



UNIVERSITE ABDELMALEK ESSAADI
FACULTE DES SCIENCES et
TECHNIQUES
TANGER



Centre d'Etudes Doctorales :
« Sciences et Techniques de l'Ingénieur »
Formation Doctorale :
« Sciences et Techniques de l'Ingénieur »
FST, Tanger

Programme Doctoral :
« Doctoral Program in Chemical and
Biological Engineering »
FEUP, Porto

THESE DE DOCTORAT EN COTUTELLE

Présentée
Pour l'obtention du

DOCTORAT EN SCIENCES ET TECHNIQUES

Par:

Hanane Boumeriame

Discipline: *Materials and Chemical Engineering*

Spécialité: *Materials and Chemical Engineering, Energy and Environment*

Development of a Novel Family of 2D Photocatalysts for Water Splitting in Solar Applications

Soutenue le 13/11/2021 devant le Jury

Président :

Pr. Jones ALAMI (Université Mohammed VI Polytechnique)

Rapporteurs :

Pr. Pascal WONG WAH CHUNG (Aix-Marseille Université)

Pr. Valérie KELLER (Université de Strasbourg)

Pr. Khalid DRAOUI (Université Abdelmalek Essaadi)

Examineurs :

Pr. Abdelkrim EL KADIB (Université Euro-Méditerranéenne de Fès)

Directeur de thèse :

Pr. Tarik CHAFIK (Université Abdelmalek Essaadi)

Pr. Joaquim Luís Bernardes Martins de FARIA (Université de Porto)

Co-Directeur de thèse

Doctor Eliana Sousa Da SILVA (Université de Porto)

Structure de recherche: Références : UAE/U14FST : Laboratoire de Génie Chimique et valorisation des ressources de la FST de Tanger

Structure de recherche de l'institution étrangère : Références : Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Portugal

A ceux qui m'ont amené jusqu'ici

Et un peu à moi aussi...

“It is your road, and yours alone. Others may walk it with you, but no one can walk it for you.”

— Jalaladim Rumi

“And, when you want something, all the universe conspires in helping you to achieve it.”

— Paulo Coelho

Acknowledgements

The following entities and projects are acknowledged for providing the material support for the fulfilment of the present Thesis research: Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC). Project 2DMAT4FUEL (POCI-01-0145-FEDER-029600 - COMPETE2020 – FCT/MCTES – PIDDAC). Erasmus+ Program (European Commission)-Mobility scholarship (Mobility 3+). OeaD-Ernst Mach Grant worldwide (Vienna, Austria).

I acknowledge the Laboratory of Chemical Engineering and Valorisation of Resources (LGCVR) at Université Abdelmalek Essaâdi for aiding the start of my PhD studies and the Associate Laboratory LSRE-LCM (Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials) for all the resources available to me during this project. I also thank the directors, professors and researchers of these institutions for their availability and assistance.

Foremost, I would like to express my deepest gratitude to my supervisors Professor Joaquim Luís Faria and Professor Tarik Chafik, for the encouragement, personal guidance, assistance, and valuable suggestions enabling me to steer my research work efficiently and effectively. For their friendship, support, and patience. Their wide knowledge and logical approach was extremely useful for my research work and provided an excellent basis for my Thesis.

My profound and sincere thanks go to my co-supervisor Doctor Eliana Sousa Da Silva. She guided me through this journey by creating the combination of serious perfection and good humour, her friendship, constant support, personal guidance, assistance and encouragement during all this process. For all the corrections, advice, conversations and all the help while I was in Porto.

I want to thank Professor Dominik Eder for accepting me and helping me during my stay at the Institute of Materials Chemistry Technische Universität Wien. His help and technical advice have made me gain many experiences in both writing and experimentation. Danke schön!

A big thank is addressed to Dr Alexey Cherevan at Technische Universität Wien, for accepting me in his wonderful team and for his guidance that made me advance in my work. For his friendship and for all the wonderful moments during my stay in Vienna. Спасибо!

I want to thank the co-authors on the papers written and in preparation, Prof. Philippe Serp, Prof. Adélio Mendes, Prof. Luísa Andrade, Prof. Manuel Prieto, Dr Dogukan Apaydin, Dr Bruno Machado, Dr Nuno Moura, Dr Tânia Lopes, Dr Ana Coutinho, for their contributions and their support with sample characterisation.

During this journey, I am blessed to meet true friends. For my colleagues in LGCVR: Mohammad Said and Mouad ‘شكرا على كل شي’. For my colleagues in LCM: Prof. Cláudia Silva,

Dr Inmaculada Velo-Gala, Dr Maria José Sampaio, Joana, Amélia, Sofia, Liliana and all others from the team “Muito Obrigada”. For my colleagues at TU Wien: Samar, Jasmin, Sreejith, Shaghayegh, Tushar, Paolo, Pablo Stephan, Jakob, Vivien and all others from the team, thanks for your friendship and your technical help and assistance. For Samar, our adventures in Vienna will never be forgotten.

Special thanks go to my colleague and friend André Torres Pinto for helping me out in my lowest times, with appreciation to my research. He always consoled me and made my stay in Porto pleasant and enjoyable.

For all the international friends and Moroccan friends that I met during my stay in Europe, Muito obrigada, Tack, Спасибо, Hvala ti, Gracias, Grazie, Danke, Merci, Děkuji, Xièxiè, شكرا, for all the unforgettable moments together.

My great and deep thanks go to my friends that are like my sisters Khalifa, Chaymae, Wiame and Zahra, for their love, advice, support, help, kindness, courage, prayers and for listening to me during my bad and good times.

My heartfelt sincere thanks go to my beloved parents; to my mom Fatima and my father Lahcen; who have been instrumental in raising me to the heights I am in at present with their love, courage, and support. I dedicate this Thesis to them. My special appreciation and gratitude go to my siblings: Mohamed, Abdoallah, Ismail, Meryem, Ghizlane, Souad, Fatima and Chorouk for their love, kindness, courage, and their financial and moral support. Everything that I achieved today is thanks to them.



Abstract

Nowadays, there is a crescent concern regarding sustainability in the energy sector. Fossil fuels have been a global topic of discussion since they present a menace to the ecosystem and affect life on Earth. Therefore, research towards green energy sources is being propelled worldwide to answer this emergent issue. For instance, solar is the most potent renewable energy and photon conversion into usable energy would help solve the global energy crisis. Photocatalytic water splitting can be considered as a promising method that can be used to directly apply this energy to produce hydrogen (H_2) as a clean fuel.

Heterogeneous semiconductor photocatalysis has received significant attention, with many studies being recently reported on the development of new materials and the modification of pre-existing photocatalysts for water splitting. Many of the reported semiconductors depict some drawbacks, including limited efficiency under visible light irradiation and fast recombination of electron/hole (e^-/h^+) pairs. The design of heterostructured photocatalysts, based on composites by combining two or more optical semiconductors, has proven to be an effective method to achieve enhanced visible light absorption and reduced photogenerated charge carrier recombination through a strong interfacial contact between the materials.

The scope of this Thesis is to develop novel materials by creating heterostructure systems based on graphitic-like carbon nitride, $g-C_3N_4$ (GCN), a metal-free semiconductor, for superior photocatalytic performance towards hydrogen and oxygen generation *via* water splitting. The bulk GCN material presents limited visible light absorption, small surface area and fast recombination of photogenerated e^-/h^+ pairs. Therefore, the architectural design of distinct nanohybrids was investigated to improve the photocatalytic activity of this material.

The research involved combining GCN with different promising materials, such as graphene-derivatives and layered double hydroxides. The first work presented in this Thesis is the synthesis of few-layer graphene (FLG)/GCN heterostructures, aiming to improve the e^-/h^+ pairs separation and the light absorption of bulk GCN. Two different types of FLG were prepared, and different loadings were added to GCN to study the morphology effect and the loading impact on the activity of bulk GCN. The prepared FLG/GCN materials presented high photocatalytic H_2 generation under Vis-LED irradiation, with the best performing material being 2%FLG/GCN, which also showed to be stable up to 4 consecutive runs of reuse.

In the next step, bulk GCN was thermally exfoliated at 500 °C under air conditions, resulting in a material with thinner layers (GCNN; nanosheets), increased surface area, and enhanced photocatalytic performance. The GCNN was then assembled with a new type of

two-dimensional (2D) layered double hydroxide (LDH) photocatalysts. These materials possess a layered structure, are easily synthesised and possess tunable bandgap energies.

The ternary NiCeAl-LDH was prepared by a simple hydrothermal method and coupled with GCNN nanosheets *via* an impregnation process while varying the loading of the LDH. The NiCeAl-LDH/GCNN hybrids were tested for photocatalytic H₂ production under Vis-LED irradiation. A beneficial effect of the loading NiCeAl-LDH into the GCNN matrix was observed during the photocatalytic reactions. The results show that a small amount of NiCeAl-LDH (1.5 wt.%) leads to enhanced photocatalytic activity of the exfoliated GCN catalyst. This improvement is mainly attributed to the interfacial contact and a synergistic effect between both layered materials.

Due to the observed positive effects of creating LDH/GCNN nanohybrids, another type of LDH (*i.e.*, binary CuAl-LDH) was also investigated and tested towards water splitting under Vis-LED illumination. The hybrids were prepared through an electrostatic co-assembly method, varying the loading amount of CuAl-LDH. The photocatalytic performance towards H₂ and O₂ generation with the CuAl-LDH/GCNN hybrid materials showed improved activity without using any additional cocatalyst, with the best loading being 0.2 wt.%. This enhanced performance is owed to the efficient e⁻/h⁺ separation and transport at the interface, enhanced visible light absorption, narrower bandgap and higher surface area.

The achievements of this Thesis will propel the future development of novel hybrids by modulated morphology and bandgap engineering for optimising heterostructures for various photocatalytic applications.

Résumé

L'énergie est l'un des domaines les plus importants aujourd'hui. La production mondiale de ces énergies est principalement issue des méthodes de génération conventionnelles qui ont des impacts néfastes sur l'environnement en utilisant des combustibles fossiles comme le pétrole, le gaz et le charbon. Ces ressources sont en demande progressive et continue à cause de la croissance démographique mondiale et l'émergence économique des pays en voie de développement d'où leurs épuisements et la nécessité de trouver des alternatives propre, renouvelable, abordable et fiable, tel que l'énergie solaire.

L'énergie solaire constitue l'un des plus grandes sources d'énergie renouvelable disponible pour l'humanité. L'utilisation de cette énergie pour la dissociation de l'eau (water-splitting) par voie photo-catalytique est considéré comme une méthode innovante et prometteuse pour produire de l'hydrogène (H_2) en tant que carburant propre.

Les semi-conducteurs hétérogènes a fait l'objet de plusieurs travaux. Des études récentes ont été publiées sur le développement de nouveaux matériaux semi-conducteur et sur la modification de photo-catalyseurs préexistants pour la séparation de l'eau. La plupart des semi-conducteurs étudiés présentent certains inconvénients, notamment une efficacité limitée sous la lumière visible et une recombinaison rapide des paires électron/trou (e^-/h^+). La conception des photo-catalyseurs hétérostructurés, en utilisant deux semi-conducteurs ou plus, s'est avérée être une méthode efficace pour améliorer l'absorption de la lumière visible et réduire la recombinaison des paires e^-/h^+ grâce à un contact interfacial fort entre les matériaux.

Cette thèse, a donc pour objectif de développer des nouveaux matériaux à base de nitrure de carbone graphitique ($g-C_3N_4$; renommer comme GCN), pour la production photocatalytique d'hydrogène et d'oxygène. Le matériau GCN sous forme "vrac" présente une absorption limitée de la lumière visible, une faible surface spécifique et une recombinaison rapide des paires e^-/h^+ . Aussi plusieurs modifications structurales ont été effectuée afin d'améliorer l'activité photo-catalytique de ce matériau.

Cette recherche consiste à combiner le GCN avec différents matériaux prometteurs, tels que les dérivés du graphène et les hydroxydes en couches doubles. L'étude a été déclenché par la synthèse d'hétérostructures, FLG/GCN de graphène à quelques couches (few-layer graphene, FLG), pour but d'améliorer la séparation des paires e^-/h^+ et l'absorption de la lumière du GCN. Deux différents types de FLG ont été préparés et différentes quantités ont été ajoutées au GCN afin d'étudier l'effet de la morphologie et l'impact de la quantité de FLG sur l'activité du GCN. Les hétérostructures FLG/GCN synthétisés présentent une forte génération de H_2 sous la

lumière visible-LED (light emitting diodes) avec une meilleure performance pour le matériau 2 wt.% FLG/GCN, qui a une stabilité de 4 cycles consécutifs.

Dans une deuxième étape, le GCN en vrac a été exfolié thermiquement à 500 °C sous l'air, ce qui a permis d'obtenir un matériau avec des couches plus fines (GCNN ; nano-feuilles), une surface spécifique plus grande et d'une performance photo-catalytiques améliorées (comparé au GCN en vrac). Le GCNN a ensuite été assemblé avec un nouveau type de photo-catalyseur bidimensionnel (2D) c'est l'hydroxyde double lamellaire (LDH). Ces matériaux possèdent une structure en couches qui sont facilement synthétisés et possèdent une énergie de bande interdite accordable.

Un nouveau matériau NiCeAl-LDH a été préparé par une simple méthode hydrothermale et assemblé avec le nano-feuilles GCNN par imprégnation tout en faisant varier le pourcentage (%) de LDH.

Les hybrides NiCeAl-LDH/GCNN ont été testés pour la production photocatalytique de H₂ sous l'irradiation visible-LED. Un effet bénéfique de la quantité de NiCeAl-LDH dans la matrice GCNN a été observé lors des réactions photocatalytiques. Les résultats montrent qu'une faible quantité de NiCeAl-LDH (1.5 %) améliore l'activité photo-catalytique du catalyseur GCN exfolié. Cette progression est principalement attribuée au contact interfacial et à l'effet synergique entre les deux matériaux stratifiés.

En raison de l'effet bénéfique de l'introduction de LDH dans la matrice GCNN, des nano-hybrides utilisant un autre type de LDH (le binaire CuAl-LDH) ont également été synthétisés et testés pour la dissociation de l'eau sous l'irradiation visible-LED. Les hybrides ont été préparés par la méthode de co-assemblage électrostatique, en variant la quantité de CuAl-LDH en GCNN.

La performance photo-catalytique pour la génération de H₂ et O₂ avec les matériaux CuAl-LDH/GCNN montre une activité améliorée sans utilisation de cocatalyst supplémentaire, le meilleur matériau hybride est celui qui contient 0.2% de CuAl-LDH. Cette amélioration des performances est due à l'efficacité de la séparation, au transport efficaces e⁻/h⁺ à l'interface, à l'augmentation de l'absorption de la lumière visible, à la bande interdite étroite et à l'augmentation de la surface spécifique.

Les résultats de ces travaux propulseront le développement futur de nouveaux hybrides par la modulation de la morphologie et l'ingénierie de bande interdite pour optimiser les hétérostructures pour diverses applications photo-catalytiques.

Resumo

Atualmente, há uma crescente preocupação com a sustentabilidade no setor energético. Os combustíveis fósseis são um tema de discussão global, uma vez que constituem uma ameaça para o nosso ecossistema e afetam a vida na Terra. Por conseguinte, a investigação no sentido de desenvolver fontes de energia verdes está a ser impulsionada a nível mundial para se responder a esta questão emergente. Por exemplo, a energia solar é a energia renovável mais potente e a conversão dos fotões em energia útil poderia ajudar a resolver a atual crise energética. A desagregação fotocatalítica da água é considerado um método promissor para a aplicação direta desta energia na produção de hidrogénio (H_2) a ser utilizado como um combustível limpo.

A fotocatalise heterogénea por semicondutores tem recebido grande atenção, tendo sido recentemente reportado um grande número de estudos sobre o desenvolvimento de novos materiais e sobre a modificação de fotocatalisadores pré-existentes para a desagregação da água. Muitos dos semicondutores reportados possuem desvantagens, que incluem a limitada eficiência sob a irradiação de luz visível e a ocorrência de rápida recombinação dos pares de electrão/buraco (e^-/h^+). A conceção de fotocatalisadores heteroestruturados, baseados em compósitos constituídos por dois ou mais semicondutores óticos, provou ser um meio eficaz para se obter uma melhor absorção de luz visível e a diminuir a recombinação de cargas fotogeradas, por meio de um forte contacto interfacial entre os materiais.

O objetivo primordial desta tese é desenvolver novos materiais, por meio da criação de sistemas heteroestruturados baseados em nitreto de carbono grafitico ($g-C_3N_4$; GCN), um fotocatalisador isento de metais, capaz de um desempenho fotocatalítico superior na produção de hidrogénio e oxigénio através da desagregação da água. O GCN em bruto apresenta uma absorção de luz visível limitada, uma área superficial baixa e uma rápida recombinação de pares e^-/h^+ fotogerados. Por isso a investigação centrou-se na conceção arquitetónica de nanohíbridos dedicados a melhorar a atividade fotocatalítica desse material.

A pesquisa descrita envolveu a combinação de GCN com diferentes materiais promissores, como derivados de grafeno e hidróxidos duplos laminados. O primeiro trabalho apresentado nesta tese é a síntese de heteroestruturas de grafeno de poucas camadas (FLG)/GCN, com o objetivo de melhorar a separação de pares e^-/h^+ e a absorção de luz do GCN em bruto. Prepararam-se dois tipos diferentes de FLG e foram adicionadas ao GCN em diferentes proporções para estudar o efeito sobre a morfologia e o impacto da composição ponderal na atividade do GCN em bruto. Os materiais preparados de FLG/GCN mostraram uma elevada

performance na geração de H_2 pela via fotocatalítica assistida por irradiação usando LEDs com emissão no visível (Vis-LED), tendo o material 2%FLG/GCN apresentado o melhor desempenho, com uma estabilidade comprovada até 4 ciclos de utilização consecutiva.

Na etapa seguinte, o GCN em bruto foi exfoliado por acção térmica a 500 °C em atmosfera de ar, resultando num material com camadas mais finas (GCNN; nanofolhas), maior área superficial e um desempenho fotocatalítico melhorado. O GCNN foi então combinado com um novo tipo de fotocatalisadores bidimensionais (2D) de hidróxidos duplos laminados (LDH). Estes materiais possuem uma estrutura lamelar, são facilmente sintetizados e possuem energias de hiato moduláveis.

O sistema ternário NiCeAl-LDH foi preparado por um método simples de via hidrotermal e seguidamente acoplado com nanofolhas de GCNN por meio de um processo de impregnação, variando a composição de LDH. Os híbridos NiCeAl-LDH/GCNN foram testados para produção de H_2 fotocatalítica assistida por Vis-LED. Foi observado um efeito positivo com a introdução da carga de NiCeAl-LDH na matriz de GCNN durante as reacções fotocatalíticas. Os resultados demonstram que uma pequena quantidade de NiCeAl-LDH (1.5%) produz uma melhoria da atividade fotocatalítica relativamente ao catalisador GCN exfoliado (GCNN). Esta melhoria é principalmente atribuída ao contacto interfacial e ao efeito sinérgico entre os dois materiais lamelares.

Na sequência dos efeitos positivos observados na criação de nanohíbridos à base de LDH/GCNN, um outro tipo de LDH (na circunstância, um sistema binário de CuAl-LDH) foi também investigado e testado para a desagregação da água sob iluminação Vis-LED. Os híbridos foram preparados através de um método de co-montagem eletrostática mútua, variando a composição de CuAl-LDH. O desempenho fotocatalítico na produção de H_2 e O_2 com os materiais híbridos CuAl-LDH/GCNN apresentou uma melhoria na atividade, sem o recurso à adição de nenhum co-catalisador, tendo-se determinado como composição ótima 0.2%. Este melhor desempenho deve-se à separação e transporte eficiente dos pares e^-/h^+ para a interface dos materiais, maior absorção de luz visível, uma estrutura de bandas mais favorável e maior área superficial.

A realização desta tese irá impulsionar o futuro do desenvolvimento de novos materiais híbridos, através da modulação da morfologia e manipulação da estrutura de bandas, capaz de otimizar heteroestruturas para diversas aplicações fotocatalíticas.

ملخص البحث

يشكل قطاع الطاقة أحد أهم المجالات العالمية اليوم، حيث يرجع إنتاج الطاقة العالمي اليوم إلى حد كبير إلى الأساليب التقليدية التي تستخدم الوقود الأحفوري مثل النفط والغاز والفحم. غير أن هذه الموارد محدودة وتقترب من الاستنفاد بسبب استمرار الطلب بسبب النمو الديمغرافي، بالإضافة إلى آثارها السلبية على البيئة. لذلك فإن إيجاد مصادر طاقة متجددة، نظيفة وغير مكلفة هو أمر أساسي لتغلب على التحديات الحديثة. على سبيل المثال، الطاقة الشمسية التي تعتبر إحدى أقوى الطاقات المتجددة وتحويلها إلى طاقة قابلة للاستخدام من شأنه أن يساعد في حل مشاكل الطاقة. ويمكن اعتبار التقسيم الضوئي للمياه وسيلة واحدة يمكنها استخدام هذه الطاقة لإنتاج الهيدروجين كوقود نظيف.

لقد حظيت المحفزات الضوئية غير المتجانسة باهتمام كبير، حيث نشر مؤخراً عدد كبير من المقالات العلمية بشأن تطوير محفزات ضوئية جديدة أو تعديل الموجودة سابقاً لتقسيم المياه. إلا أن العديد من أشباه الموصلات الموجودة لها بعض العيوب، والتي تتضمن كفاءة محدودة لامتصاص الضوء تحت إشعاع المرئي للضوء وإعادة التكوين السريع لأزواج الإلكترونات/الثقوب (e^-/h^+ electron/hole) وقد ثبت أن تصميم المحفزات الضوئية الغير المهيكلة، باستخدام اثنين أو أكثر من أشباه الموصلات، وسيلة فعالة لتحقيق امتصاص أفضل للضوء المرئي وتقليل إعادة تفاعل الزوج e^-/h^+ من خلال الاتصال القوي بين هذه المواد.

يتلخص نطاق هذه الأطروحة في تطوير مواد جديدة من خلال إنشاء محفزات غير هيكليّة تعتمد على الجرافيت كربون نيتريد ($g-C_3N_4$; GCN) وهو محفز ضوئي خالي من المعادن، لإنتاج الهيدروجين والأكسجين (H_2 و O_2) من خلال التقسيم الضوئي للمياه. تقدم المادة المتراكمة ل (GCN) امتصاصاً محدوداً للضوء المرئي، ومساحة سطحية صغيرة، وسرعة إعادة تشكيل (e^-/h^+) ولذلك، تم تصميم وصنع للأجسام النانوية المتميزة من أجل تحسين النشاط الضوئي لهذه المادة.

شمل هذا البحث الجمع بين GCN ومواد واحدة مختلفة، مثل مشتقات الجرافين والهيدروكسيدات المزدوجة. العمل الأول الذي تم تقديمه في هذه الأطروحة هو توليف الجرافين ذو الطبقات القليلة (few-layer graphene, FLG) مع GCN، بهدف تحسين فصل أزواج e^-/h^+ والامتصاص الضوئي الخفيف ل GCN. وقد أعد نوعان مختلفان من FLG وأضيفت كميات مختلفة إلى شبكة GCN لدراسة تأثير المورفولوجيا وتأثير الكمية على نشاط GCN. قدمت مواد FLG/GCN إنتاجاً عالياً من H_2 تحت إشعاع (ثنائي باعث للضوء visible-LED)، وأفضل محفز كان FLG/GCN 2٪، والذي أظهر أيضاً استقراراً عالياً بعد 4 تفاعلات متتالية.

في الخطوة التالية، تم تَوْسُفُ GCN حرارياً عند 500 درجة مئوية، مما أدى إلى إنتاج طبقات رقيقة (صفائح نانو; GCNN) وزيادة المساحة السطحية وتحسين الأداء الضوئي. ثم تم جمع GCNN بنوع جديد من ثنائي الأبعاد (2D) الهيدروكسيد مزدوج الطبقات ((layered double hydroxide (LDH)). تمتلك هذه المواد بنية طبقية صفائحية، ويتم صنعها بسهولة وتمتلك فجوة نطاق الطاقة قابلة للضبط.

أُعدَّت المادة الثلاثية NiCeAl-LDH بطريقة مائية حرارية بسيطة (hydrothermal) وأدمجت مع GCNN عن طريق التشريب مع تغيير كمية مادة LDH. تم اختبار هجينات NiCeAl-LDH/GCNN لإنتاج H_2 تحت إشعاع الضوئي-LED. ولوحظ أثر مفيد لإضافة NiCeAl-LDH إلى GCNN خلال التفاعلات الكيميائية. وأظهرت النتائج أن قدراً ضئيلاً من NiCeAl-LDH (1.5%) يؤدي إلى تحسين النشاط الضوئي ل GCNN. يرجع هذا التحسن إلى الاتصال القوي وإلى التأثير التآزري بين كل من هذه المواد.

نظراً للتأثيرات الإيجابية الملحوظة الناجمة عن إنشاء مركبات نانوهيبريدات LDH/GCNN، قد تم أيضاً تأليف نوع آخر من مركبات (ثنائي CuAl-LDH) واختباره لتقسيم الضوئي للمياه تحت إشعاع LED. وقد تم إعداد هذه المركبات من خلال طريقة الكهروستاتيكي، مع تفاوت في كمية CuAl-LDH. أظهرت نتائج الأداء الضوئي نحو إنتاج H_2 و O_2 بالمواد الهجينة من CuAl-LDH/GCNN إلى تحسن النشاط دون استخدام أي cocatalyst، وأفضل محفز هو الذي يحتوي على كمية 0.2% من CuAl-LDH. يرجع هذا التحسن إلى الفصل والنقل الفعالين لـ e^-/h^+ ، وتحسين امتصاص المرئي للضوء، وتضييق فجوة نطاق الطاقة، وزيادة مساحة السطح. ستمكن نتائج هذه الأطروحة إلى تطوير المحفزات المهجنة الغير المتجانسة في المستقبل عن طريق هندسة المورفولوجيا وهندسة فجوة نطاق الطاقة لتحسين الهياكل غير المتجانسة لمختلف التطبيقات الضوئية.

Table of contents

Abstract	I
Résumé.....	III
Resumo	V
المبحث ملخص.....	VII
Table of contents.....	XI
List of figures	XVII
List of tables	XXI
List of schemes	XXIII
List of abbreviations and symbols.....	XXV
Materials nomenclature	XXIX
List of publications	XXXI
List of communications	XXXIII
Chapter 1 General introduction.....	1
1. Energy context.....	3
2. Solar energy.....	4
2.1 Hydrogen fuel	5
2.2 Photocatalytic water splitting.....	6
2.2.1 General principles and mechanism	7
2.2.2 Photocatalysis and semiconductors	8
3. 2D semiconductors for water splitting	9
4. Aim of the work and Thesis outline	13
Chapter 2 Literature review.....	17
2.1 Graphitic carbon nitride.....	19
2.1.1 Generality.....	19
2.1.2 Synthesis and modification of GCN	20

2.1.3 GCN for photocatalytic water splitting	30
2.2 Layered double hydroxides (LDHs)	39
2.2.1 Properties and synthesis	39
2.2.2.1 Functionalisation of LDH-based materials for water splitting.....	44
2.2.2.1.1 Calcination	45
2.2.2.1.2 Pyrolysis	46
2.2.2.1.2 Cationic doping	47
2.2.2.1.3 Hybrid formation	48
2.2.2.2 LDH as catalytic support for photocatalytic water splitting.....	52
2.3. Graphene-derivatives	60
2.3.1 Properties and synthesis	60
2.3.2 Graphene-derivatives for photocatalytic water splitting	64
Chapter 3 Characterisation techniques	71
3.1 Electron microscopy	73
3.1.1 Scanning electron microscopy	73
3.1.1.2 Energy-dispersive X-ray spectroscopy	74
3.1.2 Transmission electron microscopy	74
3.2 X-ray methods	75
3.2.1 X-ray diffraction	75
3.2.2 X-ray photoelectron spectroscopy	76
3.3 Attenuated total reflectance - Fourier transform infrared spectroscopy.....	77
3.4 Surface area measurements	78
3.5 Optical spectroscopy	79
3.5.1 UV-Vis diffuse reflectance spectroscopy	79
3.5.2 Photoluminescence spectroscopy	80
3.6 Electrochemical techniques	82
3.6.1 Mott-Schottky method	82

3.6.2 Linear sweep voltammetry	83
3.7. Zeta potential	84
Chapter 4 FLG/g-C₃N₄ hybrids for photocatalytic H₂ generation.....	89
4.1 Introduction	91
4.2 Experimental section	91
4.2.1 Materials	91
4.2.2 Catalyst preparation	91
4.2.3 Photocatalytic tests	92
4.3. Results and discussion.....	93
4.3.1 Characterisation of the photocatalysts	93
4.3.2 Photocatalytic hydrogen generation.....	106
4.3.3 Proposed photocatalytic mechanism.....	109
4.4. Conclusions	111
Chapter 5 LDH/g-C₃N₄ hybrids for photocatalytic water splitting	115
5.1 NiCeAl-LDH/GCNN hybrids for photocatalytic H₂ generation	117
5.1.1. Introduction.....	117
5.1.2. Materials and methods	117
5.1.2.1 Materials.....	117
5.1.2.2 Catalyst preparation.....	118
5.1.2.3 Photocatalytic tests.....	119
5.1.3. Results and discussion	120
5.1.3.1 Materials characterisation	120
5.1.3.2 Photocatalytic hydrogen generation	127
5.1.4. Conclusions.....	128
5.2. CuAl-LDH/GCNN hybrids for photocatalytic H₂ and O₂ evolution.....	130
5.2.1. Introduction.....	130
5.2.2. Materials and Methods.....	130

5.2.2.1. Materials	130
5.2.2.2. Catalyst preparation	130
5.2.2.3. Photocatalytic experiments	131
5.2.3. Results and discussion	132
5.2.3.1 Catalyst characterisation	132
5.2.3.2 Photocatalytic water splitting	141
5.2.3.3. Charge carrier dynamics and photocatalytic mechanism	143
5.2.4. Conclusions	147
Chapter 6 Summary and future work.....	151
6.1 Summary	153
6.2 Future work	154
References	159

List of figures

Figure 1. World energy consumption by fuel type, 2010-2050 (quadrillion Btu) Reproduced from International Energy Outlook 2021.	4
Figure 2. Hydrogen production and its integration in different energy fields.	6
Figure 3. Schematic showing the energy band structure and e^-/h^+ pair separation in the p-n heterojunction.	10
Figure 4. Types of semiconductors heterojunctions according to the band position.....	11
Figure 5. a) Sensitisation mechanism; b) type II heterojunction, and c) direct Z-scheme.	12
Figure 6. a) Triazine, b) tri-s-triazine (heptazine) GCN structures, c) thermal polymerisation of various GCN precursors undergoing thermal polymerisation. The black, blue, white, red, and yellow balls denote C, N, H, O, and S atoms, respectively.	21
Figure 7. Relationship between the thermal duration and layer thickness of GCN and diagram for the layer-by-layer exfoliation and splitting mechanism of GCN with decreased thickness and size. TEM images of GCN synthesised at 550 °C for (b–c) 0 min, (d–e) 60 min, and (f–g) 240 min, excluding the heating-up time.	24
Figure 8. Schematic illustration of the proposed mechanism for CO ₂ photoreduction in the GCN/NiAl-LDH heterojunctions.	29
Figure 9. a) UV-Vis DRS of GCN nanomesh and the bulk counterpart, and its corresponding Tauc plots (inset). b) PL emission spectra of GCN nanomesh and the bulk, the inset in b) shows transient photocurrents under visible light illumination of both materials. c, d) XPS valence band spectra and electronic band structure of the GCN nanomesh and the bulk counterpart. .	31
Figure 10. Schematic diagram illustrating the enhanced photocatalytic performance of Pt-rGO/GCN photocatalysts. Step (1): rGO as an electron sink to capture the photogenerated electrons from the GCN; Step (2): rGO as an electron mediator to transfer electrons from the capture sites to the Pt nanoparticles; Step (3): Pt nanoparticles as the reduction active sites for the H ₂ generation.	34
Figure 11. Schematic illustration of MoS ₂ on GCN for boosting H ₂ generation.	35
Figure 12. Representative structure of LDH materials.	40
Figure 13. a) Schematic illustration of the procedure for preparing MgAl-LDH/NiS hybrids; TEM images of b) pure MgAl-LDH and c) MgAl-LDH/NiS-0.7.	44

Figure 14. a) Schematic illustration of the electron localization on the polar facet and the hole localization on the non-polar facet for hexagonal $\text{Zn}_{0.67}\text{Cd}_{0.33}\text{S}$ nanosheet. b) Proposed photocatalytic water splitting mechanism over 2D ultrathin $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheet.	47
Figure 15. a) PL spectra of TbZnCr-LDH samples. b) Schematic illustration of the oxygen evolution process over the TbZnCr-LDH under visible light irradiation.	48
Figure 16. a, b) TEM images of CNMMO. c) Mechanistic pathways of photocatalytic water splitting.....	50
Figure 17. Schematic of band structure and charge transfer process in ZnCr-LDH/GCN for photocatalytic H_2 generation.	53
Figure 18. a) Structure of pristine GR; b) Armchair (blue) and zigzag (red) edges in monolayer GR.	61
Figure 19. Synthesis methods of GR.....	62
Figure 20. Schematic of different signals produced by interactions of an electron beam with the sample. Each signal comes from a different depth of the sample.	73
Figure 21. Bragg diffraction scheme. Black circles represent atoms of two parallel periodic lattice planes with a distance between them equal to d . Ingoing (1 and 2) and outgoing (1' and 2') parallel X-ray beams possess a difference in path length of $2\Delta l$ after the scattering..	76
Figure 22. IUPAC classification of physisorption isotherm types.....	78
Figure 23. Light scattering at smooth surfaces: normal or regular (grey) and diffuse (black) reflection.	79
Figure 24. a) Potential waveforms for linear sweep voltammetry and b) its corresponding voltammogram.	84
Figure 25. Illustration of zeta potential showing the surface charge, the Stern layer, and the slipping layer.....	85
Figure 26. Upper row: UV-Vis DRS of a) GCN, FLG ₁₀ and xFLG ₁₀ /GCN; and b) GCN, FLG ₆₀ and xFLG ₆₀ /GCN composites. Lower row: visual aspect of the colours of the materials i) GCN, ii) 2FLG ₁₀ /GCN, and iii) 2FLG ₆₀ /GCN, respectively.....	94
Figure 27. N_2 adsorption-desorption isotherms at -196°C and BJH pore size distribution curves of a, b) GCN; c, d) 2FLG ₁₀ /GCN and e, f) 2FLG ₆₀ /GCN.....	96
Figure 28. SEM (left) and TEM (right) images of (a, b) GCN, (c, d) FLG ₁₀ , (e, f) FLG ₆₀ , (g, h) 2FLG ₁₀ /GCN and (i, j) 2FLG ₆₀ /GCN. See text for arrow meaning.....	98
Figure 29. X-ray diffraction patterns of a) FLG ₁₀ , FLG ₆₀ , and of b) GCN, 2FLG ₁₀ /GCN, and 2FLG ₆₀ /GCN (inset: magnification of the (002) peaks of FLG and GCN); c and d) Deconvolution of the (002) peaks of both composites presented in b).....	99

Figure 30. FTIR spectra of GCN, 2FLG ₁₀ /GCN and 2FLG ₆₀ /GCN.....	101
Figure 31. Raman spectra of 2FLG ₁₀ /GCN, FLG ₁₀ and FLG ₆₀	102
Figure 32. Survey spectra of a) GCN and b) 2FLG ₁₀ /GCN. High-resolution XPS spectra of C1s, N1s and O1s for GCN (c, d, e) and 2FLG ₁₀ /GCN (f, g, h) materials.....	104
Figure 33. Steady-state PL emission spectra of GCN and a) xFLG ₁₀ /GCN, and b) xFLG ₆₀ /GCN, c) comparison of PL emission spectra of GCN, 2FLG ₁₀ /GCN, and 2FLG ₆₀ /GCN upon excitation at 370 nm.	106
Figure 34. a) Rate of H ₂ production over GCN, xFLG ₁₀ /GCN, and xFLG ₆₀ /GCN after 3 h of visible-LED irradiation in the presence of EDTA (10% vol) and Pt (3 wt.%). b) Variation in H ₂ production of the catalyst 2FLG ₁₀ /GCN over four cycles of visible light irradiation (LED, λ_{em} = 420 nm) in the presence of EDTA and Pt. c) HER profile run of 2FLG ₁₀ /GCN hybrid.....	107
Figure 35. Correlation between the optical/surface parameters (PL, S_{BET} and PL/ S_{BET} ratio) and the photocatalytic activity for the materials GCN and xFLG _y /GCN (x = 0.5, 1 and 2 wt.%).	108
Figure 36. a) Mott-Schottky plots and b) transient photocurrent response (constant applied potential of 0.2 V vs Ag/AgCl, with 60 s simulated solar light (100 mW·cm ⁻²) on/off cycles during 1000 s for GCN and 2FLG ₁₀ /GCN materials.....	110
Figure 37. a) Band structure diagram of GCN and 2FLG ₁₀ /GCN materials, b) Proposed diagram of charge carrier transfer and H ₂ production on 2FLG ₁₀ /GCN.	111
Figure 38. ATR-FTIR spectra of a) NiCeAl-LDH, b) GCN and GCNN, c) GCNN and xNiCeAl-LDH/GCNN materials.	121
Figure 39. X-ray diffraction patterns of a) GCN and GCNN, b) GCNN, NiCeAl-LDH and xNiCeAl-LDH/GCNN materials.	122
Figure 40. a) N ₂ adsorption-desorption isotherms at -196 °C and b) the pore size distribution of GCNN, NiCeAl-LDH and 1.5NiCeAl-LDH/GCNN heterostructures.....	123
Figure 41. SEM images of a) GCNN, b) NiCeAl-LDH, c) 1.5NiCeAl-LDH/GCNN, and d) 7NiCeAl-LDH/GCNN materials.	124
Figure 42. UV-Vis DRS of a) GCN and GCNN, b) NiCeAl-LDH, c) GCNN and xNiCeAl-LDH/GCNN hybrids, d) Tauc plot of GCNN, NiCeAl-LDH and 1.5NiCeAl-LDH/GCNN hybrids.....	125
Figure 43. Solid steady-state PL spectra of a) GCN and GCNN, b) GCNN and xNiCeAl-LDH/GCNN materials.	126
Figure 44. a) Photocatalytic H ₂ production for GCN, GCNN, NiCeAl-LDH and xNiCeAl-LDH/GCNN composites under visible-LED irradiation, in the presence of EDTA and	

Pt. b) H ₂ production profile for 1.5NiCeAl-LDH/GCNN catalyst after 3h or irradiation. c) Reusability test of 1.5NiCeAl-LDH/GCNN material for four cycles (3 h each).	128
Figure 45. Photograph representation of the experimental setup used during photocatalytic HER reactions.	132
Figure 46. SEM (a, c, e, g) and TEM (b, d, f, h) images of CuAl-LDH, GCNN, 0.2CuAl-LDH/GCNN and 7CuAl-LDH/GCNN, respectively.	133
Figure 47. EDX spectrum of 7CuAl-LDH/GCNN hybrid.	134
Figure 48. N ₂ adsorption-desorption isotherms at –196 °C and BJH pore size distribution curves obtained from adsorption of a, b) GCNN; c, d) CuAl-LDH and e, f) 0.2CuAl-LDH/GCNN, respectively.	135
Figure 49. X-ray diffraction patterns of GCNN, CuAl-LDH and xCuAl-LDH/GCNN materials.	136
Figure 50. ATR-FTIR spectra of GCNN, CuAl-LDH and xCuAl-LDH/GCNN materials. .	137
Figure 51. XPS spectra a) Cu 2p, b) Al 2p, and c) O 1s of CuAl-LDH.....	138
Figure 52. a) C1s and b) N1s XPS spectra of GCNN and xCuAl-LDH/GCNN materials (x = 0.2 and 7). The dashed lines indicate the shifted peaks.....	139
Figure 53. a) UV-Vis DRS GCNN, CuAl-LDH and xCuAl-LDH/GCNN materials; b) Tauc plot determination of GCNN, CuAl-LDH and 0.2CuAl-LDH/GCNN materials.	141
Figure 54. a) Photocatalytic H ₂ generation rate for GCNN, CuAl-LDH and xCuAl-LDH/GCNN materials under visible-LED irradiation. b) Photocatalytic H ₂ generation over 0.2CuAl-LDH/GCNN catalyst using different hole scavengers (MeOH, TEOA and EDTA (10% v/v)). c) Wavelength irradiation dependent H ₂ evolution of GCNN and 0.2CuAl-LDH/GCNN catalysts in the presence of TEOA scavenger. d) OER evolution rate of GCNN, CuAl-LDH and 0.2CuAl-LDH/GCNN materials under visible-LED irradiation. ...	143
Figure 55. a) Solid steady-state PL spectra of GCNN and xCuAl-LDH/GCNN materials. b) Relative quenching factor vs wt.% of CuAl-LDH spectra of 0.2CuAl-LDH/GCNN materials. c) Fluorescence intensity decays of GCNN and 0.2CuAl-LDH/GCNN materials.	145
Figure 56. Current potential curves of a) GCNN, b) CuAl-LDH, and c) 0.2CuAl-LDH/GCNN materials in dark conditions.	146
Figure 57. Proposed mechanism for water splitting over CuAl-LDH/GCNN under visible-light irradiation (type I heterojunction).	147

List of tables

Table 1. Examples of published works regarding GCN and GCN-based composites and their photocatalytic applications.	36
Table 2. Summary of LDH-based nanomaterials for photocatalytic water splitting.	54
Table 3. Some reported H ₂ generation of several GCN/GRDs based heterostructures.	68
Table 4. Optical (bandgap energy) and textural (surface area, pore volume, and size) properties of the prepared materials.	95
Table 5. Structural parameters of the materials for the (002) peak obtained from the XRD data. FWHM is the full width at half-maximum of the peak, d_{002} is the interlayer distance, L_C is the crystallite size, and 2θ is the diffraction angle.	100
Table 6. Peak position (cm ⁻¹) and ratio peak intensities (I_D/I_G) of the materials FLG ₁₀ , FLG ₆₀ and 2FLG ₁₀ /GCN obtained by Raman spectroscopy.	103
Table 7. Peak position (eV) and relative composition (at.%) of the materials obtained by XPS analysis.	104
Table 8. Textural properties of GCNN, NiCeAl-LDH and xNiCeAl-LDH/GCNN heterostructures determined by N ₂ adsorption-desorption isotherms at -196 °C.	123
Table 9. Fluorescence lifetimes (τ_i , τ_{av}), normalised amplitudes (A_i) and chi-square (χ^2) for GCNN and 1.5NiCeAl-LDH/GCNN materials ($\lambda_{ex} = 335$ nm; $\lambda_{em} = 433$ nm).	127
Table 10. Textural properties (surface area, pore volume and size) and optical (bandgap energy) properties xCuAl-LDH/GCNN (x = 0.2, 1, 3 and 7) materials.	134
Table 11. Fluorescence lifetimes (τ_i , τ_{av}), normalised amplitudes (A_i) and chi-square (χ^2) of GCNN and 0.2CuAl-LDH/GCNN materials ($\lambda_{ex} = 375$ nm; $\lambda_{em} = 451$ nm).	145

List of schemes

Scheme 1. Principle of water splitting on semiconductor photocatalysts.	8
Scheme 2. General representation of the post-modification processes for LDH-based materials.	45
Scheme 3. a) Image and b) schematic representation of the photocatalytic setup used during photocatalytic reactions.	93
Scheme 4. The synthesis process of NiCeAl-LDH.	118

List of abbreviations and symbols

AQY	Apparent quantum yield
ACN	Amorphous carbon nitride
ATR	Attenuated total reflection
AE	Auger electrons
BSE	Backscattered electrons
CB	Conduction band
c-CVD	Catalytic chemical vapour deposition
DFT	Density functional theory
DMF	N,N-dimethylformamide
DCN	Dicyandiamide
EDX	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
EDTA	Ethylenediaminetetraacetic acid
EtOH	Ethanol
E_g	Energy bandgap
e^-/h^+	Electron/hole pair
Eq	Equation
FTIR	Fourier transform infrared spectroscopy
FLG	Few-layer graphene
FHWM	Full width at half maximum
GC	Gas chromatography
GCN	Graphitic carbon nitride
GCNN	Graphitic carbon nitride nanosheets
GR	Graphene
GRDs	Graphene derivatives

GO	Graphene oxide
GrO	Graphite oxide
HER	Hydrogen evolution reaction
HT	Hydrotalcite
$h\nu$	Energy of the photon
h	Hour
IR	Infrared
IPA	Isopropanol
KM	Kubelka-Munk
LDHs	Layered double hydroxides
LED	Light emitting diode
LSV	Linear sweep voltammetry
MMOs	Mixed metal oxides
MeOH	Methanol
NHE	Normal hydrogen electrode
NPs	Nanoparticles
NIR	Near-infrared
NMP	<i>N</i> -methyl-pyrrolidone
OER	Oxygen evolution reaction
PL	Photoluminescence
Pt	Platinum
QY	Quantum yield efficiency
rGO	Reduced graphene oxide
RE	Reference electrode
SPR	Surface plasmon resonance
SEM	Scanning electron microscopy
SE	Secondary electrons

SC	Semiconductor
S_{BET}	Brunauer–Emmett–Teller specific surface area
TEM	Transmission electron microscopy
TEOA	Triethanolamine
t	Time
T	Temperature
UV	Ultraviolet
UV-Vis DRS	UV-Vis diffuse reflectance spectroscopy
VB	Valence band
Vis	Visible
WE	Working electrode
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
wt. %	Weight %
2D	Two-dimensional
λ	Wavelength

Materials nomenclature

GCN	Bulk graphitic carbon nitride
GCNN	GCN subjected to thermal treatment at 500 °C
FLG	Few layer graphene
FLG _y /GCN	Hybrids of FLG x% (0.5, 1, 2, and 3 wt.%) with GCN
NiCeAl-LDH	NiCeAl- layered double hydroxide
CuAl-LDH	CuAl- layered double hydroxide
NiCeAl-LDH/GCNN	Hybrids of NiCeAl-LDH x% (0.5, 1, 1.5, 3, and 7 wt.%) with GCNN
CuAl-LDH/GCNN	Hybrids of CuAl-LDH x% (0.2, 1, 3, and 7 wt.%) with GCNN

List of publications

Hanane Boumeriame, Eliana S. Da Silva, Alexey S. Cherevan, Tarik Chafik, Joaquim L. Faria, Dominik Eder. Layered double hydroxide (LDH)-based materials: a mini-review on strategies to improve the performance for photocatalytic water splitting. *J. Energy Chem.* 46, 2022, 406.

Raquel A. Fernandes, Maria J. Sampaio, Eliana S. Da Silva, Hanane Boumeriame, Tânia Lopes, Luísa Andrade, Adélio Mendes, Joaquim L. Faria, Claudia Gomes Silva. Sustainable production of value-added chemicals and fuels by using a citric acid-modified carbon nitride optical semiconductor. *Appl. Catal. A*, 609, 2020, 117912.

Hanane Boumeriame, Bruno F. Machado, Nuno M. M. Moura, Philippe Serp, Luísa Andrade, Tânia Lopes, Adélio Mendes, Tarik Chafik, Eliana S. Da Silva, Joaquim L. Faria. Graphitic carbon nitride doped with few-layer graphene: an efficient 2D/2D heterostructure to separate charge carriers for improved LED-visible-light photocatalytic hydrogen generation. (Under review, November 2021, *Int. J. Hydrog. Energy*).

Hanane Boumeriame, Ana Coutinho, Manuel Prieto, Luísa Andrade, Tânia Lopes, Adélio Mendes, Nuno M. M. Moura, Tarik Chafik, Eliana S. Da Silva, Joaquim L. Faria. Enhanced visible-LED photocatalytic hydrogen generation from novel 2D/2D NiCeAl-LDH/g-C₃N₄ hybrids. (To be submitted).

Hanane Boumeriame, Eliana S. Da Silva, Dogukan H. Apaydin, Dominik Eder, Tarik Chafik, Alexey S. Cherevan, Joaquim L. Faria. Novel 2D/2D CuAl-LDH/g-C₃N₄ nanohybrids for visible light-driven photocatalytic H₂ and O₂ generation. (To be submitted).

List of communications

- Hanane Boumeriame, Eliana S. Da Silva, Dominik Eder, Tarik Chafik, Alexey S. Cherevan, Joaquim L. Faria. “Effective construction of a 2D/2D CuAl-LDH/g-C₃N₄ heterostructure for photocatalytic H₂ and O₂ generation”. European Congress and Exhibition on Advanced Materials and Processes – EUROMAT, 12 to 16 September 2021, Graz, Austria. (Oral communication).
- Hanane Boumeriame, Eliana S. Da Silva, Dogukan H. Apaydin, Dominik Eder, Tarik Chafik, Alexey S. Cherevan, Joaquim L. Faria. “CuAl-LDH/g-C₃N₄ Nanohybrids for Photocatalytic H₂ and O₂ Generation *via* Water Splitting”. XXVII Encontro Nacional da Sociedade Portuguesa de Química, 14 to 16 July 2021, Braga, Portugal. (Poster presentation).
- Hanane Boumeriame, Eliana S. Da Silva, Ana I. Coutinho, Manuel Prieto, Tânia Lopes, Luísa Andrade, Adélio Mendes, Nuno M.M. Moura, Tarik Chafik, Joaquim L. Faria. “Photochemical H₂ generation by a novel 2D/2D NiCeAl-LDH/g-C₃N₄ nanohybrid”. 14º Encontro Nacional de Química Física, 29 to 31 March 2021, Coimbra, Portugal. (Oral communication).
- Hanane Boumeriame, Eliana S. Da Silva, Dominik Eder, Tarik Chafik, Alexey S. Cherevan, Joaquim L. Faria. “2D/2D CuAl-LDH/g-C₃N₄ nanohybrid photocatalysts for visible-light-driven hydrogen production”. Eder Group Seminars, 16 October 2020, Vienna, Austria. (Oral communication).
- Raquel A. Fernandes, Maria J. Sampaio, Hanane Boumeriame, Eliana S. Da Silva, Joaquim L. Faria, Cláudia G. Silva. “Sustainable production of high value-added chemicals by citric acid modified carbon nitride optical semiconductor”. SP7 - 7th International Conference on Semiconductor Photochemistry, 11 September 2019, Milan, Italy. (Oral communication).
- Hanane Boumeriame, Eliana S. Da Silva, Bruno F. Machado, Philippe Serp, Tarik Chafik, Joaquim L. Faria. “Polymeric carbon nitride doped with graphene for light-driven hydrogen generation”. XXVI Encontro Nacional da SPQ, 24 to 26 July 2019, Porto, Portugal. (Poster presentation).
- Hanane Boumeriame, Eliana S. Da Silva, Bruno F. Machado, Philippe Serp, Tarik Chafik, Joaquim L. Faria. “Light-driven hydrogen generation by means of modified polymeric semiconductors”. DCE 2019 - Doctoral Congress in Engineering, 27 to 28 June 2019, Porto, Portugal. (Oral communication).

- Hanane Boumeriame, Eliana S. Da Silva, Tarik Chafik, Joaquim L. Faria. “NiCeAl-LDH/g-C₃N₄ as photocatalyst for light-driven hydrogen production”. XXIV Encontro Luso-Galego de Química, 21 to 23 November 2018, Porto, Portugal. (Poster presentation).

Chapter 1

General introduction

This chapter aims to provide a general overview regarding the current energetic challenges giving insights on the processes that can photochemically generate solar fuels (hydrogen) from water and sunlight. General motivation will be addressed focusing on the world's energy context, which is considered one of the primary challenges of the current century. According to recent research, the exploitation of renewable energy sources will become a trending key in science and industry. Solar light is an example of this renewable energies. However, new technologies are needed to harness its power, store and distribute it to customers. At the same time, a "hydrogen generation system" could be developed to solve the adverse effects of fossil fuels along with their increasing depletion; and provide a high-quality energy resource for a wide range of applications in an efficient, clean, and sustainable way. In this context, the photocatalytic water splitting process seems a viable approach to link those mentioned above, by providing a direct solar light-induced water conversion method to H_2 . However, for this to be successful is of primordial importance in designing novel photocatalytic materials that can respond to this demand. Therefore, a general introduction to the mechanism of photocatalytic water splitting by semiconductors is addressed. Emphasis will be given to the developments of semiconductors materials, especially two-dimensional (2D) materials. The research aims and objectives of this Thesis are included at the end of this chapter. The Thesis outline is also presented as means to initiate the discussion of the project's results.

1. Energy context

Nowadays, our society faces crucial issues that will affect our future. The highest concerning problems arising from the worldwide population growth include energy, water and food scarcity, environmental issues, diseases,^{1, 2} to name a few. One of the most critical factors that affect each of these concerns is the topic of energy. Without a reliable source of energy, it is not possible to answer adequately to these problems.¹ Therefore, a clean, secure, affordable and reliable energy supply is essential to overcome the modern challenges and govern our society towards sustainable growth.¹ Therefore, transitioning to new energy sources to fulfil the current fossil-based supplies such as oil, coal, and natural gas is required.

According to the U.S. Energy Information Administration International Energy Outlook 2021 (IEO2021), the world energy consumption will increase by around 60% in 2050,³ fossil fuels being the primary energy supply, marking a whopping 80% of world energy usage. However, renewable sourced energies are the world's fastest-growing energy sources, increasing 4.5% *per year* (**Figure 1**).³ It is also predicted that the actual fossil fuel usage will shrink due to their limited availability and significant threat to the environment.^{3, 4} As an additional consequence of this high carbon fuels consumption is the increase in CO₂ emissions (almost 50%) until 2040, which will have an obligatory negative impact on our climate.³ Decarbonising fossil fuels and future investment in nuclear energy and renewable energy sources are considered the only possibilities for solving our current and future energy issues.⁵⁻⁷ Decarbonisation of fossil fuels is a process where the amount of CO₂ involved is reduced during the utilisation of oil, coal and natural gas by a method of carbon capture and sequestration (CCS). In this process, the CO₂ produced by the power plant is collected and stored in oceanic or geological reservoirs.^{5, 6} The major limitation regarding these fuels is related to CO₂ storage. The nuclear energy option is considered carbon-free energy. However, the low availability of uranium restricts its long-term utilisation, as well as the dangers related to its use.^{5, 7} Renewable energy sources, such as solar, hydropower, wind, biomass, and geothermal, are inexhaustible non-harmful and considered as the optimal solution for the long-term. Being freely available and carbon-neutral makes renewable energy a feasible solution to overcome worldwide energy concerns.^{8, 9}

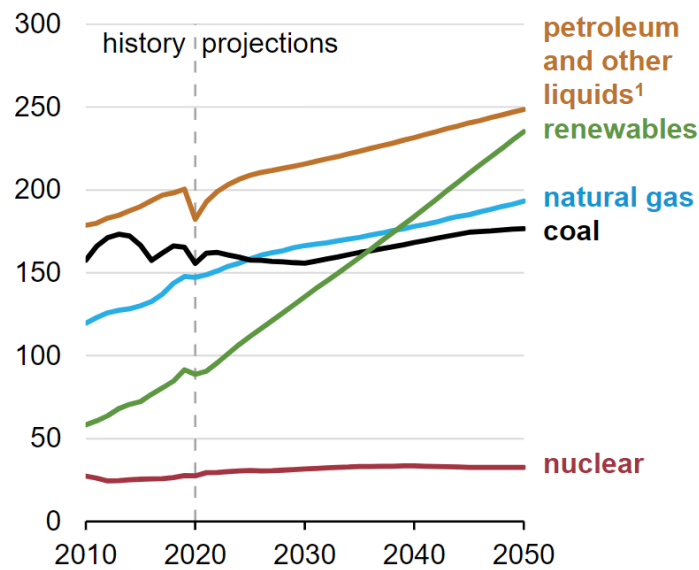


Figure 1. World energy consumption by fuel type, 2010-2050 (quadrillion Btu) Reproduced from International Energy Outlook 2021. Adapted from ref.³

The employment of renewable energy sources also shows some limitations as it often requires technological innovation, advances in materials science and manufacturing techniques. At present, rapid progress is being made in establishing methods of usage for all of the renewables as mentioned earlier, but so far, the most progress has been made in the conversion of solar energy and biomass use.^{9, 10}

2. Solar energy

Solar energy-based technologies are the most promising alternative due to the most potent energy source, *i.e.*, the Sun. This energy is transmitted to the Earth by electromagnetic waves being the driving force that sustains all life on our planet.^{8, 11}

Solar energy received at the top of the Earth's atmosphere is around 174 PW (petaWatt = 10^{15} Watt).¹¹ However, the energy intensity varies according to the Earth's position and orbital cycle, and with the longitude of a given point on the Earth's surface. The amount of energy hitting the top of the Earth's atmosphere when the Sun is directly overhead averages at 1366 W m^{-2} .^{8, 11}

Sunlight delivers energy to the Earth's surface through light photons with a wide wavelength range, accounting for ultraviolet (UV, 10 – 380 nm), visible (Vis, 400 – 700 nm), and near-infrared (NIR, 700 nm – 10^6 nm) light ranges with a total power of about 1000 W m^{-2} measured at sea level and distributed as 5, 42 and 53% for the UV, Vis and NIR ranges, respectively.¹¹ Broadly speaking, the Earth's surface receives only around 70% of the overall

radiation filtered by the atmosphere, and about 30% of it is reflected back into space. Further, the amount of solar energy striking the Earth in one hour is similar to the energy consumed by the world in one year, making solar power the most significant available energy source.^{8, 11}

Various technologies can convert, capture, and use photons. The photon energy can be converted to (i) electricity through photovoltaic solar cells, (ii) thermal energy by heating, and (iii) chemical energy, for instance, water splitting or CO₂ reduction.⁸⁻¹² However, and despite the promising potentialities of these technologies, they also show some drawbacks. Namely, solar cells can produce electricity directly from light, and therefore, this electricity can be used for any other application, including heating and chemical synthesis. However, the critical point is how costly solar cell energy and solar cell technologies are compared to others and, solar light availability.⁸⁻¹² Solar thermal energy can be extracted without any advanced technology using heat collectors, but it also depends on the availability of sunlight. Lastly, photon energy to chemical energy conversion requires more innovative methods yet has the advantage of accumulating and storing energy in chemical bonds, *i.e.*, hydrogen (H₂), which can be used as a fuel, alternative to fossil fuels, opening new prospects and possibilities for diverse applications.^{11, 13, 14}

2.1 Hydrogen fuel

Hydrogen (H₂) is the lightest of all existing elements and the most abundant chemical element in the universe.¹³⁻¹⁵ Besides being a very light and clean-burning fuel, it reacts quickly and easily with other chemical compounds, making it a very effective reactant. For that, H₂ can be used as a fuel for either direct combustion in an internal combustion engine or a fuel cell, generating only water as a by-product, with no greenhouse gas emissions (*e.g.*, CO₂), rendering it a storable and renewable fuel. Further, hydrogen possesses a higher gravimetric energy density (33.3 kWh kg⁻¹) if compared with traditional fuels like methane (12.8 kWh kg⁻¹), gasoline (12.4 kWh kg⁻¹) and diesel (11.8 kWh kg⁻¹).^{10, 15}

The hydrogen economy is an industrial system in which H₂ is the universal energy carrier. The idea of a hydrogen economy began in 1970 when John Bockris displayed the idea of generating H₂ through water electrolysis (both fresh and seawater) that would employ electricity produced by solar energy.^{14, 15} However, hydrogen economy concept has received much attention only during the last decades due to the increased concerns over energy supply security and the ensuing environmental issues. This H₂-based energy system is an advantageous option for providing high-quality energy services for a wide range of applications (**Figure 2**) in an

efficient, clean and safe way while achieving the United Nations proposed Sustainable Development Goals (SDGs).^{14, 16} The SDGs are a recent set of objectives to ensure a healthy lifestyle and commodity in daily life to every human, animal and plant, contemplating energy, water, food, education, safety and equality, among other factors.¹⁶ Hydrogen production *via* renewable means follows the need to comply with the SDGs due to the clear advantages it shows.

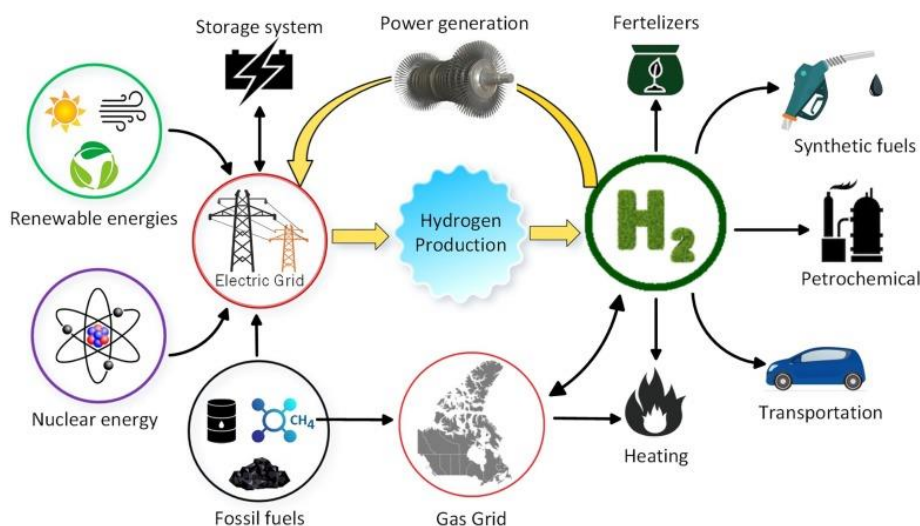


Figure 2. Hydrogen production and its integration in different energy fields. Adapted from ref.¹⁷

To ensure a sustainable pathway to H_2 production, photocatalytic water splitting appeared as an efficient way to directly generate clean H_2 from water using light (solar or simulated).^{18, 19}

2.2 Photocatalytic water splitting

Photocatalytic water splitting derives its inspiration and tries to mimic a natural mechanism that transforms sunlight into fuel, *i.e.*, photosynthesis, where plants consume sunlight and turn it into energy that is then used to feed the plant itself.^{20, 21} It is often referred to as artificial photosynthesis. Photocatalytic water splitting aims to use solar as an energy source and semiconductor photocatalysts as light absorbents and energy converters to generate H_2 , using it as a renewable fuel. Research studies into water splitting are in progress and increasing year after year. Major steps towards process application have already been made; however, most existing semiconductor materials suffer from low catalytic rates restricted by poor light absorption or rapid charge carriers recombination.²⁰⁻²² The following section aims to explain the features of the water-splitting process together with semiconducting systems.

2.2.1 General principles and mechanism

The concept of photocatalytic water splitting is based on a semiconductor (SC) and a light source to form electrons and holes (Eq. 1), which subsequently drive half-reactions of water oxidation and reduction yielding O₂ and H₂, following Eqs. 2 and 3.



Generally, water decomposition can be divided into two half-reactions:

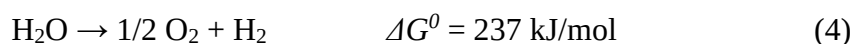
(i) water reduction to produce H₂ (Eq. 2)



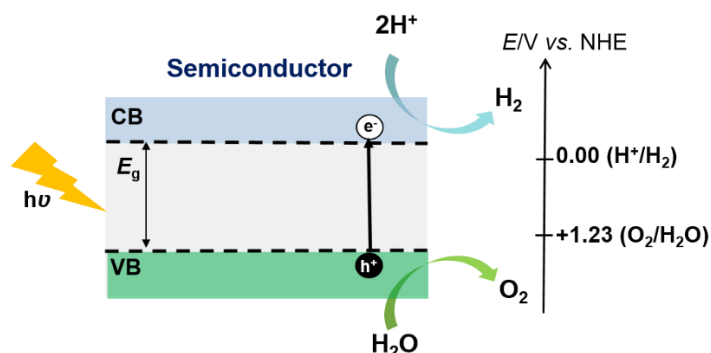
and (ii) water oxidation to produce O₂ (Eq. 3)



Thermodynamically, the overall water splitting reaction to generate hydrogen and oxygen (Eq. 4) is an energetically uphill and endothermic reaction with a standard Gibbs free energy change (ΔG^0) of 237 kJ/mol.²²⁻²⁴



From the thermodynamic perspective, photocatalytic water splitting can only proceed when the conduction band (CB) minimum of an SC is more negative than the reduction potential of H⁺/H₂ (0 vs normal hydrogen electrode (NHE)) and its valence band (VB) maximum is more positive than the oxidation potential of O₂/H₂O (+1.23 V vs NHE). This reaction occurs in three steps (**Scheme 1**): (i) the photocatalyst absorbs one photon with energy greater than the bandgap energy of the material, generating e⁻/h⁺ pairs, (ii) these photoexcited charge carriers separate and migrate to the surface of the photocatalysts (electrons to the CB and holes to the VB), and (iii) surface redox reactions between the charge carriers and the adsorbates take place according to the Eq. 2 and 3.²²⁻²⁵ The first two steps are highly dependent on the structural and electronic properties of the photocatalyst. Generally, high crystallinity positively affects the activity as the density of defects acting as recombination centres between photogenerated carriers decreases with increasing crystallinity.^{24, 26} On the other hand, the third step is promoted by the presence of a suitable cocatalyst.^{24, 27} The efficiency of each step contributes to the overall performance. Therefore, it is essential to consider all three steps when it comes to designing photocatalysts.



Scheme 1. Principle of water splitting on semiconductor photocatalysts.

2.2.2 Photocatalysis and semiconductors

Concerning photocatalysis, to comprehend it better, and according to its etymology, the term "photocatalysis" is derived from the Greek word "photo" (light) and the word "catalysis" material (substance) that modifies the activation energy of the reaction, thereby influencing its kinetics.^{26, 28} Hence, photocatalysis is a process in which the reaction is accelerated through the actuation of light.^{26, 28}

The concept of photocatalysis originated in 1911 from the study on the illumination of zinc oxide (ZnO) in the whitening of the dark blue pigment of Prussian blue by Alexander Eibner.²⁹ However, few studies have been done in that period.³⁰ The most well-known and cited publication in photocatalysis refers to the pioneering work of Honda and Fujishima in 1972 on photoelectrochemical water splitting using titanium dioxide (TiO_2) as a semiconductor anode under UV light irradiation.³¹ Following their discovery, great efforts have been made to develop new materials and entirely photocatalytic processes.

An SC is a solid-state material with a band structure in which the CB is separated from VB by a suitable bandgap (**Scheme 1**). The working principles were aforementioned, following light absorption, electron excitation and migration and e^-/h^+ pairs reaction and recombination. To be a suitable catalyst for photocatalytic water splitting reactions, the VB of an SC should be more positive than the oxidation potential to oxidise water, and the CB should be more negative than the reduction potential.³²⁻³⁵ However, the width of the bandgap determines the irradiation that can be used for the water-splitting process. So far, most of the catalysts developed are active under UV irradiation. UV is only about 4% of the solar spectrum and Vis light is about 46%.⁸ Therefore, an SC capable of absorbing Vis light could improve the efficiency of the process. The limit wavelength between Vis and UV light is 400 nm, which corresponds to an energy of 3.0 eV; hence, the bandgap of a Vis-active catalyst for water splitting should be in the range of

$1.23 \text{ eV} < E_g < 3.00 \text{ eV}$.³²⁻³⁴ Even if all these requirements are met, charge recombination can prevent the material from being active and efficient for water splitting. As electrons and holes migrate to the surface, they may recombine. This phenomenon reduces the number of charges required for redox reactions and decreases catalyst activity.³²⁻³⁵

Several parameters, such as bandgap energy, band-edge position, light absorption ability and charge separation, should be considered when selecting an SC catalyst for photocatalytic water splitting. Among various other SC photocatalysts, two-dimensional (2D) materials are promising candidates for water splitting applications due to their sheet-like structures and electronic, optical, and mechanical properties.³⁵⁻³⁸

3. 2D semiconductors for water splitting

Since the first synthesis of the 2D material, graphene (GR), by Novoselov and Geim in 2004,³⁹ the application of 2D materials has become an enticing topic for both theoreticians and experimentalists. 2D materials are classified as free-form crystal with a plane size of more than 100 nm and a thickness of only one or a few atomic layers, and usually possess a very high surface area that provides active catalytic sites.^{36, 38, 40-42} In addition, the ultrathin thickness of layered structure of 2D materials aids the process of light absorption even at a low flux density and shorten the distance for charge carriers migration, hence, reducing the recombination rate.^{36, 40-42} Moreover, the dimension reduction of the material may change the energy band structure. The visible light response and photocatalytic efficiency of the material can be improved by changing the positions of the CB and the VB edges.^{36, 40-42}

Furthermore, the optoelectronic properties of 2D materials-based photocatalysts are expected to offer intriguing features and benefits developing new prospects of materials design compared to other dimensionalities. In one example, Yang *et al.*⁴³ synthesised a 2D graphitic carbon nitride (g-C₃N₄, labelled as GCN) nanosheets material by liquid-phase exfoliation for photocatalytic hydrogen evolution reaction (HER). The 2D GCN exhibited an H₂ evolution rate of 93 $\mu\text{mol h}^{-1}$ and a quantum yield of 3.75% at 420 nm, in the presence of 3 wt.% of platinum (Pt). In another example, using layered double hydroxides (LDH) as 2D nanomaterials, Silva *et al.*⁴⁴ investigated a series of ZnTi, ZnCe and ZnCr-LDH at different Zn-to-metal atomic ratio (from 4:2 to 4:0.25) for O₂ evolution through photocatalytic water splitting, in which ZnCr-LDH proved to be the best matching case, with an atomic ratio of 4:2.

However, some 2D semiconductors often suffer from the low process efficiency and fast recombination of e^-/h^+ pairs. Significant efforts have been made to develop and modify

semiconductor photocatalysts that are capable of using visible light.^{38, 45} The process includes metal ion or non-metallic element doping, dye sensitisation, copolymerisation, morphological tuning and creation of 2D heterojunctions by assembling with another SC material.^{24, 36, 38, 45} The latter process is considered one of the most effective and feasible approaches due to the unique advantages, that include (i) accessible interfacial contact, which consequently increases active catalytic sites, (ii) low intrinsic resistance and short transport path which facilitates charge transfer, therefore, decreasing the charge carrier recombination, (iii) ultrathin thickness which is beneficial for light absorption.^{24, 45, 46} As a result, the construction and use of 2D/2D heterostructures materials have become one of the hottest research topics.

Another exciting field in nanomaterials science is the formation of heterojunctions between two or more materials. For photoresponsive applications, there are two fundamentally different types of semiconductor-semiconductor heterojunctions: p-n heterojunction and *non*-p-n heterojunction system.^{33, 45, 46}

The semiconductor p-n junctions are when p- and n-type semiconductors come into contact. They form a p-n junction with a space-charge region at the interface, which creates a built-in electric field that can transfer electrons and holes in the opposite direction (**Figure 3**).³³ Generally, the electrons are transferred to the CB of the n-type semiconductor and the holes are transported to the VB of the p-type semiconductor within the space-charge region. Numerous advantages can be achieved in this type of heterostructures: (i) rapid charge transfer to the catalyst surface; (ii) longer lifetime of charge carriers; and (iii) more effective charge separation.³³ All of these features provide the p-n heterostructures with improved photocatalytic activity.

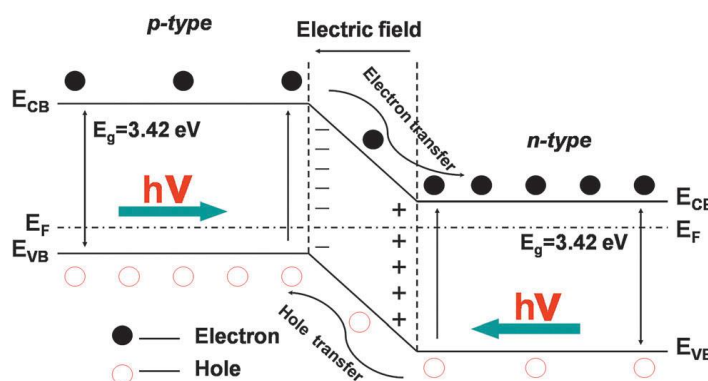


Figure 3. Schematic showing the energy band structure and e^-/h^+ pair separation in the p-n heterojunction. Adapted from ref.³³

The semiconductor materials can be branded into either an n- or p-type based on the nature of the donor and acceptor proprieties. Hence, the synthesis method is a crucial step to obtain a composite with an effective p-n junction. Nerveless, the morphology and crystallinity of the heterojunction play an essential role in photocatalytic activity.^{33, 45, 46} For example, Liu *et al.*⁴⁷ synthesised a p-n junction composite of GCN and Cu₂O by the *in-situ* growth method. The good photocatalytic activity towards degradation of tetracycline was attributed to effective charge carrier separation due to the formation of a p-n junction.

The *non*-p-n heterojunction systems are composed of two SC with staggered band structure configuration, and they can be n-n or p-p type heterojunctions. These band gap and band positions of the two semiconductors are tightly bonded with each other, therefore facilitate the transfer of photogenerated electrons and holes.^{33, 45, 46} The difference between this type of junction and the p-n junction is that the p-n junction contains a space-charge region and a built-in electric field from charge transfer during equilibration. While in a *non*-p-n junction, the photocarrier collection happens *via* band offsets.^{33, 45, 46, 48}

There are three systems of heterojunctions that are differentiated based on the semiconductors bandgap and its relative band positions (**Figure 4**).^{33, 48} The heterojunction type-I with a straddling gap, in which the CB of SC-I is higher than the CB of SC-II and the VB of SC-I is lower than VB of SC-II (**Figure 4a**); type II (staggered bandgap) in which the CB and VB of SC-I are above the VB of SC-II, respectively, thereby the CB of SC-II is acting as an electron sink, and the VB of SC-I serves as a hole sink (**Figure 4b**); and type-III with broken bandgap, the CB of the SC-II is below the VB SCI (**Figure 4c**); thus, the holes are transferred to SC-II and the protons can be reduced on both materials.^{33, 45, 46, 48, 49}

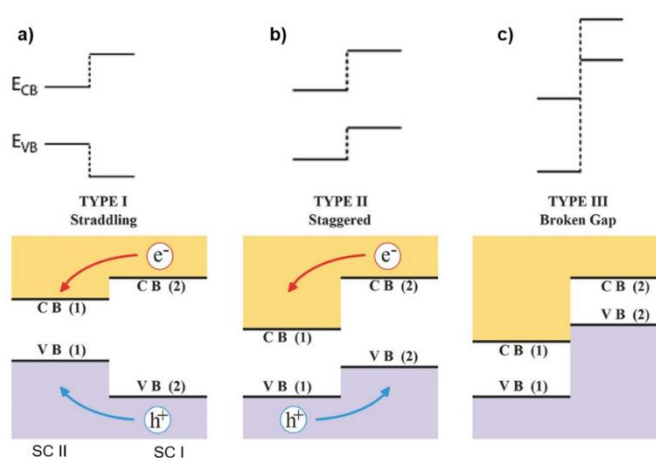


Figure 4. Types of semiconductors heterojunctions according to the band position. Adapted from ref.⁴⁸

In addition to heterojunctions types, the charge transfer mechanism is also a crucial point, depending on the light activation of both or only one of the SC. Three charge transfer mechanisms are proposed in the literature.⁵⁰ One is the sensitisation mechanism (**Figure 5a**), where only one semiconductor is activated by light. In this case, the photogenerated electron migrates from SC-I with a higher CB position to the CB of SC-II; therefore, it promotes spatial separation and reduces charge recombination. The type II heterojunction mechanism happens when the two semiconductors are excited by light (**Figure 5b**). The photogenerated electrons will migrate from the CB of the SC-I to SC-II and the generated holes in the VB of SC-II will transfer to the VB of SC-I. Hence, SC-I can act as a hole sink and the SC-II as an electron sink, thus, promoting charge separation and improve the photoactivity. The third mechanism consists of the Z-scheme (**Figure 5c**), where the relative band alignment is like type II heterojunctions. The Z-scheme mechanism occurs when the semiconductors are exposed to light: the photogenerated electrons in SC-II and the photogenerated holes in SC-I remain in their respective bands; meanwhile, the photogenerated electrons on SC-I and holes on SC-II recombine.⁴⁹⁻⁵¹ In broader terms, the photogenerated holes in the VB of SC-I and the electrons in the CB of SC-II with strong redox capacity/potential are preserved and can participate in reduction and oxidation reactions, respectively. Consequently, the reductive and oxidative sites are separated, resulting in enhanced photocatalytic activity.⁴⁹⁻⁵¹

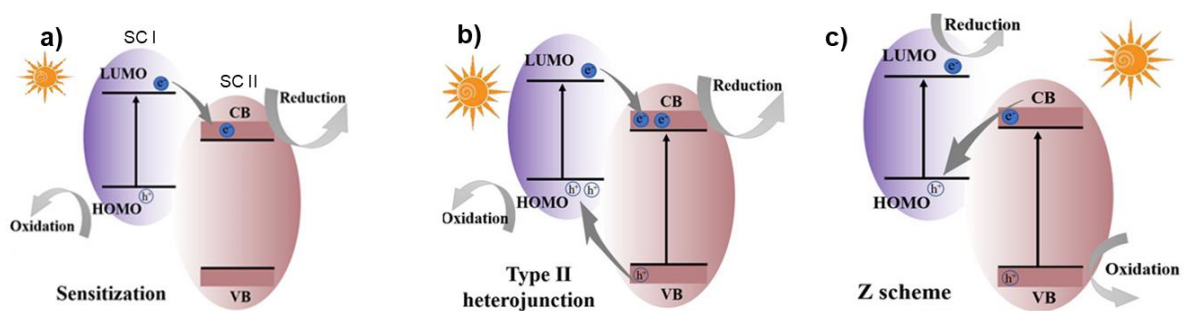


Figure 5. a) Sensitisation mechanism; b) type II heterojunction, and c) direct Z-scheme. Adapted from ref.⁵⁰

Different types of heterojunctions can be designed based on individual components, bandgaps and band positions to achieve an effective charge separation and allow for enhanced visible-light activity key parameters to enhance the activity of a particular photocatalyst. Until now, various 2D materials have been discovered by researchers. In the next chapter, promising and recent 2D materials, such as graphitic carbon nitride (GCN), layered

double hydroxides (LDH), and graphene (GR) and its derivatives (GRDs), are presented in greater detail in the context of their photocatalytic water splitting application.

4. Aim of the work and Thesis outline

Water-splitting technology as a sustainable and renewable means to photocatalytically generate H_2 is classed as a promising strategy to mitigate energy issues and produce clean and large-scale fuel energy. The selection and design of highly efficient and visible-light response SC is an undeniable challenge. On this basis, the objectives of this Thesis are focused on: (i) design and synthesis of highly active heterogeneous semiconductor photocatalyst, mainly precisely layered nanomaterials as g- C_3N_4 (GCN), LDH and few-layer graphene (FLG); (ii) engineering the properties of the semiconductor GCN in order to boost its photocatalytic activity for solar fuels production. This has been done by modulating its properties through thermal exfoliation and fabrication of 2D/2D hybrid materials of GCN/FLG and GCN/LDH; (iii) photocatalytic tests of individual and composite materials towards water splitting to generate H_2 and O_2 under visible light irradiation using green and economical light sources (*i.e.*, high-intensity light-emitting diodes LED); (iv) characterise the materials in order to correlate the GCN modifications (optical, electronic and morphological) with its photoactivity.

This dissertation is divided into six chapters, the first two chapters related to the introduction and state of the art of 2D semiconductor materials.

Chapter 1 consists of a general overview of the thematic related to energetic crisis and the technologies developed to overcome this, particularly photocatalytic water splitting processes. Chapter 2 provides the state-of-art about some type of layered semiconductor materials and their application in photocatalytic water splitting. The SC materials described in this chapter are mainly the GCN, LDH and GRDs, as these were the primary materials employed in this Thesis.

Chapter 3 provides a summarised overview of the characterisation techniques employed during this Thesis.

Chapter 4 reports the synthesis of bulk GCN and its modification with FLG, a conducting material, through an *in-situ* calcination process, aiming to obtain a high-efficient photocatalytic hydrogen production material. A LED system was used as a light source, and EDTA as sacrificial and Pt as cocatalyst. The effect of morphology and loading of FLG on the surface and the activity of GCN is discussed.

Chapter 5 reports the fabrication of LDH/GCN heterostructures and their application for photocatalytic water splitting. With this purpose, two different types of LDH photocatalysts have been synthesised; this chapter is subdivided into two parts: the first part consists of performing a thermal treatment to bulk to obtain GCN nanosheets followed by modification with LDH to design a 2D/2D heterostructure. The LDH used in this part is a ternary NiCeAl-LDH. The composites were prepared *via* impregnation while varying the loading amount of LDH. The formed heterostructures were tested for photocatalytic H₂ production using a LED system as a light source, EDTA as a sacrificial agent and Pt as cocatalyst. In the second part of chapter 5, the fabrication of a 2D/2D heterostructured composed of CuAl-LDH and GCN nanosheets through an electrostatic co-assembly strategy is addressed. The materials were tested towards both visible-light-driven photocatalytic hydrogen and oxygen generation. However, no additional cocatalyst was employed in this case, and TEOA was used as a sacrificial agent.

Chapter 6 includes the conclusions and suggestions for future work.

Chapter 2

Literature review

This chapter provides an overview of 2D semiconductor photocatalysis used in this research, namely graphitic carbon nitride (g-C₃N₄, abbreviated as GCN), layered double hydroxides (LDH) and graphene-derivatives (GRDs), along with their application for photocatalytic water splitting. Furthermore, the 2D/2D heterostructures obtained through the combination of these materials were also explored in a way to understand the synergistic effect and electrostatic bond between both individual materials. Finally, the reaction parameters that affect the photocatalytic water splitting results were reviewed, mainly type of light source, usage of cocatalyst and selection of sacrificial agents.

Part of this chapter is based on the following article:

Boumeriame H.; Da Silva E. S.; Cherevan A. S.; Chafik T.; Faria J. L.; Eder D. Layered double hydroxide (LDH)-based materials: a mini-review on strategies to improve the performance for photocatalytic water splitting. *J. Energy Chem.* 46, **2022**, 406-43.

2.1 Graphitic carbon nitride

GCN has attracted widespread interdisciplinary interest as a metal-free and visible-light-activated photocatalyst in the fields of solar energy conversion, environmental remediation, and sensors. This section will include a general description of the material, synthesis routes, and application, mainly in the field of photocatalytic water splitting.

2.1.1 Generality

GCN is one of the oldest artificial polymers reported back in 1834 by Berzelius and Liebig and named melon.^{52, 53} The resulted compound was a linear polymer-based of triazine and tri-s-triazine basic monomers connected through secondary nitrogen atoms. The first description of this structure was available at the beginning of the 1920s. In 1922, Franklin described the formation of a C_3N_4 material as the final product of heating melon.⁵⁴ In 1937, Pauling and Sturdivant suggested the coplanar tri-s-triazine unit as the basic structural motif for these polymeric derivatives.⁵⁵ Three years later, Redemann and Lucas found a formal similarity between graphite and melon, wherein the melon vacancies are filled by three carbons and one N atom.⁵⁶ For a long period (around 150 years), research on melon-based C_3N_4 was halted due to unconfirmed species caused by chemical inertness and insolubility in most solvents. Only in the beginning of the 1990s, the research in C_3N_4 was fomented, and a significant number of works focused on the synthesis and on the crystalline structure of carbon nitride materials.^{53, 57} These findings lead to an explosion of research works regarding the fabrication of different polymers based on C_3N_4 . The known functional groups for C/N compounds that allow the formation of a large number of different structures and phases of C_3N_4 are varied, namely, cyano- (NC-), isocyano- (:CN-), azido (N_3 -) and diazo- ($N=N=$) groups, among others, as described by Kroke *et al.*⁵⁸ In general, there are seven different phases of C_3N_4 , denominated as α - C_3N_4 , β - C_3N_4 , cubic C_3N_4 , pseudo-cubic C_3N_4 , g-h-triazine, g-o-triazine, and g-h-heptazine (commonly referred as g- C_3N_4) with respective bandgaps of 5.49, 4.85, 4.30, 4.13, 2.97, 0.93, and 2.88 eV. Under ambient temperature and pressure conditions, the g- C_3N_4 is the most stable allotrope, with a base unit of tri-s-triazine being energetically favoured.⁵⁹⁻⁶² In 1996, Teter and Hemley,⁵⁹ demonstrated for the first time that tri-s-triazine units are bounded through a trigonal plane coordinated by N atoms. In this sense, a graphite-like structure is formed wherein g- C_3N_4 has a planar structure and aromatic rings with delocalized π electrons. Liu and Wentzcovitch⁶² showed that the planar sheets of C_3N_4 could be stacked in rhombohedral ways (*i.e.*, ABCABC stacking), which lead to a crystalline matrix with an R3m

spacing group. Alves *et al.*⁶³ demonstrated that the layers of C₃N₄ (*sp*² hybridisation) could be constructed *via* two coordinated N atoms leading to a P2mm spacing group.^{63, 64}

All in all, the utilisation of GCN in the heterogeneous catalysis field began only around 2006. In 2009, Wang *et al.*⁶⁵ reported for the first time the use of GCN as a photocatalyst for hydrogen production through water splitting. Since then, research on GCN has grown, in specific for photocatalysis. In the coming section, it will be given an overview of the design and synthesis of GCN materials as well as its different modification approaches.

2.1.2 Synthesis and modification of GCN

In general, GCN is obtained by thermal condensation of precursors rich in N and C atoms, such as cyanamide, dicyandiamide, melamine, urea, thiourea, and others like ammonium thiocyanate and guanidine carbonate.⁵⁷ The primary tectonic units, triazine and tri-s-triazine ring structures to form GCN allotropes are shown in **Figure 6a, b**. For each precursor, the thermal decomposition can occur with different polyaddition or polycondensation mechanistic pathways (**Figure 6c**). For instance, Wang *et al.*⁶⁵ synthesised GCN by using a combination of polyaddition and polycondensation processes in which the cyanamide precursor was condensed to dicyandiamide and melamine at a temperature range of 200 – 235 °C. It was observed that melamine-based products were still remnant when the temperature was around 335 °C, and above 390 °C, the structure of melon (tri-s-triazine) was detected. Overall, at the temperature of 520 °C, the crystalline phases of GCN appear to contribute to the formation of tri-s-triazine and s-triazine-based GCN. Theoretically, at around 600 °C, tri-s-triazine becomes unstable and above 700 °C the polymeric GCN decomposes.⁶⁶

In another work, Thomas *et al.*⁵² calculated the polyaddition and condensation reactions by the *ab initio* method to clarify the reaction path with further details. Based on density functional theory (DFT) calculation using a plane-wave basis set with energy cut-off at 550 eV, the authors demonstrated that the cohesive energy of the molecules increased along the polyaddition pathway, confirming that melamine was produced upon heating of the cyanamide. Furthermore, the calculation indicated that the shape of the melon chain is determined by a rivalry between an energy gain by extending the π -electron system into a linear chain and repulsion between the lone pair of electrons located on the N atom on the edges. When the GCN linear chain formed, it remains highly distorted due to the interaction of several N atoms on the tri-s-triazine edges to optimise their distance and location. Similarly, Kroke *et al.*⁵⁸ performed another DFT analysis, indicating that the polycondensation of melamine, cyanamide, dicyandiamide or urea formed a melon polymer from the melem units, and confirming that tri-s-triazine based

structures are 30 kJ mol^{-1} more thermodynamically robust than s-triazine, making tri-s-triazine the most putative unit for GCN.

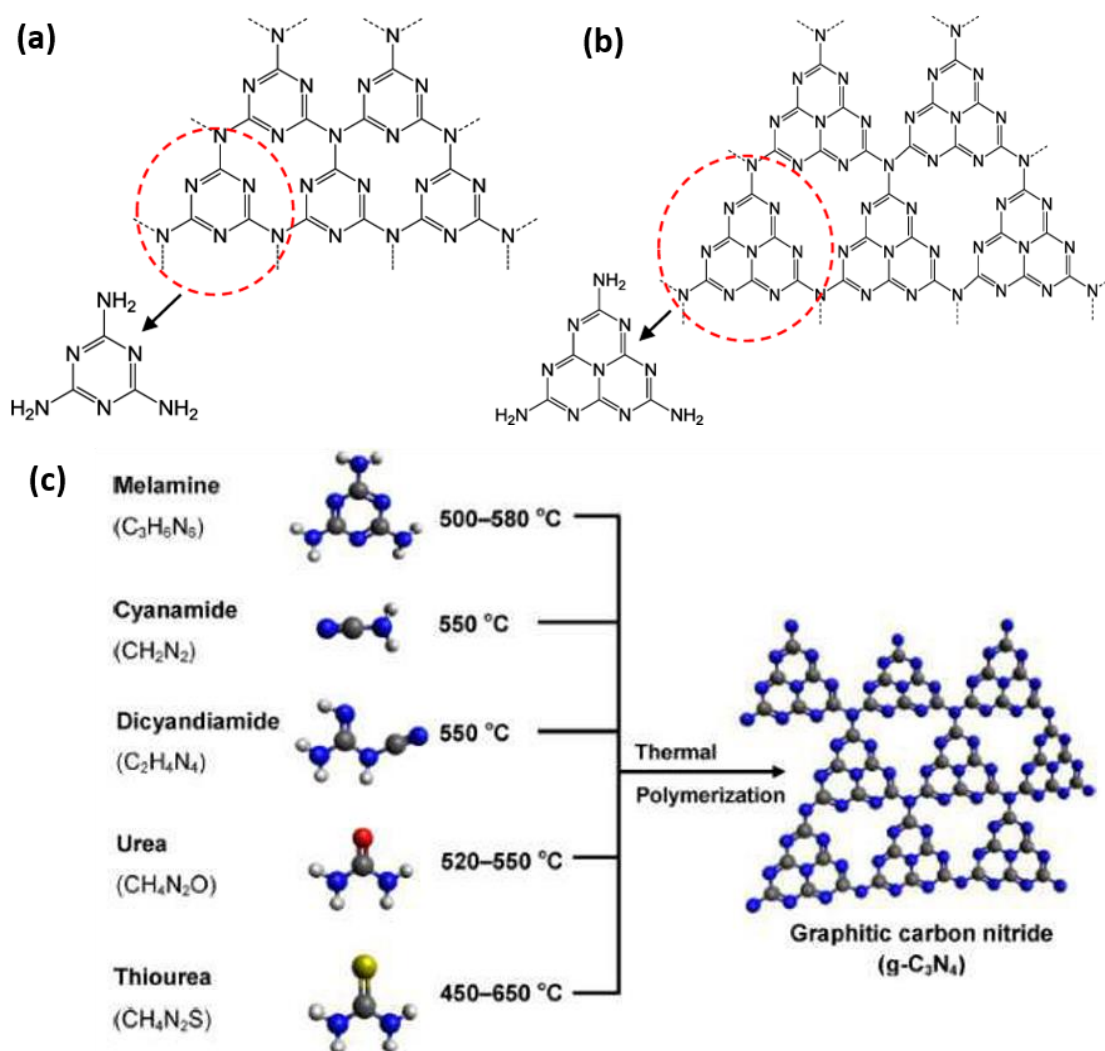


Figure 6. a) Triazine, b) tri-s-triazine (heptazine) GCN structures, c) thermal polymerisation of various GCN precursors undergoing thermal polymerisation. The black, blue, white, red, and yellow balls denote C, N, H, O, and S atoms, respectively. Reprinted from Ref.⁵⁷

Several results pointed out how various types of precursors and treatments can strongly influence the polymerisation degree and physicochemical characteristics of the reporting GCN, such as structure, specific surface area, porosity, and light absorption. A comprehensive summary of several types of synthesis techniques, as well as modification strategies, will be further elaborated in the next sections.

Precursor type, temperature, and time reaction effects

Significant efforts have been made to synthesise GCN using different C and N rich precursors. Several papers focused on the impact of the precursor on the final material. For instance, Zhang *et al.*⁶⁷ synthesised urea-derived GCN at 550 °C for 3 h. The obtained material possesses a porous structure with small flat sheets due to generated gases during the process. These generated gases NH₃ (at low temperature) and CO₂ (at a higher temperature) play a key role in the porosity of the final obtained material. The obtained urea derived GCN possess higher surface area and pore volume compared to GCN obtained with thiourea and dicyandiamide precursors, which favourite the photocatalytic activity. Another similar study performed by Martin *et al.*⁶⁸ reported the synthesis of GCN under comparable conditions using three distinct precursors (urea, thiourea, and dicyandiamide). The urea derived GCN performed higher photocatalytic H₂ evolution comparing to thiourea and dicyandiamide-derived GCN. The authors attributed this to the increased surface area, a greater degree of polymerisation, better charge carrier separation, and movement of delocalised electrons from the oxygen-containing urea precursor.

Mao *et al.*⁶⁹ reported the synthesis of GCN through a pyrolysis process of two different precursors, melamine and urea, under the same conditions (*ca.* 580 °C for 3 h). They found that the urea-derived GCN exhibited a higher surface area than the melamine-derived GCN, 39.5 and 3.7 m² g⁻¹, respectively. They also found that urea-derived precursor induces effective photoinduced charge separation and better photocatalytic CO₂ reduction. This enhancement was explained by the porous structure of urea derived GCN that increases the number of active sites and decreases the photoinduced charge carrier recombination rate. It is fundamentally observed that despite the precursor, different characteristics can be obtained.

To obtain a perfectly layered GCN material, the C/N ratio should be 0.75. This ratio can be developed by a suitable selection of precursors and condensation techniques. Yan *et al.*⁷⁰ described the design of GCN using melamine as a precursor at different heating temperatures. The study demonstrated that when the temperature increased from 500 °C to 580 °C, the C/N ratio varies from 0.721 to 0.742 and the bandgap decrease from 2.80 eV to 2.75 eV. This indicated that amine functional groups existed with about 2% of hydrogen content when the molar ratio of C/N is less than that of the ideal GCN (0.75) due to structural defects and incomplete condensation. This was attributed to the presence of NH/NH₂ amine groups within the structure which allows a better interaction between the sheets and reduces the mobility of charges within the sheet. In another work, using urea as the precursor, Liu and co-workers⁷¹ formed GCN *via* thermal decomposition process at a temperature from 400 to 550 °C and under ambient pressure. Concerning the influence of temperature, authors have experimented with

different calcination heating ramps and stages, altering the time and temperature. The authors observed with XRD analysis that there was no detected shift for the peak at 27.5° when the temperature was lifted to 550°C , which was due to graphitic-like structure. However, when the temperature increased from 400 to 450°C , the peak at 10.7° shifted to 13.1° ; further, this peak showed no shift when the calcination temperature increased from 450 to 550°C . This indicates that the graphitic-like layered structure was initially developed, followed by the creation of in-planar ordering occurred at temperatures greater than 450°C . Mo *et al.*⁷² studied the effect of temperature used during the thermal condensation process. They reported that GCN is formed only after a temperature of 500°C using melamine as the precursor. The authors also observed the formation of several melamine derived compounds at 450°C , and with increasing temperature from 600°C to 650°C , the material becomes highly porous. The difference in the structure led to an obvious redshift in the maximum absorption, which corresponds to an increase of π -plane conjugation and to an enhanced degree of polymerisation. This resulted in a better charge carrier separation and narrowing bandgap. Gu *et al.*⁷³ tailored the structures of melamine-derived GCN photocatalysts by varying the calcination temperature through air-assisted thermal polymerisation and etching processes. The samples structures evolved from bulk GCN to nanosheets, rolled nanosheets, nanotubes, nanoflakes, and nanoparticles when synthesised at various temperatures. Dong *et al.*⁷⁴ were interested in the impact of the heat treatment time. The authors prepared urea-derived GCN at 550°C , and they observed that the surface area was increased from 31 to $288\text{ m}^2\text{ g}^{-1}$ when the time thermal-treatment was prolonged from 0 to 240 min due to the increased porosity and decreased layer thickness (**Figure 7**). Moreover, as the treatment time increases, the stacking of the sheets decreases, which assigned to the hydrogen bonds between the melon units and the NH/NH_2 groups. In other words, when the treatment time increases, the number of NH/NH_2 groups decreases, leading to a decrease in the number of sheets. The further increased time treatment leads to a layer-by-layer exfoliation of the GCN (**Figure 7**), thus increasing the specific surface area. The effects of thermal process duration and temperature on GCN can serve to gain a better understanding of bandgap and nanoarchitecture engineering for superior photocatalysis.

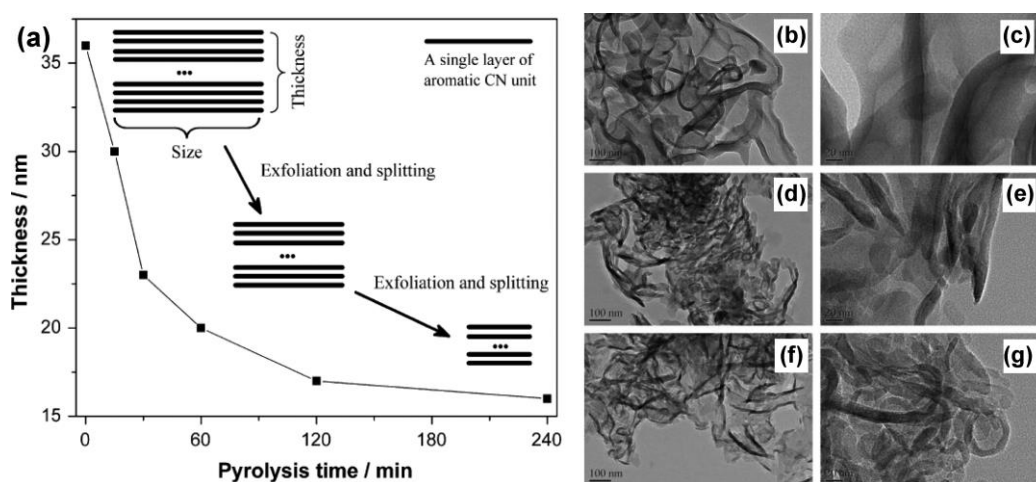


Figure 7. Relationship between the thermal duration and layer thickness of GCN and diagram for the layer-by-layer exfoliation and splitting mechanism of GCN with decreased thickness and size. TEM images of GCN synthesised at 550 °C for (b–c) 0 min, (d–e) 60 min, and (f–g) 240 min, excluding the heating-up time. Reprinted from ref. ^{57, 74}

The nature of the reaction atmosphere is another parameter that determines the final structure of GCN. It is assumed that based on the atmosphere used, it might induce disordered structure defects and greater or lower degrees of C and N vacancies. Defects on the GCN structure are interesting in photocatalysis since the controlled mesoporosity increases the number of active sites within the material without destroying its structure. In parallel, C and N vacancies incorporate intermediate energy levels within the GCN electronic structure, *e.g.*, additional energy bands between the VB and the CB, thereby increasing the optical reaction of the photocatalyst.⁷⁵ For instance, Niu *et al.*⁷⁶ used H₂ atmosphere as a post-calcination step to introduce N vacancies on GCN structure. The authors demonstrated that the small size of H₂ could easily access the channels among the layers to interact, therefore react with the skeleton atoms in GCN to form vacancies, which leads to enhanced optical absorption of GCN (above 460 nm) and to narrow bandgap (from 2.78 to 2.03 eV). Furthermore, the deduction of higher hydrogen bonding interactions facilitates distortion in the planar structure of the GCN, forming lone pairs on the edge of N atoms in tri-s-triazine-based GCN units within the π -conjugated system. This new location leads to a new electronic transition $n \rightarrow \pi^*$, which enables a higher electron density in the π -conjugated system, facilitates electron mobility in the CB and initiates the photocatalytic process. In another study, Dong *et al.*⁷⁷ reported the use of N₂ during GCN synthesis. The introduction of N vacancies has contributed to a better photocatalytic N₂ fixation ability, possibly due to the improved separation performance of photogenerated charge carriers and the electron transfer from GCN to adsorbed N₂. The existence of lattice disorders and

defects within the GCN structure, regardless of the atmosphere used, contributes to the development of midgap states, also known as "band tail" states. These modifications to GCN structure help to improve the excitation of e^-/h^+ pairs and the optical response of the photocatalyst.^{78, 79}

Precursor treatment effect

Pre-treatments of precursors by various methods, namely using acid solution (HCl, H₂SO₄, HNO₃), is considered as an easy technique to ameliorate the physicochemical properties of GCN. Yan *et al.*⁸⁰ report the synthesis of GCN by thermal polymerisation of melamine treated with H₂SO₄. It was found that the specific surface area of the treated precursor was higher than the one synthesised without treatment (15.6 m² g⁻¹ vs 8.6 m² g⁻¹). The authors attributed the results to the different condensation process during which the sublimation of melamine was suppressed. Gao *et al.*⁸¹ demonstrated that treating melamine with HNO₃ and ethylene glycol results in the forming of GCN with nanotube-like morphology, which leads to better charge carriers transfer and separation. Another modification strategy proposed by He *et al.*⁸² consisted of employing sulphur as a solvent mediator to obtain melamine-derived GCN. The obtained GCN has uniform pores with an average pore size of 50 nm, accompanied by increased surface area from 17 m² g⁻¹ to 46 m² g⁻¹ for bulk GCN and sulphur-mediated GCN, respectively.

In general, one step pre-treatment of GCN precursors might result in GCN with various morphologies, such as belt-like or ribbon-like porous with aggregated bundles.^{67, 83, 84}

Besides the above-mentioned strategies, the elemental doping, exfoliation and heterostructure and/or hybridisation techniques show a substantially influential impact on the structural, morphological and electronic properties of GCN.

Doping

Doping is an effective approach to tailor the electronic structure and to narrow the bandgap, therefore modifying the light absorption ability. Generally, two types of elemental doping, *i.e.*, non-metal and metal doping, are employed. In 2010 Wang *et al.*⁸⁵ reported fluorine (F)-doped GCN by introducing NH₄F into the GCN framework, thus leading to change in the hybridisation of C atoms (sp^2 to sp^3) and therefore a change in the HOMO-LUMO structure. The authors attributed this change to the electronegativity of fluorine that binds easily to the C instead of N. The F-doped GCN exhibits a narrower bandgap compared to the non-doped GCN (2.69 vs 2.63 eV), which therefore resulted in an enhanced photocatalytic H₂ generation.⁸⁵ In the same year, Liu *et al.*⁸⁶ reported sulphur-doped GCN by post-synthesis treatment in H₂S. The resulted

material exhibited upshifting of the VB width and enlarged CB minimum due to the homogeneous distribution of the S element and to reduced particle size after the doping process. Thus, enhanced the photoactivity of H₂ generation under visible light irradiation, being 8 times higher than pristine GCN. In another study, Dong *et al.*⁸⁷ prepared carbon self-doped GCN by treating melamine with absolute ethanol. The C self-doping lead to the substitution of bridging N atoms by C atoms which alter the intrinsic electronic and band structures (narrowing the bandgap from 2.72 eV to 2.65 eV). The C-doped GCN enhanced the visible-light-driven H₂ evolution by about 1.42 times compared to the pristine GCN.

Exfoliation

The exfoliation procedure involves the use of mechanical, physical or chemical force to separate the individual GCN layers. This means that the bulk thickness will decrease, and the surface area will increase. This phenomenon is likely due to the weak van der Waals forces between the GCN layers. The most known approaches to exfoliate bulk GCN are post-thermal, chemical, mechanical, and ultrasonication-assisted liquid techniques.^{43, 88-94} Yang *et al.*⁴³ reported the synthesis of GCN nanosheets *via* liquid exfoliation process using various organic mediums such as isopropanol (IPA), *N*-methyl-pyrrolidone (NMP), acetone and ethanol. The authors found that IPA was the most appropriate solvent, resulting in a material with a high surface area *ca.* 384 m² g⁻¹ and a thickness of 2 nm. Furthermore, no precipitation was observed after 4 months of storage, proving the well-dispersion stability, dissimilar to the GCN prepared in ethanol and acetones, which showed precipitation after only 2 days of storage. In addition to that, the charge transfer resistance was substantially reduced by about 75% after exfoliation compared to the bulk GCN, as confirmed by electrochemical impedance spectroscopy (EIS) measurements, which therefore enhanced the photocatalytic activity towards H₂ production. In another study, Lin *et al.*⁸⁹ synthesised monolayer GCN nanosheets through liquid exfoliation by controlling the volume ratio of solvent and GCN concentration (0.1–3 mg mL⁻¹). The authors studied different solvents mixtures, *i.e.*, ethanol/H₂O, IPA/H₂O, and dimethylformamide (DMF)/H₂O, and found out that the combination of ethanol/H₂O solvents contributes to the formation of free-standing GCN nanosheets with high concentration. The obtained GCN nanosheets showed a thickness of 0.4 nm with high 2D anisotropy, high surface area, lower surface defects, effective separation of photogenerated charge carrier, increased photoelectric response, thus, improved photocatalytic performance compared to the bulk structure. Exfoliation of GCN in alkaline or acid mediums is another strategy to obtain thin layer GCN. Xu *et al.*⁹⁰ effectively-prepared thin-single layer of GCN nanosheets *via* chemical exfoliation process

using concentrated H_2SO_4 acid solution. The H_2SO_4 was intercalated into the interlayer of GCN and dissociate the hydrogen bonding; further, the $-\text{NH}-$ linking group was cleaved, yielding small-sized fragments of GCN. The obtained GCN nanosheets exhibited a thickness of 0.4 nm and a surface area of $205 \text{ m}^2 \text{ g}^{-1}$, being 50 times larger than bulk GCN. The chemical exfoliation by H_2SO_4 yielded about 60% of separate GCN nanosheets. In another example, Sano *et al.*⁹¹ synthesised GCN nanosheets through alkaline hydrothermal treatment using 0.1 M NaOH solution. The authors found that the C/N ratio did not change, and the H and O content was increased. This conduct to the removal of unstable domains of GCN and to the formation of a mesoporous structure with higher surface area compared to bulk GCN.

In an environmentally friendly and cost-effective process, the thermal exfoliation technique of bulk GCN in air conditions create a gradual decrease in its thickness, achieving nanoscale range. One of the first examples in 2012 by Niu *et al.*⁹² reported the thermal exfoliation of GCN by heating dicyandiamide in an open crucible under static air at either 550 or 600 °C. The obtained GCN nanosheets exhibited thickness of 2 nm corresponding to 6–7 multilayers, the high surface area of $306 \text{ m}^2 \text{ g}^{-1}$, increased lifetime and enhanced charge carriers transferability due to the quantum confinement effect, which therefore enhances the photoactivity. Nonetheless, the obtained yield of GCN nanosheets was about 6%. In a parallel study, Dong *et al.*⁹³ reported the preparation of GCN nanosheets by pyrolysis of thiourea followed by a thermal exfoliation at 550 °C. The resulted GCN possess a higher surface area of $151 \text{ m}^2 \text{ g}^{-1}$ and decreased layer thickness of about 2 nm.

Following a different approach, Qiu *et al.*⁹⁴ investigated the thermal exfoliation of bulk GCN under an H_2 atmosphere to form GCN nanosheets with a thickness of around 2 nm. The authors found that the yield of formed GCN calcined in H_2 was higher than the yield of those calcined in air. Moreover, the exfoliated GCN exhibits a longer lifetime of charge carrier (9.79 ns) compared to the bulk GCN (5.15 ns), thus confirm the slower decay kinetics in GCN nanosheets and hinder the recombination of charge carriers. The photocurrent studies show that the GCN treated in H_2 exhibits a higher photocurrent compared to the one treated under air or N_2 . This demonstrates that the treatment under H_2 atmosphere improved the exfoliation of GCN and enhanced the π -conjugated electronic structure. In a comparative manner, Lima *et al.*⁸⁸ reported the exfoliation of GCN using dicyandiamide as a precursor by different processes, such as thermal, chemical and mechanical techniques. The authors tested several temperatures (400, 450 and 500 °C), different times of mechanical treatment (1.5, 3.0 and 8.0 h) and different protic acids (H_2SO_4 , HCl and HNO_3). It was found that the post-thermal treatment at 500 °C resulted in a material with reduced bandgap energy and higher BET surface area ($87 \text{ m}^2 \text{ g}^{-1}$) as compared

to the mechanical and chemical treatments processes, which leads to chemical defects (oxygen functionalities), thus changing the electronic properties of the resulting materials.

Generally, the creation of mesoporous and nanosheets structure by exfoliation process significantly increases the surface area and improves the photocatalytic activity performance of GCN.

Heterostructure construction

Another effective approach to enhance the separation efficiency of the photogenerated charge carriers of GCN is by constructing 2D heterojunctions by assembling them with other semiconductors. The creation of these composites is considered an ideal choice for photocatalytic applications due to the synergistic effects arising from the layer structure and optical and electronic properties of each individual material.^{46, 95} It is expected that the combination of two pre-selected materials will give greater charge carrier mobility through the heterojunction interface, thereby reducing the recombination rate of e^-/h^+ , which is a key parameter in the process of photocatalytic water splitting. For example, Nayak *et al.*⁹⁶ employed a GCN/NiFe-layered double hydroxide (LDH) composite to obtain high efficiency for photocatalytic water splitting. In another approach, Tonda *et al.*⁹⁷ combined GCN with NiAl-LDH. The GCN/NiAl-LDH heterojunctions exhibited excellent performance for photocatalytic CO₂ reduction, being CO produced with a rate of 5 times higher than the pure GCN and 9 times higher than the pure NiAl-LDH. The 2D structures of both materials enable effective physical contact and strong electronic coupling between them, thus promoting photocatalytic activity. The authors suggested the photocatalytic mechanism of the nanocomposite (**Figure 8**) based on the calculation of the band edge positions of each individual material. Upon visible-light irradiation, both GCN and NiAl-LDH can be excited to generate the electrons and holes in CB and VB, respectively. The excited electrons on the CB of GCN can transfer into the CB of NiAl-LDH, while the formed holes on the VB of NiAl-LDH can pass to the VB of GCN. Therefore, promoting charge separation and suppressing charge recombination.

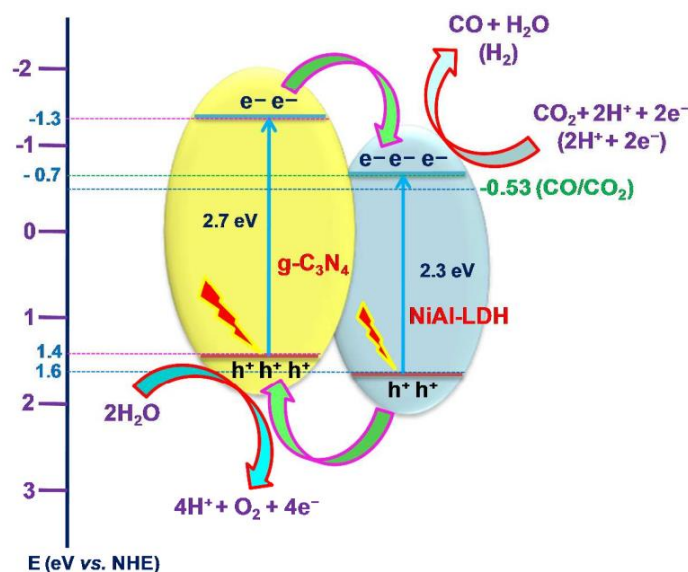


Figure 8. Schematic illustration of the proposed mechanism for CO₂ photoreduction in the GCN/NiAl-LDH heterojunctions. Reprinted from ref.⁹⁷

In the case of CdS, a well-known semiconductor, Ge *et al.*⁹⁸ prepared a composite of GCN with CdS quantum dots by chemisorption and calcination process. The composite with 30 wt.% CdS loading displayed a higher H₂ generation rate being 9.1-times superior compared to pure GCN. Besides, the composites show high stability during H₂ evolution with no photocorrosion observed during 28 h of irradiation. Similarly, Cao *et al.*⁹⁹ adapted a solvothermal process to prepare GCN/CdS composite. The photocatalytic performance was further improved, and the H₂ evolution rate over 12 wt.% CdS/GCN increased by a factor of 60 compared to the pristine GCN under visible light irradiation.

Metal oxides such as TiO₂ are considered the benchmark of optical semiconductors efficient for photocatalysis. In this way, it is also interesting to couple GCN with metal oxides. For instance, Chai *et al.*¹⁰⁰ fabricated GCN-Pt-TiO₂ by calcination method, and they found that the composite with a mass ratio of 70:30 (GCN:TiO₂) shows the maximum photoactivity towards H₂ production with an average rate of 178 $\mu\text{mol h}^{-1}$. This composite also exhibited a higher photocurrent being 1.5 times higher than the bare GCN. Zhou *et al.*¹⁰¹ reported the construction of the composite composed of GCN and TiO₂ nanotube arrays from anodic oxidation and electrodeposition method. These TiO₂/GCN composites exhibited an enhanced photocatalytic performance and quenched photoluminescence (PL) intensity, suggesting the suppression of photoexcited e⁻/h⁺ recombination. Besides LDH, CdS and TiO₂, many other photocatalysts have been coupled with GCN, such as BiPO₄, BiVO₄, ZnO, ZnWO₄, Co₃O₄, MoS₂, graphene and so on.¹⁰²⁻¹⁰⁸ All the GCN-based composites showed excellent photocatalytic performance

due to the differences in the band energy levels (CB and VB), enhanced light absorption, narrow bandgap, and better separation and transfer of charge carriers.

2.1.3 GCN for photocatalytic water splitting

GCN has been used in different applications such as gas sensor design,^{109, 110} oxidation of hydrocarbons,¹¹¹⁻¹¹³ degradation of organic pollutants,^{114, 115} hydrogen storage,¹¹⁶⁻¹¹⁸ photocatalytic CO₂ reduction,^{119, 120} and particularly photocatalytic water splitting.¹²⁰⁻¹²² In **Table 1**, some reported works using GCN-based materials and their application for photocatalytic water splitting, mainly H₂ generation, are listed. The photocatalytic water splitting application over GCN was reported for the first time in 2009 by Wang *et al.*⁶⁵ In this work, the authors prepared GCN using cyanamide precursor, which was subjected to a heat treatment. The HER rate over bare GCN was found to fluctuate and differ from batch to batch (0.1–4 $\mu\text{mol h}^{-1}$). By depositing 3 wt.% Pt into GCN, the amount of H₂ generated increased and reached 770 μmol after 72 h of irradiation. The authors explored the OER by introducing RuO₂ into GCN and using AgNO₃ as a sacrificial electron acceptor and obtained 53 μmol after 8 h under ultraviolet irradiation. Furthermore, from the DFT calculations of the HOMO-LUMO position, it was confirmed that GCN could generate both H₂ and O₂. The calculations show that the reduction sites for H⁺ to H₂ are C atoms, while the oxidation sites for H₂O to O₂ collapse into N atoms.⁶⁵ Following this initial study, GCN has received a significant amount of attention to further improve its activity for H₂ generation under visible light. Maeda *et al.*¹²³ published an investigation on GCN with various cocatalysts. A screening of a few transition metals was carried out, and the results indicate that the best cocatalyst is indeed Pt followed by Pd. After selecting Pt as the optimum cocatalyst, they investigated the influence of loading amount, and they reported that a 1 wt.% loading gave the best performance. Other metals such as Ni, Au and Ag have also been tested as cocatalysts to enhance the efficiency of the GCN for H₂ and O₂ evolution.¹²⁴⁻¹²⁷

Modified GCN shows promising properties, as explained in section 2.1.2. These characteristics can be expected to lead to higher photocatalytic activity. For instance, thermal exfoliation has been thoroughly explored. Yang and co-workers⁴³ used liquid exfoliation to prepare GCN nanosheets (thickness around 2 nm) which shown to produced higher H₂ from a water/triethanolamine (TEOA) solution than the bulk GCN; using 3wt.% of Pt, achieving a rate of 93 $\mu\text{mol h}^{-1}$ and quantum yield (QY) of 3.75% at 420 nm. Han *et al.*¹²⁸ prepared thin mesoporous GCN nanomesh by the solvothermal process. The obtained porous GCN nanomesh possessed a high surface area and better alignment of CB and VB edges (**Figure 9**) and exhibits

an excellent photocatalytic H_2 generation affording a rate of $8510 \mu\text{mol h}^{-1} \text{g}^{-1}$ (AQE of 5.1% at 420 nm), higher than the $1560 \mu\text{mol h}^{-1} \text{g}^{-1}$ reached over non-porous 2D GCN nanostructures or $350 \mu\text{mol h}^{-1} \text{g}^{-1}$ detected for bulk GCN (AQE of 3.75% at 420 nm). The superb performance was attributed to the unique structural advantages for aligned energy levels, enhanced light absorption and reduced charge carriers recombination (**Figure 9**).

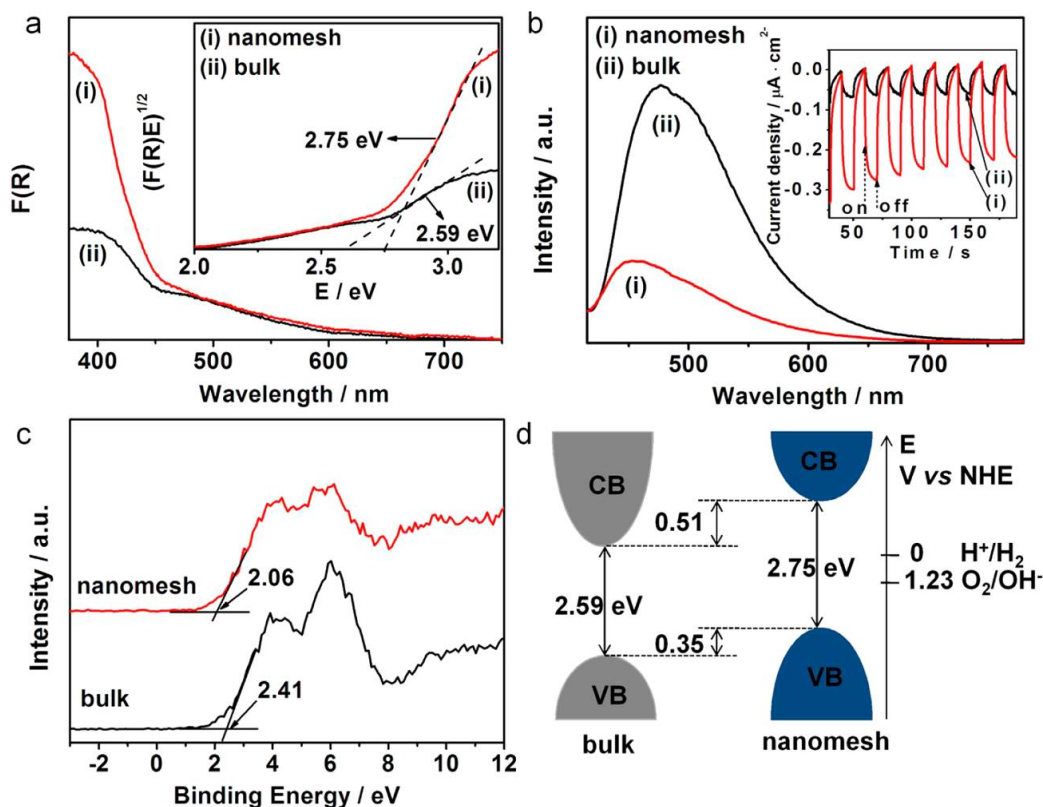


Figure 9. a) UV-Vis DRS of GCN nanomesh and the bulk counterpart, and its corresponding Tauc plots (inset). b) PL emission spectra of GCN nanomesh and the bulk, the inset in b) shows transient photocurrents under visible light illumination of both materials. c, d) XPS valence band spectra and electronic band structure of the GCN nanomesh and the bulk counterpart. Reprinted from ref.¹²⁸

In another report, Zeng *et al.*¹²⁹ demonstrated that GCN nanotubes synthesised *via* water-induced morphological transformation process performs superior visible-light H_2 generation than the bulk or nanosheets GCN, affording a rate of $28.5 \mu\text{mol h}^{-1}$ in the presence of 3 wt.% Pt cocatalyst. The authors attributed the superior photocatalytic activity to the tubular nanostructure of GCN with high photogenerated carriers transfer efficiency and enhanced light utilisation efficiency. In addition, the disorder in the GCN structure demonstrated to achieve the higher photocatalytic activity. These disorders can be caused by stacking defects, grain

boundaries, surface termination sites, and substitution of heteroatom. Martin *et al.*⁶⁸ studied the effect of protonation and polymerisation of pristine GCN using different precursors. The resulted in GCN displayed an H₂ generation rate of 20000 $\mu\text{mol h}^{-1} \text{g}^{-1}$ and 3300 $\mu\text{mol h}^{-1} \text{g}^{-1}$ under the full arc and visible-light irradiation, respectively. Moreover, the material showed high stability over 30 h and QY of 26.5% under visible light. The authors also determined the effect of polymerisation and protonation on H₂ production rates by modelling protonation using DFT simulations. They found that the density of states (DOS) of the CB edge was downshifted by 0.34 eV, indicating a modification of the electrochemical properties, resulting in a lower overpotential for reduction reactions, and thus enhanced photocatalytic H₂ production. Construction of nanoporous and microspheres GCN have also shown high photocatalytic photoactivity towards H₂ generation. Gu *et al.*¹³⁰ reported the synthesis of nanoporous GCN microspheres through a solvothermal method, and the resulted material showed significant improvements in H₂ generation with a rate of 1.80 $\mu\text{mol h}^{-1} \text{g}^{-1}$ (AQE was 1.62% at 420 nm), being 2.3 times superior to the bulk GCN (0.784 $\mu\text{mol h}^{-1} \text{g}^{-1}$, AQE is 0.75% at 420 nm), using TEOA and 3 wt.% Pt as a cocatalyst under visible light. The enhancement was ascribed to the wider-range visible light absorption and more effective transport and separation of photogenerated charge carriers. Accordingly, Zhang *et al.*¹³¹ reported that the nanospherical GCN comprised of nanosheets with 3 wt.% Pt cocatalyst showed significant improvements in H₂ production, with an AQY of 9.6% at 420 nm, which was superior to the pristine GCN nanosheets (AQY of 3.75%). Hollow GCN nanospheres with a high AQY of 7.5% have also been stated to have high photoactivity for water splitting.¹³² The addition of MoS₂ as cocatalyst significantly enhanced H₂ evolution over these hollow GCN spheres, resulting in the formation of MoS₂/GCN heterojunctions, increasing light-harvesting and charges carriers separation.¹³³ Han *et al.*¹³⁴ demonstrated that the seaweed-like GCN structure prepared by a 3-step process – hydrothermal pre-treatment followed by freeze-drying self-assembly and then by calcination under inert atmosphere –. This material showed highly efficient light-harvesting, charge separation and active sites as compared to its bulk GCN. The porous GCN seaweed-like structure exhibited a superior H₂ generation affording a rate of 9900 $\mu\text{mol h}^{-1} \text{g}^{-1}$ under visible light irradiation, accompanied by an AQY of 7.8% at 420 nm. Controlling the nanostructure of GCN via different processes to design nanoporous, microspheres, hollow nanospheres or seaweed-like structures showed high photocatalytic activity towards H₂ evolution compared to their bulk counterparts.

GCN has also been combined with other 2D structure semiconductors materials to broaden its spectral range. Such heterojunctions provide improved separation of photoexcited charge

carriers, and hence reduced the recombination and improve the photoactivity. TiO₂/GCN heterojunction have been fabricated by a two-step hydrothermal calcination process, using melamine as GCN precursor, followed by an *in-situ* solid-state reaction approach. The resulted heterojunctions material possess a narrow bandgap and enhanced photoactivity of H₂ produced (556 $\mu\text{mol h}^{-1} \text{g}^{-1}$) under visible-light irradiation as compared to pure GCN (108 $\mu\text{mol h}^{-1} \text{g}^{-1}$) and TiO₂ (130 $\mu\text{mol h}^{-1} \text{g}^{-1}$).¹³⁵ In the same perspective using TiO₂ as semiconductor, Mao *et al.*¹³⁶ synthesised GCN/N–TiO₂ photocatalyst doped with a noble metal-free Ni_xP as cocatalyst by the combination of ammonia etching and photoreduction deposition technique. The N–TiO₂ composite was formed and stood vertically on the surface of the GCN matrix, forming a 3D structure. The deposition of Ni_xP cocatalyst leads to enhance the photocatalytic H₂ production with an amount of around 5438 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which was 7.5 times higher than that of N–TiO₂/GCN under UV-Vis irradiation. The core-shell heterostructures composites have additional advantages due to the high interfacial contact area between the shell and core components.^{137, 138} For instance, core-shell Cu₂O/GCN heterostructure were prepared *via* combined solvothermal and chemisorption methods.¹³⁸ The Cu₂O/GCN heterostructure showed higher photocurrent intensity compared to that of Cu₂O and pure GCN, indicating the high separation and transport efficiency of photoexcited species through the interfacial connection of GCN and Cu₂O, resulted in enhanced photocatalytic H₂ production of 795 $\mu\text{mol g}^{-1}$ for 5 wt.% GCN under visible light irradiation.¹³⁸

Graphene (labelled here as GR) has received significant interest among other 2D structures materials due to its structural similarities to GCN, which makes it suitable for nanocomposite formation. Xiang *et al.*¹⁰⁸ interfaced GR with GCN to generate a metal-free GR/GCN composite through a combined impregnation-chemical reduction technique. The maximum H₂ evolution rate was with the hybrid contain 1 wt.% of GR with an amount of 451 $\mu\text{mol h}^{-1} \text{g}^{-1}$, being 3.07 times higher than pure GCN. The function of GR as a good acceptor of photogenerated electrons, which effectively suppressed the recombination of charge carriers, was supported by both PL and photocurrent response characterisations. In another example, Sun and co-workers,¹³⁹ reported the construction of a reduced graphene oxide (rGO) composite with GCN by an *in-situ* hydrothermal process. The obtained rGO/GCN photocatalysts had a cotton-like structure and could be well suspended in water due to the good coupling between rGO and GCN nanosheets, which is favourable for photocatalytic reactions. The loading of Pt cocatalyst as an active site for H₂ evolution reaction to the rGO/GCN photocatalysts lead to enhance its photoactivity, and the highest photoactivity was obtained with an optimal loading of 0.08 wt.% rGO, affording a rate of 87.4 $\mu\text{mol h}^{-1} \text{g}^{-1}$ which was greater than that of Pt/GCN.

The improved photocatalytic performance was attributed to the synergistic effect of rGO and Pt, wherein rGO nanosheets act as electron-transfer mediators, and the Pt nanoparticles act as active reduction sites (**Figure 10**) to efficiently promote the H_2 evolution reaction.

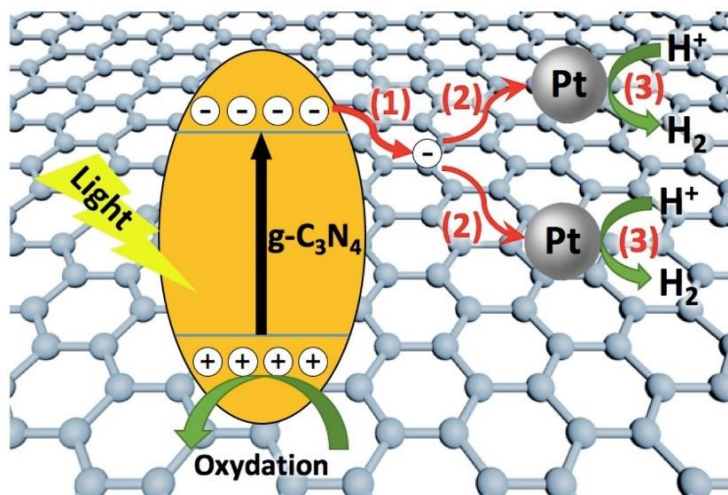


Figure 10. Schematic diagram illustrating the enhanced photocatalytic performance of Pt-rGO/GCN photocatalysts. Step (1): rGO as an electron sink to capture the photogenerated electrons from the GCN; Step (2): rGO as an electron mediator to transfer electrons from the capture sites to the Pt nanoparticles; Step (3): Pt nanoparticles as the reduction active sites for the H_2 generation. Reprinted from ref. ¹³⁹

More recently, Song *et al.*¹⁴⁰ prepared rGO/two-phase GCN (GCN2) using a simple hydrothermal reduction method. The GCN2 was found to be strongly integrated, which resulted in a substantial decrease in its agglomeration, and rGO was evenly overlaid onto the GCN surface and interlayers. The H_2 yield obtained with the composite 0.4% rGO loaded GCN2 was about $55.8 \mu\text{mol h}^{-1} \text{g}^{-1}$ without the use of cocatalyst, under visible light irradiation, which was 15 times higher than pure GCN. The electronically conductive channels given by rGO resulted in the interfacial separation of photogenerated charge carriers, thus improved photoactivity.

As mentioned above, the 2D MoS_2 can enhance the photocatalytic activity of GCN, being used either as a cocatalyst or as a supporting material to GCN. For instance, Ge *et al.*¹⁴¹ incorporate MoS_2 into GCN by a facile impregnation method. MoS_2 and cyanamide were used as starting materials for MoS_2 and GCN. It demonstrates that MoS_2 cocatalysts can promote the separation of photoexcited e^-/h^+ pairs in GCN and thus increase the efficiency of H_2 generation (**Figure 11**). The GCN/0.5wt.% MoS_2 heterostructure exhibited the highest photocatalytic H_2 performance with a rate of $23.10 \mu\text{mol h}^{-1}$ being 11.3-folds superior to the pristine GCN. Hou

*et al.*¹⁴² found that a heterojunction could be fabricated between MoS₂ and GCN due to the resemblance of layered structures. The MoS₂/GCN heterojunction is advantageous for charge transport at the interface of GCN and MoS₂, preventing charge carrier recombination. Consequently, the photocatalytic H₂ evolution rate with 0.5 wt.% MoS₂/GCN enhanced significantly (20.6 $\mu\text{mol h}^{-1}$), which is higher than that of 0.5 wt.% Pt/GCN (4.8 $\mu\text{mol h}^{-1}$) under the same conditions. In another example, Shi *et al.*¹⁴³ investigated the use of MoS₂ doped on GCN (MoS₂/GCN) composite for photocatalytic H₂ evolution, using lactic acid as a sacrificial electron donor and under visible light illumination. The MoS₂ was doped successfully on the surface of GCN *via* an *in-situ* photodeposition process. The photocatalytic activity of GCN was greatly improved after doping MoS₂ nanodot compared to the MoS₂ monolayer. Therefore, MoS₂/GCN nanodots showed 7.9 times higher photoactivity (660 $\mu\text{mol h}^{-1} \text{g}^{-1}$) than the GCN/MoS₂ monolayer (83.8 $\mu\text{mol h}^{-1} \text{g}^{-1}$).

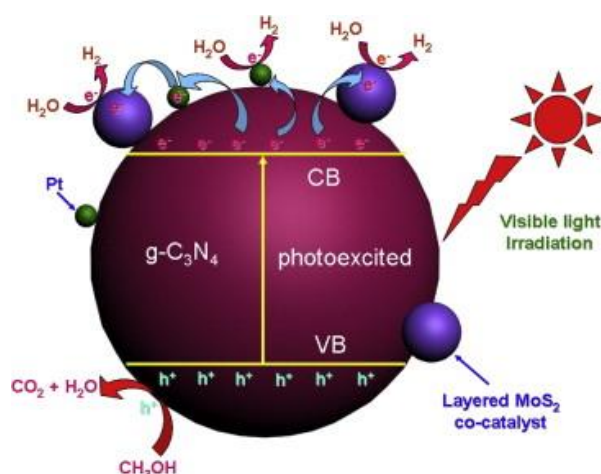


Figure 11. Schematic illustration of MoS₂ on GCN for boosting H₂ generation. Reproduced from Ref.¹⁴¹

In addition, using LDH to create heterojunctions with GCN has also been shown to be a highly effective approach for improving photocatalytic performance. In one example, Shi *et al.*¹⁴⁴ designed a 2D/2D calcined Mg-Fe-LDH/GCN photocatalyst and achieved an increased H₂ generation under visible light irradiation.

More details will be given about 2D/2D heterojunctions of GCN, LDH, and GRDs nanomaterials in the next sections.

Table 1. Examples of published works regarding GCN and GCN-based composites and their photocatalytic applications.

Catalyst	Catalyst Preparation	Cocatalyst	Light source	H ₂ generation	Apparent quantum yield (AQY)	Ref.
GCN	Thermal condensation	Pt	300 W Xe lamp $\lambda > 420$ nm	770 μmol	0.1% at 420–460nm	65
GCN	Thermal condensation	Pt	300 W Xe lamp $\lambda > 420$ nm	20 $\mu\text{mol h}^{-1}$	-	123
GCN nanosheets	Liquid exfoliation	Pt	300 W Xe lamp $\lambda > 420$ nm	93 $\mu\text{mol h}^{-1}$	3.75% at 420 nm	43
GCN nanomesh	Solvothermal	Pt	300 W Xe lamp $\lambda > 420$ nm	8510 $\mu\text{mol h}^{-1} \text{g}^{-1}$	5.1% at 420 nm	128
GCN nanotubes	Ultrasonic exfoliation	Pt	300 W Xe lamp $\lambda > 400$ nm	28.5 $\mu\text{mol h}^{-1}$	-	129
GCN protonation	Thermal condensation	Pt	300 W Xe lamp $\lambda > 395$ nm	3300 $\mu\text{mol h}^{-1} \text{g}^{-1}$	26.5% at 400 nm	68
GCN microspheres	Solvothermal	Pt	300 W Xe lamp $\lambda > 420$ nm	1.80 $\mu\text{mol h}^{-1} \text{g}^{-1}$	1.62% at 420 nm	130
GCN nanospherical	Thermal polymerisation with Silica spheres template	Pt	300 W Xe lamp $\lambda > 420$ nm	574 $\mu\text{mol h}^{-1}$	9.6% at 420 nm	131

GCN nanospherical	Thermal polymerisation with Silica spheres template	Pt	300 W Xe lamp $\lambda > 420$ nm	574 $\mu\text{mol h}^{-1}$	9.6% at 420 nm	131
GCN hollow- nanospheres	Thermal condensation with Silica template	Pt	300 W Xe lamp $\lambda > 420$ nm	224 $\mu\text{mol h}^{-1}$	7.5% at 420 nm	132
GCN seaweed-like structure	Hydrothermal - Self- assembly - Calcination	Pt	300 W Xe lamp $\lambda > 420$ nm	9900 $\mu\text{mol h}^{-1} \text{g}^{-1}$	7.8% at 420 nm	134
GCN/TiO ₂	Two-step hydrothermal Calcination	-	300 W Xe lamp AM 1.5 G filter	556 $\mu\text{mol h}^{-1} \text{g}^{-1}$	-	135
GCN/N-TiO ₂	Hydrothermal - ammonia etching - Photochemical reaction	Ni _x P	300 W x Xe lamp $\lambda > 350$ nm	5438 $\mu\text{mol h}^{-1} \text{g}^{-1}$	-	136
Cu ₂ O/GCN	Solvothermal- Chemisorption	Pt	300 W Xe lamp $\lambda > 420$ nm	795 $\mu\text{mol g}^{-1}$	-	138
GR/GCN	Impregnation - Chemical Reduction	Pt	350 W Xe lamp $\lambda > 400$ nm	451 $\mu\text{mol h}^{-1} \text{g}^{-1}$	2.6%	108
rGO/GCN	<i>In-situ</i> hydrothermal	Pt	LEDs at 420 nm	87.4 $\mu\text{mol h}^{-1} \text{g}^{-1}$	6.18% at 420 nm	139
rGO/GCN	Hydrothermal	-	Xe lamp $\lambda > 420$ nm	55.8 $\mu\text{mol h}^{-1} \text{g}^{-1}$	-	140

MoS ₂ /GCN	Impregnation	MoS ₂	300UV Xe lamp $\lambda > 420$ nm	23.10 $\mu\text{mol h}^{-1}$	-	141
MoS ₂ /GCN	Impregnation-sulfidation	Pt	300 W Xe lamp $\lambda > 420$ nm	20.6 $\mu\text{mol h}^{-1}$	2.1% at 420nm	142
MoS ₂ /GCN nanodots	<i>In-situ</i> photodeposition	-	Xe lamp $\lambda > 400$ nm	660 $\mu\text{mol h}^{-1} \text{g}^{-1}$	5.67% at 400 nm	143

2.2 Layered double hydroxides (LDHs)

Among the various photocatalysts that have been explored to date, LDH-based materials have gained recent attention, owing to their unique 2D and compositionally tunable structures in combination with attractive optical and electrochemical properties.¹⁴⁵⁻¹⁴⁹ These materials have tunable bandgap and high adsorption capacity, are suitable for cation-anion-exchange, and able to provide spatially separated reduction and oxidation reaction sites for the active production of H₂ and O₂ from water splitting.¹⁵⁰ Herein, a brief overview regarding the properties, synthesis and application of this material for photocatalytic water splitting reactions will be given.

2.2.1 Properties and synthesis

LDH, also known as hydrotalcite (HT)-like compounds, are a large family of 2D natural and/or synthetic anionic clay materials. These materials were discovered around 1842 in Sweden, but it was only in 1915 when Manasse reported the exact formula of the natural mineral hydrotalcite, [Mg₆Al₂(OH)₁₆]CO₃·4H₂O.¹⁵¹ Since then, a great deal of interest in these structures has been shown, and extensive research was carried out in recent years, leading to various fields of application.

The general formula of an LDH is [M²⁺_(1-x) M³⁺_x (OH)₂]^{x+} (Aⁿ⁻)_{x/n} • mH₂O, where M²⁺ is a divalent cation such as Mg²⁺, Zn²⁺, Ni²⁺, Ca²⁺, etc.; M³⁺ is a trivalent cation, *e.g.*, Al³⁺, Fe³⁺, Cr³⁺, etc.; Aⁿ⁻ is the interlayer anion of valence *n* (CO₃²⁻, SO₄²⁻, porphyrins, polyoxometalates, etc.) and *x* is the molar ratio of M³⁺/(M²⁺+M³⁺), which usually varies between 0.2 and 0.4 due to structural stability factors.¹⁵²⁻¹⁵⁵ The structure of LDH is based on the brucite Mg(OH)₂ layers, composed of edge-sharing Mg(OH)₆ octahedral units in which the metal cations are accommodated in the centres; each cation is thus surrounded by six OH⁻ ions that are pointed towards the corners and form infinite sheets (**Figure 12**).¹⁵²⁻¹⁵⁶ The positively charged layer comprises two or more types of divalent or trivalent metal hydroxides and the interlayer region is composed of water molecules and anions, which are responsible for balancing charge neutrality. The basal spacing of the LDH materials (*d*) is defined by the distance between the centre of one layer to the centre of the adjacent layer, *i.e.*, is given by the total of the brucite-like layer and the interlayer space (**Figure 12**).¹⁵²⁻¹⁵⁶

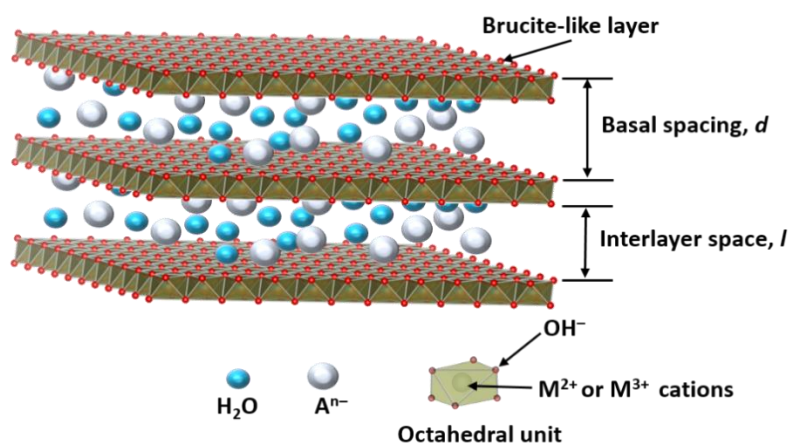


Figure 12. Representative structure of LDH materials.

The sheet-like structure of LDH makes them prone to stacking or aggregation due to the electrostatic forces between the layers.^{157, 158} This process can decrease the specific surface area and active site exposure, which typically weakens the functional properties of LDH in catalytic applications. Research on developing LDH preparation with various irregular morphologies has been carried out to solve this problem, resulting in flower-like, core-shell, and hollow-sphere LDH structures.¹⁵⁹⁻¹⁶² The main goal of this approach is to increase the specific surface area and provide better access to the active catalytic sites. On the other hand, due to relatively weak interlayer bonding between LDH domains, various exfoliation methods have been looked at to prepare low-dimensional LDH nanostructures.^{150, 163}

The broad modulation capability - including the type of cations, molar ratios of M^{2+}/M^{3+} , and the nature of interlayer compensation anions - results in a variety of compositional LDH combinations, which in turn yields LDH-based nanostructures with flexible physical and chemical properties.^{156, 164-166} In addition to that, the specific combinations of M^{2+} and M^{3+} can also lead to the emergence of new properties. For example, LDH materials consisting of transition metals (*e.g.*, Zn^{2+} , Ni^{2+} , Fe^{2+}) usually feature attractive catalytic properties.^{158, 160, 167, 168} Recently, some layered triple hydroxides with three types of metal cations have been reported.¹⁶⁹⁻¹⁷² Once again, the choice of cations and cations ratio affects the resulting specific surface as well as the catalytic performance of the resulting LDH.

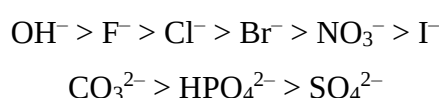
LDH can be synthesised using several techniques, such as coprecipitation, anion exchange, hydrothermal and solvothermal methods, urea and sol-gel.^{164, 173-175}

Coprecipitation is the most common method to synthesise LDH. Its advantage consists of being easily scaled up for synthesising larger amounts of LDH material. It involves the simultaneous precipitation of a mixture solution of metal cations (M^{2+} and M^{3+}) by the addition of a basic

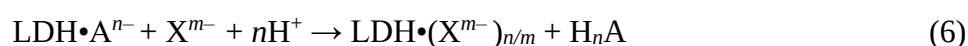
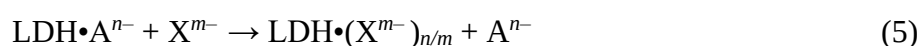
solution (*e.g.*, sodium hydroxide and sodium carbonate) at constant or increasing pH, in which the counter anions of the metal salts become the interlayer anions.^{164, 173, 174, 176, 177} This reaction allows controlling the morphology and particle size, depending on the supersaturation of the solution. Moreover, the pH value is dependent on the metal cations nature, and has, therefore, a significant impact on the chemical, structural and textural properties of the final obtained LDH. Consequently, the pH of the solution must be controlled (a pH value too low does not allow the complete precipitation of all metallic ions, while a too high value results in the leaching of one or more metallic ions) to achieve LDH with high chemical homogeneity and good crystallinity.^{164, 173, 174, 176, 177}

The *anion exchange* technique is based on the exchange properties of the LDH interlayer anions.^{174, 175} This method is useful when the coprecipitation method is inapplicable, for example, when the anions or metal cations (M^{2+} and M^{3+}) are unstable in alkaline solution, or when the direct reaction between metal ions and guest anions is more favourable.^{164, 174, 175}

In thermodynamic terms, the anionic exchange in the LDH mainly depends on the electrostatic interactions between the brucite sheets and the exchanging interlayer anions. Furthermore, this process is correlated with several parameters, including pH value and suitable solvent that facilitates the anion exchange. For instance, at pH values lower than 4.0 the hydroxyl layers can be broken, and the layered structure disappears. Besides, the process also depends on the chemical composition of the LDH host layers.^{164, 174, 175} In addition, the anion exchange properties of LDH depend on the affinity of incoming anions. Generally, the exchange ability of incoming anions increases with increasing charge and decreasing ionic radius. The easiness of exchange of monovalent anions and divalent anions occurs in the following order.^{175, 178}



Overall, the anion exchange approach can be carried out in two possible ways, as described by Eq. (5) and (6), where A represents the anion existing in the LDH and to be exchanged by the X anion.^{164, 174, 175}



In Eq. (5), the precursor $\text{LDH} \cdot \text{A}^{n-}$ usually contains univalent anions such as Cl^- or NO_3^{2-} , which possesses weak electrostatic interaction with the LDH layers. While, in Eq. (6), the precursor $\text{LDH} \cdot \text{A}^{n-}$ contains anions susceptible to acid attack, such as CO_3^{2-} or carboxylates.^{174, 175}

Hydrothermal and solvothermal synthesis is considered a simple way to synthesise LDH materials with good crystallinity and increased particle sizes at controlled temperature and pressure.^{164, 173, 179} It consists of dissolving the metallic salts mixture into a solvent before putting the solution into a stainless-steel reactor and heating under thermal conditions and steam pressure, with different synthesis times. In addition, this method can be used to optimise LDH synthesised by coprecipitation or anion exchange method a second post-treatment.^{164, 173} The advantage of this method is that the reaction conditions are controllable and generate highly crystallised LDH materials.¹⁸⁰ Moreover, compared to the above-mentioned processes, the hydrothermal and solvothermal methods are not as time-consuming and do not require the usage of salt-based solvents. In addition to these techniques, sol-gel and urea hydrolysis method were also reported to prepare LDH.^{164, 173, 181, 182}

In the end, in this Thesis the hydrothermal and solvothermal methods were selected to prepare different LDH materials, due to the promising features they promote, cost-effectiveness and employment of innocuous solvents (*i.e.*, water and ethanol).

In the following sections, pristine LDH, modified LDH and LDH-based nanohybrids will be overviewed and discussed to understand the relation between their structure, properties, and photocatalytic performance towards the reactions of water splitting. Various strategies to enhance the performance of LDH-based materials will be focused on thermal treatment (in air and in an inert atmosphere), doping of suitable cations, and the formation of heterostructures. All these modifications are summarised in the following sections, along with the corresponding experimental conditions of the photocatalytic tests and their outcomes. The list of relevant studies conducted between 2016 and 2021 on LDH-based photocatalysts for water splitting is presented in **Table 2**.

2.2.2 LDHs for photocatalytic water splitting

Significant attention has been paid to LDH materials and their applications in solar energy conversion and storage. Silva *et al.*⁴⁴ pioneered using LDH as a semiconductor for photocatalytic water splitting. The authors investigated a series of ZnTi, ZnCe, and ZnCr-LDH catalysts with different Zn-to-metal atomic ratios (from 4:2 to 4:0.25) for visible-light O₂ generation. In this study, ZnCr-LDH with a 4:2 atomic ratio proved to be the optimal material. The photocatalyst exhibited two absorption bands in the visible region at λ_{max} of 410 and 570 nm. The efficiency of the ZnCr-LDH for O₂ generation was 1.6 times higher than the WO₃ benchmark material under the same conditions. The higher efficiency was attributed to the high

degree of crystallinity and increased light absorbance, as confirmed with XRD and solid-state UV-vis measurements.

More recently, Xu *et al.*¹⁸³ provided a comprehensive study aiming to relate the electronic properties and the OER for 14 types of LDH $M^{+2}_nM^{+3/+4}_n\text{-A-LDH}$ ($M^{+2} = \text{Mg, Co, Ni, Cu, Zn}$; $M^{+3} = \text{Cr, Fe}$; $M^{+4} = \text{Ti}$; $n = 2, 3, 4$; $A = \text{Cl}^-, \text{NO}_3^-, \text{CO}_3^{2-}$) using a density functional theory plus U (DFT + U) method. The band structure, density of state, bandgap energies and band edge positions calculation results designate that all 14 LDH can absorb visible light, and their (003) planes are the most preferably exposed surface. The OER driving force and overpotential values further indicate that 10 types of these LDHs ($\text{Ni}_2\text{Ti-Cl-}$, $\text{Cu}_2\text{Ti-Cl-}$, $\text{Zn}_2\text{Ti-Cl-}$, $\text{Ni}_2\text{Cr-Cl-}$, $\text{Zn}_2\text{Cr-Cl-}$, $\text{Co}_2\text{Fe-Cl-}$, $\text{Ni}_2\text{Cr-NO}_3\text{-}$, $\text{Ni}_2\text{Cr-CO}_3\text{-}$, $\text{Ni}_3\text{Cr-Cl-}$, and $\text{Ni}_4\text{Cr-Cl-LDH}$) can drive the reaction with a sufficiently high oxidation potential of the *as*-photogenerated holes, while the other LDH need an external bias (*i.e.*, photoelectrochemistry) to conduct OER. The photocatalytic activity of these LDH series towards water splitting was also evaluated under solar light irradiation and in the presence of AgNO_3 as an electron acceptor. Experimental results demonstrate the efficient photocatalytic performance of $\text{Ni}_2\text{Cr-Cl-LDH}$, $\text{Zn}_2\text{Cr-Cl-LDH}$, $\text{Ni}_2\text{Cr-NO}_3\text{-LDH}$, $\text{Ni}_2\text{Cr-CO}_3\text{-LDH}$, $\text{Ni}_3\text{Cr-Cl-LDH}$, and $\text{Ni}_4\text{Cr-Cl-LDH}$ with O_2 generation rates of 1037, 1079, 669, 614, 871, and 714 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. The O_2 generation rate of $\text{Ni}_2\text{Cr-Cl-LDH}$ (1037 $\mu\text{mol g}^{-1} \text{h}^{-1}$) was the highest among the $\text{Ni}_n\text{Cr-A-LDH}$ family ($n = 2, 3, 4$; $A = \text{Cl}^-, \text{NO}_3^-, \text{CO}_3^{2-}$), which matched well with the theoretical predictions of bandgap energies and band edges positions.

Mostafa and coworkers¹⁸⁴ reported the preparation of one-dimensional CoTi-LDH nanorods (denoted as CTN-LDH) using a one-pot synthesis strategy. The CTN-LDH was prepared by direct diffusion of titanium tetrachloride vapours into a cobalt solution under an inert atmosphere. The authors tested the photoactivity of CTN-LDH for OER under UV-vis and Infrared (IR) light without adding any noble metal or scavenger. This LDH material achieved the highest O_2 evolution rate of 5300 $\mu\text{mol g}^{-1} \text{h}^{-1}$ under IR irradiation at 55 °C. The high IR-light photocatalytic activity was ascribed to the multilayered structure of the CTN-LDH composed of ultra-thin nanorods (20-50 nm) – which allowed for a narrow bandgap (1.4 eV) and subsequent efficient separation of e^-/h^+ pairs – and as well as to strong electromagnetic absorption in the high wavelength region (750-1200 nm), as was further confirmed by photoluminescence (PL) and UV-vis measurements.

More recently, Chen *et al.*¹⁸⁵ fabricated MgAl-LDH with NiS as HER cocatalyst using a two-step hydrothermal and precipitation method (**Figure 13a**). The weight ratio of NiS nanoparticles was varied from 0.1 to 1.5 wt.% with respect to the parent LDH. The TEM results

showed that the ultrafine NiS nanoparticles were uniformly anchored on MgAl-LDH hexagonal nanoflakes (**Figure 13b, c**).

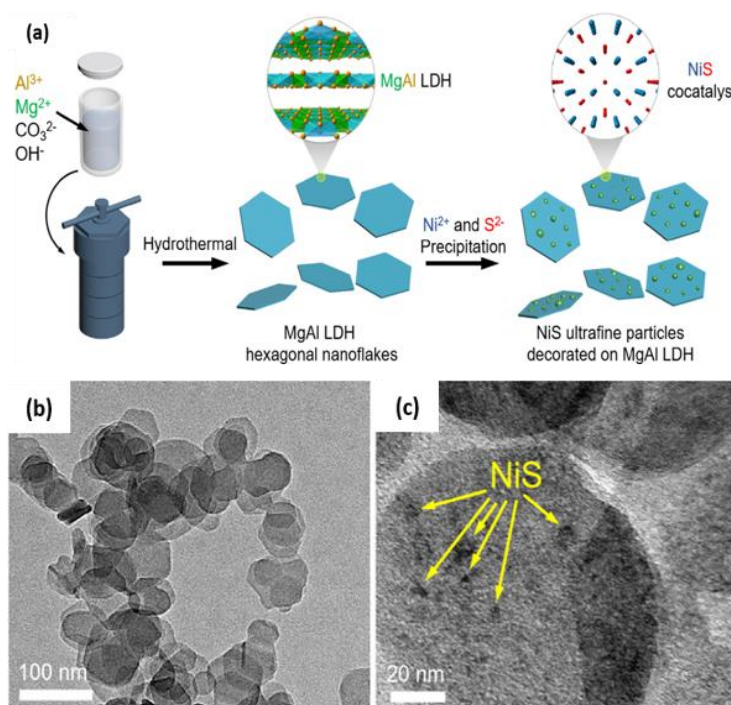


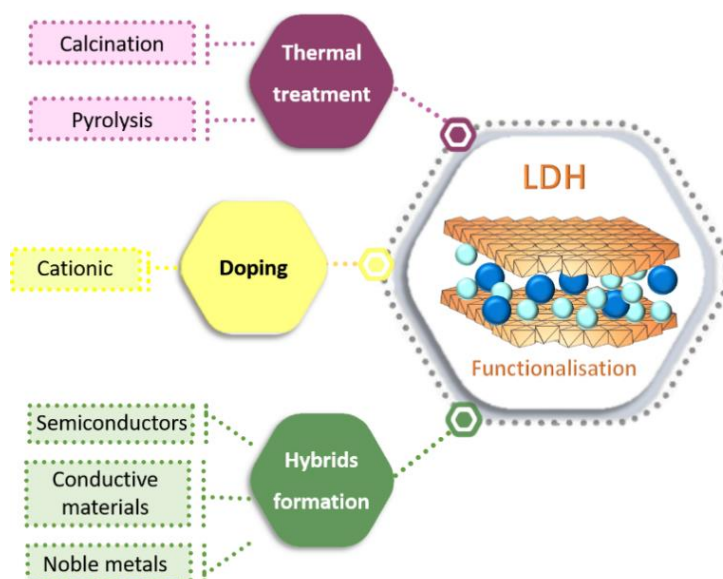
Figure 13. a) Schematic illustration of the procedure for preparing MgAl-LDH/NiS hybrids; TEM images of b) pure MgAl-LDH and c) MgAl-LDH/NiS-0.7. Adapted from ref.¹⁸⁵

The presence of NiS led to enhanced visible light absorption, narrower bandgap and promoted the separation and transfer of photogenerated charge carriers, thereby enhancing the photocatalytic H₂ production activity. Compared with pristine MgAl-LDH, the MgAl-LDH/NiS hybrid with a 0.7 wt.% of NiS showed a 13.3-fold increase in the photocatalytic H₂ evolution rate (35.8 $\mu\text{mol h}^{-1}$ and 2.7 $\mu\text{mol h}^{-1}$ for MgAl-LDH/NiS-0.7 and MgAl-LDH, respectively) under visible light irradiation. For comparison, the authors modified the MgAl-LDH with 0.5 wt.% Pt, which resulted in 33.4 $\mu\text{mol h}^{-1}$ of H₂ – the value lower than the one obtained for the MgAl-LDH/NiS-0.7 hybrid.

2.2.2.1 Functionalisation of LDH-based materials for water splitting

Despite some promising results, bulk LDH materials often face several challenges, such as limited access to active sites due to aggregation, short-living e^-/h^+ pairs, and low electrical conductivity. To address these restraints, a series of efficient approaches have been proposed, including calcination, doping and building of heterojunction systems. A general overview of

relevant studies conducted between 2016 and 2021 on the functionalisation of LDH-based materials is presented in **Scheme 2**, which will be explored below.



Scheme 2. General representation of the post-modification processes for LDH-based materials.

2.2.2.1.1 Calcination

Calcination of pristine LDH is a facile technique for synthesising mixed metal oxides (MMOs) with uniformly distributed M^{2+} and M^{3+} , generating materials with narrow bandgap and high surface areas.^{164, 186} Three main steps are involved in the thermal decomposition of LDH: (i) release of interlayer and adsorbed water; (ii) dehydroxylation of the layers; and (iii) decomposition of anions leading to MMO. Importantly, MMOs with tunable properties are seen as very attractive candidates for photocatalytic applications due to their advantages. For instance, Suárez *et al.*¹⁸⁷ investigated the preparation of mixed metal oxides (MMOs) by calcination of ZnAl-LDH at different temperatures (400, 500, 600 and 700 °C), which resulted in ZnO/Zn₆Al₂O₉ and ZnO/ZnAl₂O₄ heterojunctions. The H₂ evolution yield was higher as the annealing temperature increased due to the formation of the heterojunctions of ZnO with the Zn₆Al₂O₉ and ZnAl₂O₄ oxides, with the highest H₂ production amount of approximately 8000 µmol reached with the sample calcined at 600 °C (ZnO/Zn₆Al₂O₉) under UV light irradiation. The material calcined at 700 °C (ZnO/ZnAl₂O₄) showed lower photocatalytic performance even though its crystallinity was higher. The authors attributed this behaviour to the higher recombination rate of the ZnO/ZnAl₂O₄ heterojunction in comparison with that of ZnO/Zn₆Al₂O₉. In another example, Nayak *et al.*¹⁸⁸ synthesised MgCr-LDH using a coprecipitation method, employing DMF as a chelating agent, and further subjected it to heat

treatments to obtain 2D porous MgO/MgCr₂O₄(*x*) MMOs nanocomposites, *x* being the molar ratio between Mg²⁺ and Cr³⁺ (*x* = 2/1, 3/1, and 4/1). The resulting MgO/MgCr₂O₄(*x*) nanocomposites possess a unique form of crystalline, porous nanosheets made of nanoparticles and have a high surface area as compared to the bulk MgCr-LDH. Among the synthesised materials, the MgO/MgCr₂O₄(3/1) nanocomposite exhibited the highest H₂ production rate of 420 μmol g⁻¹ h⁻¹, which was 2 times higher than that of the MgCr₂O₄ (210 μmol g⁻¹ h⁻¹). The increased photocatalytic activity of the composites was attributed to their high surface area, the formation of Schottky junction, and the interstitial oxygen vacancy of porous MgO sheets, which behaves as an electron trapping site, thus restricting the e⁻/h⁺ recombination in the composite.

2.2.2.1.2 Pyrolysis

Besides calcination, several novel materials have been obtained through the so-called topotactic pyrolysis.^{189, 190} In this process, the use of an inert atmosphere and temperature causes a transformation within the LDH crystal lattice and involves the displacement or exchange of oxygen atoms. Experimentally, this is achieved by subjecting LDH to heat treatments in the presence of sulphur or nitrogen sources.^{189, 190} In this way, bulk LDH can be used to construct 2D nanosheets with ultrathin thickness and a compact interface allowing for short charge transfer distances and accelerated carrier migration and transfer. In one example, Shi *et al.*¹⁸⁹ reported the fabrication of 2D ultrathin Zn_{*x*}Cd_{1-*x*}S nanosheets by the sulphurisation process using trimetallic ZnCdAl-LDH as precursor and thiourea as a sulphur source. The topological sulphuration pyrolysis of ZnCdAl-LDH allowed to generate Zn_{*x*}Cd_{1-*x*}S in ultrathin sheet-like morphology and exposed their polar facets (**Figure 14a**). The ultrathin ZnCdAl-LDH were prepared with different molar ratios (Zn/Cd/Al: 1/2/1, 1.5/1.5/1, 2/1/1) and evaluated towards photocatalytic H₂ production under visible light irradiation and in the presence of Na₂S/Na₂SO₃ as a sacrificial electron donor. The Zn_{0.67}Cd_{0.33}S nanosheets displayed the highest photocatalytic H₂ generation activity (6.69 mmol g⁻¹ h⁻¹) without any additional cocatalyst, which was also superior to that of pristine ZnS and CdS. The enhanced activity was attributed to the 2D ultrathin structure with exposed cubic (111) or hexagonal (002) polar facets (**Figure 14**). In the polar facet structure, the sulphur ions (S²⁻) were alternatively distributed along the (111)/(001) direction to form a -M-S-M-S- system (M is Zn or Cd) with alternating cation/anion layers. In contrast, in the non-polar facet (002), cations and anions coexist on the same plane. Moreover, the authors demonstrated that in the exposed polar facet (111) or (002) structure, the electrons are located on the metal layers (Zn or Cd), whereas holes are located on

the S layers (**Figure 14a**). In this way, the polar facet promoted the separation and transport of photogenerated electrons and holes to the surface sites (**Figure 14b**). This provides a fascinating strategy to fabricate highly efficient $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheets from LDH precursors, using a simple, low-cost, and environmentally friendly process. The photogeneration of electrons and holes can be enriched in different crystal facets. The investigation of crystal facets engineering can help properly modulate the band structure between various crystal facets to form a facet junction. Thus, a more facile e^-/h^+ transfer to different facets can be obtained, resulting in effective charge carrier separation.^{149, 191, 192}

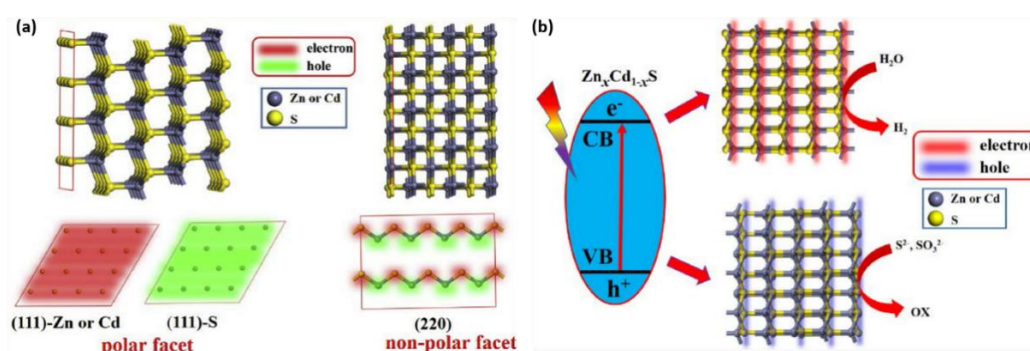


Figure 14. a) Schematic illustration of the electron localization on the polar facet and the hole localization on the non-polar facet for hexagonal $\text{Zn}_{0.67}\text{Cd}_{0.33}\text{S}$ nanosheet. b) Proposed photocatalytic water splitting mechanism over 2D ultrathin $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheet. Reprinted from ref.¹⁸⁹

2.2.2.1.2 Cationic doping

Doping is another generally used and well-accepted strategy that aims to tune the electronic characteristics of a given photocatalyst (such as its electronic band structure and charge carrier mobility) and to improve its visible light absorption by modifying the crystal lattice of the parent compound and creating new interband gap states.¹⁹³⁻¹⁹⁵ Parida *et al.*¹⁹⁶ first studied the use of LDH as photocatalysts for H_2 generation from water splitting. The authors reported the synthesis of Fe-doped MgAl-LDH by a simple coprecipitation technique. In this work, a series of Fe-doped MgAl-LDH was prepared by varying Al:Fe ratio from 1:4, aiming to lower the concentration of Fe, thus obtaining samples with different contents on Fe in the brucite layers to assess the role of Fe in the photocatalytic performance of the materials. The highest photocatalytic H_2 evolution activity was obtained with an Al:Fe ratio of 3:2, yielding $493 \mu\text{mol g}^{-1} \text{h}^{-1}$ under visible irradiation. Moreover, an excess of Fe ion resulted in the formation of amorphous Fe_2O_3 , which might accelerate the charge transfer recombination, thus

causing a decrease in H_2 generation. In another work, Yi *et al.*¹⁹⁴ reported the preparation of Tb doped ZnCr-LDH (TbZnCr-LDH) photocatalysts through a coprecipitation method by loading different molar ratios of Tb ion (Tb^{3+}) into the initial ZnCr-LDH ($(\text{Tb}^{3+}/(\text{Tb}^{3+} + \text{Cr}^{3+})) = 0, 0.1, 0.5, 1$ and 5%). The photocatalytic performance of the materials was evaluated towards OER under visible light irradiation using AgNO_3 as an electron acceptor. The highest photocatalytic activity was observed for ZnCr-LDH doped with 0.5% of Tb^{3+} , affording a rate of $1022 \mu\text{mol g}^{-1} \text{h}^{-1}$, which was twice as high compared to the pristine ZnCr-LDH. The authors attributed the large photocatalytic improvement to the effective separation of photoinduced charge carriers (from PL studies; as shown in **Figure 15a**), narrow bandgap (from 2.3 to 2.09 eV), higher surface area, and stronger photocurrent response of the Tb^{3+} doped LDH. Moreover, the authors showed that Tb incorporation results in the creation of hole acceptor states within the LDH matrix, facilitating the charge extraction (**Figure 15b**).

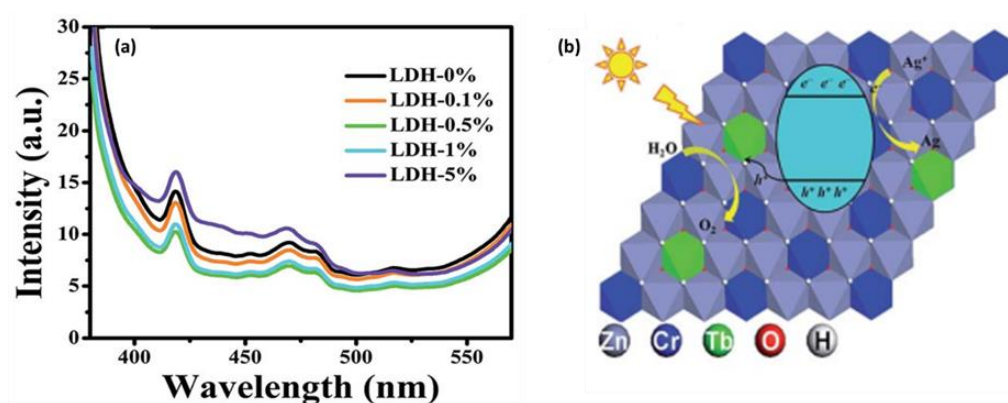


Figure 15. a) PL spectra of TbZnCr-LDH samples. b) Schematic illustration of the oxygen evolution process over the TbZnCr-LDH under visible light irradiation. Reprinted from ref.¹⁹⁴

2.2.2.1.3 Hybrid formation

The hybridisation of LDH with other semiconductors, either used as the main catalyst or used as catalytic support, to construct nanosheet heterostructures has thus been shown as a highly effective strategy for enhancing photocatalytic performance of both individual materials. For instance, Megala *et al.*¹⁹⁷ constructed 2D/2D heterojunction of NiAl-LDH/GCN nanocomposite with a different weight percentage of GCN for photocatalytic H_2 generation. The composites were prepared by a one-step *in-situ* hydrothermal process. TEM of the resulting nanocomposites showed that GCN sheets were wrapped on the surface of NiAl-LDH plates, confirming the formation of a heterojunction system. The nanocomposites exhibited a remarkable enhancement of photoactivity after loading of GCN. The highest H_2 evolution rate

was obtained with the composite containing 30 wt.% of GCN that showed 100- and 1000-folds higher performance than those of the pristine GCN and pure NiAl-LDH, respectively. The reached H₂ evolution rate was 3170 $\mu\text{mol g}^{-1} \text{h}^{-1}$ after 4 h of reaction under simulated solar irradiation and in the presence of TEOA as a sacrificial agent. The photocatalytic enhancement was attributed to the synergistic effect between 2D layered materials and the formation of n-n heterojunction.

Patnaik *et al.*¹⁹⁸ synthesised a triple junction between GCN and ZnCr₂O₄@ZnO *via* calcination to obtain porous composite materials (labelled as CNMMO). The growth of ZnO and ZnCr₂O₄ from ZnCr-LDH resulted in the exfoliation of GCN during the preparation process, which facilitated the stoichiometric evolution of H₂ and O₂ under visible light irradiation. The obtained composite materials were highly porous, exhibited smooth surfaces, and resembled thin 2D layers, where the oxide components were well-embedded within the GCN matrix, as was confirmed with TEM analysis (**Figure 16a, b**). The lifetimes of the charge carriers of the composites were studied, and the results were in this order: CNMMO (45.01 ns) > MMO (37.93 ns) > GCN (31.11 ns), which suggested an inhibited recombination tendency of the charge carriers and improved activity in the composite. The best photocatalytic activity was obtained with the composite containing 60% of GCN, producing 847 μmol and 455 μmol of H₂ and O₂ in the presence of methanol and AgNO₃ as sacrificial reagents, respectively, and under visible light irradiation. The better photocatalytic activity was attributed to the enhanced visible-light harvesting capacity and surface area, low PL emission intensity, and the formation of GCN nanosheets. Furthermore, according to the authors, the synergistic catalytic effect can be attributed to strong coordination bonding between GCN (N as Lewis base sites) and Zn²⁺ ions (as Lewis acid sites). The possible mechanism for the carrier transfer is illustrated in **Figure 16c**. Under visible light irradiation, photoelectrons generated from the VB of GCN and ZnCr₂O₄ can be excited and moved to the CB of ZnO, which lies at lower potential and can thus act as an electron sink to favour the water reduction reaction. Holes are transferred from the VB of ZnO to the VB of GCN to favour the water oxidation reaction.

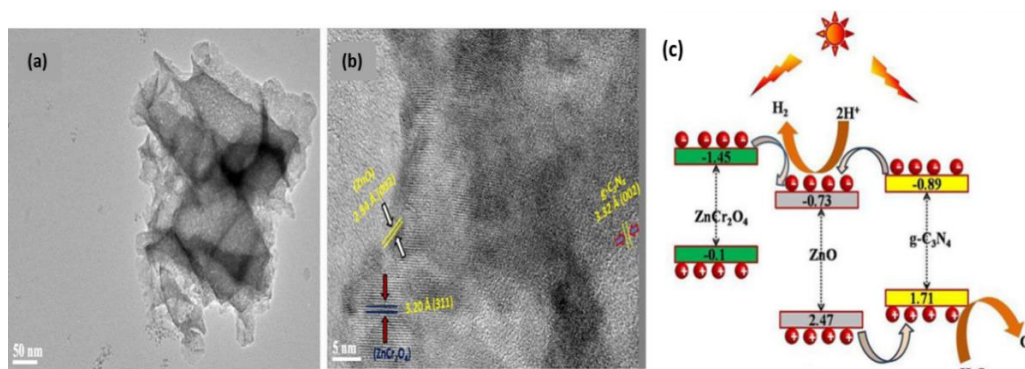


Figure 16. a, b) TEM images of CNMMO. c) Mechanistic pathways of photocatalytic water splitting. Adapted from ref.¹⁹⁸

Mancipe *et al.*¹⁹⁹ synthesised CdS/MgAl-LDH composites by a coprecipitation method using different wt.% of CdS (5, 10, 15, and 20 wt.%) with a fixed molar ratio of Mg/Al (3/1). The 5%CdS/MgAl-LDH photocatalyst showed the highest H₂ production with 1148 $\mu\text{mol g}^{-1}$ generated after 7 h under UV light irradiation in the presence of methanol as a sacrificial agent. The excellent photocatalytic activity was assigned to the crystallite size effect, in which the uniform dispersion of the active phase in the lamellar material prevents agglomeration of CdS particles and consequently reduces the recombination of the e^-/h^+ pair. Another critical contribution stemmed from the presence of carbonate ions (CO_3^{2-}) in the lamellar region of the MgAl-LDH, which act as traps for the photogenerated holes helping the formation of hydrogen. Nayak *et al.*²⁰⁰ reported that creating a Z-scheme involving a p-type MoS₂ and an n-type NiFe-LDH as composite components leads to the efficient separation and migration of photoinduced e^-/h^+ pairs, therefore, enhancing the photoactivity. The MoS₂/NiFe-LDH nanocomposites with different wt.% of MoS₂ loaded over NiFe-LDH were prepared by hydrothermal and electrostatic self-assembly methods. The morphology of the composites shows the interconnection between layers of NiFe-LDH and MoS₂. The maximum H₂ production rate (550.9 $\mu\text{mol h}^{-1}$) was obtained with the hybrid containing 3 wt.% of MoS₂, in an aqueous methanol solution under visible light irradiation. This result is 10.9- and 19.2-fold higher than that of NiFe-LDH and MoS₂, respectively. The improved catalytic activity was attributed to a suitable electric field at the interface between NiFe-LDH and MoS₂, which allowed effective charge carrier separation.

GRDs, such as rGO, are well recognised due to their attractive chemical and physical properties, such as good electronic conductivity, high specific surface area, high mechanical properties and thermal stability.^{201, 202} Kumaresan *et al.*²⁰³ designed and prepared a nanocomposite of

CoAl-LDH and rGO through a simple solvothermal method. The CoAl-LDH/rGO materials were prepared by adding different amounts of rGO into CoAl-LDH suspensions. The morphology of the composites showed the attachment of the nanoflower-like CoAl-LDH onto the rGO surface, which promised high conductivity of CoAl-LDH/r-GO. The photocatalytic ability of the nanocomposites was studied for HER under visible light illumination, and the HER results revealed that CoAl-LDH/rGO with 50 mg loading of rGO exhibited the highest activity with a rate of $1571.84 \mu\text{mol g}^{-1} \text{h}^{-1}$, which was 3.6 times higher than that of the pristine CoAl-LDH. This enhanced performance was shown to be due to the strong electronic coupling at the interface of CoAl-LDH and rGO, which led to a higher separation efficiency of charge carriers.

An alternative and promising method for designing highly efficient visible light heterojunctions are by assembling noble metal (plasmonic photocatalysts) with LDH.^{204, 205} The Ag-based photocatalyst Ag_3VO_4 has been reported as an effective catalyst for transforming solar into chemical energy due to its narrow bandgap energy (2-2.2 eV) and n-type semiconductor character, enabling oxidative properties.^{204, 206-208} In addition to this, the existence of metallic Ag results in surface plasmon resonance (SPR) – the collective oscillation of conduction electrons on the metallic surface, which interacts with electromagnetic radiation – which can significantly enhance the absorption of visible light and thus enhance overall photocatalytic activity.²⁰⁶⁻²⁰⁹ Sahoo *et al.*²⁰⁸ fabricated nanocomposites of ZnCr-LDH along with Ag/ Ag_3VO_4 plasmonic catalyst to modulate the band structure of ZnCr-LDH and to extend its photocatalytic application towards oxygen evolution. The ternary $\text{Ag}@\text{Ag}_3\text{VO}_4/\text{ZnCr-LDH}$ nano-heterostructures were prepared by *in-situ* hydrothermal syntheses followed by coprecipitation. The Ag_3VO_4 (AgV) nanoparticles were dispersed on the brucite surface of the ZnCr-LDH material, accompanied by a partial reduction of Ag^+ to metallic Ag. Among the prepared nanocomposites, the nanohybrid with 40 wt.% of Ag_3VO_4 exhibited excellent photocatalytic activity with $14250 \mu\text{mol g}^{-1} \text{h}^{-1}$ of O_2 evolution rate under visible light irradiation using AgNO_3 as an electron acceptor. The highly improved photocatalytic efficiency of the composite was ascribed to (i) the SPR effect of Ag nanoparticles, (ii) Schottky barrier formation at the interface of ZnCr-LDH and Ag_3VO_4 nanoparticles, and (iii) strong coupling between Ag, Ag_3VO_4 , and ZnCr-LDH. Furthermore, the composite showed the lowest fluorescence intensity in the PL spectra, the highest photocurrent density (4 mA cm^{-2}), a reduced arc of the Nyquist plot (50Ω), and the lowest Tafel slope (216 mV dec^{-1}), all of which support the enhanced charge carrier separation across the heterojunctions.

2.2.2.2 LDH as catalytic support for photocatalytic water splitting

In addition, to be used as a pristine photocatalyst, LDHs have also been exploited to improve other semiconductors activity. For instance, Shi *et al.*¹⁴⁴ used LDH as catalytic support to improve the photoactivity of GCN. The authors prepared hierarchical GCN/MgFe- MMO heterojunctions by the thermal decomposition method with different amounts of MgFe- MMO loaded into GCN. The heterostructure with 30 wt.% of MgFe- MMO exhibited the optimal photocatalytic H_2 production ($1.260 \text{ mmol g}^{-1} \text{ h}^{-1}$) about 6.64 times higher than that of pure GCN under visible light irradiation using TEOA as hole sacrificial agent and Pt as cocatalyst. The authors attributed the enhanced photoactivity to the increased surface areas, the decreased bandgap, the unique inter-planar 2D/2D nanostructure, and to the synergistic effect between both components, *e.g.*, spatial charge separation. Luo *et al.*²¹⁰ followed a procedure in which ZnCr-LDH was first exfoliated using formamide as a solvent, followed by hybridisation with GCN as structural support. The ZnCr-LDH/GCN nanohybrids were prepared *via* a self-assembly method with a varied mass ratio between the exfoliated ZnCr-LDH and the GCN nanosheets. Among the nanohybrids, the composite with 1 wt.% ZnCr-LDH nanosheets-modified GCN showed an enhanced photoactivity about 2.8 times higher than that of pristine GCN. The enhanced H_2 evolution activity was attributed to the promoted charge transfer and separation efficiency, owing to the formation of heterojunction and the type II band alignment between the two components. These nanohybrids possessed excellent stability and sustained their structure during the photocatalytic H_2 evolution reaction. Furthermore, the authors suggested the possible photocatalytic H_2 production mechanism, in which the photogenerated electrons in CB of ZnCr-LDH travel to the CB of GCN through strong electronic interaction and then accumulate at Pt reduction active sites to promote H_2 evolution reaction. At the same time, holes in the VB of GCN pass to the VB of ZnCr-LDH, and they react with the TEOA solution (**Figure 17**).

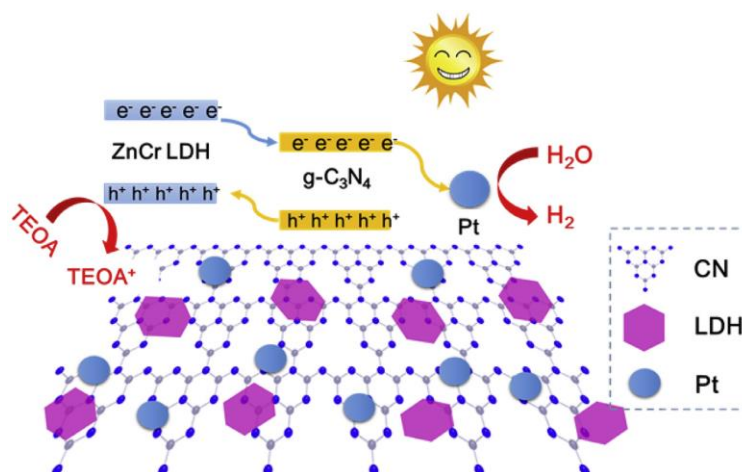


Figure 17. Schematic of band structure and charge transfer process in ZnCr-LDH/GCN for photocatalytic H_2 generation. Adapted from ref.²¹⁰

Most recently, Zhang *et al.*²¹¹ fabricated a type-II heterojunction composed of CoAl-LDH/GCN nanosheets using different amounts of CoAl-LDH (5 to 50 mol%) and applied them for photocatalytic H_2 evolution. The composites were synthesised by adding CoAl-LDH solution into GCN nanosheets suspension followed by a hydrothermal treatment. Among all heterojunctions, the hybrids with 20 mol% of CoAl-LDH displayed the highest photocatalytic HER with a rate of $680.13 \mu\text{mol g}^{-1} \text{h}^{-1}$, which was 21 times higher than that of the pristine CoAl-LDH ($32.91 \mu\text{mol g}^{-1} \text{h}^{-1}$). This superior performance towards water reduction was attributed to the high surface area of the composite, reduced fluorescence, strong photocurrent response and quenched PL of the GCN, indicating the suppression of e^-/h^+ recombination rate.

In sum, LDH-derived and LDH-based materials have shown promising performances towards water splitting reactions. Moreover, building a heterostructure system with LDH allows obtaining materials with ultrathin structures and high surface areas to capture more solar light and facilitate photoinduced charge carrier separation and transport.

In this Thesis, different LDH were prepared and were coupled with GCN semiconductor in order to build heterostructures for photocatalytic water splitting.

Table 2. Summary of LDH-based nanomaterials for photocatalytic water splitting.

LDH-based semiconductors	Preparation method of LDH	Light source	Catalyst load (g L ⁻¹)	Sacrificial agent	H ₂ evolution	O ₂ evolution	AQY	Ref.
Ni ₂ Cr-Cl-LDH	Coprecipitation	300 W Xe lamp	0.2	AgNO ₃ (0.01 M)	-	1037 μmol g ⁻¹ h ⁻¹	-	183
CoTi-LDH	-	200 W Xe lamp for both UV-vis and IR spectrum	0.15	-	-	5300 μmol g ⁻¹ h ⁻¹	-	184
ZnAl-MMO	Coprecipitation Calcination	UV lamp (254 nm 2.2 mW/cm ⁻²)	0.125	50% MeOH	~8000 μmol	-	-	187
MgCr-LDH MgO/MgCr ₂ O ₄	Coprecipitation	125 W Hg Lamp λ ≥ 400 nm	1	10% MeOH	840 μmol g ⁻¹ 2h ⁻¹	-	-	188
Zn _{0.67} Cd _{0.33} S from ZnCdAl-LDH	Coprecipitation Hydrothermal Calcination	300 W Xe lamp λ ≥ 420 nm	0.25	0.75 M Na ₂ S 1.05M Na ₂ SO ₃	6690 μmol g ⁻¹ h ⁻¹	-	-	189
Cu ₂ S/Zn _{0.67} Cd _{0.33} S-LDH	Coprecipitation	300 W Xe lamp λ ≥ 420 nm	30 mg	0.1 M Na ₂ S/Na ₂ SO ₃	15.27 mmol g ⁻¹ h ⁻¹	-	18.15% at 420 nm	190
GaZn-ON	GaZn-LDH Coprecipitation	100 W high-pressure USHIO λ > 420 nm	300 mg	pure water	84 μmol h ⁻¹	~35 μmol h ⁻¹	2.5% at 420-440 nm for HER	212

GaZnON/r-GO	GaZn-LDH Coprecipitation	100 W high pressure USHIO $\lambda > 420$ nm	400 mg	10% MeOH	$\sim 140 \mu\text{mol h}^{-1}$	-	-	213
(Ga _{1-x} Zn _x)(N _{1-x} O _x)- LDH	Coprecipitation	300 W Xe lamp $\lambda > 400$ nm	0.5	H ₂ SO ₄ ; pH =4.5	$\sim 700 \mu\text{mol g}^{-1}$	-	4.11%	214
Fe-MgAl-LDH	Coprecipitation	125 W Hg Lamp $\lambda > 420$ nm	1	10% MeOH	$493 \mu\text{mol g}^{-1} \text{h}^{-1}$	-	-	196
Tb-ZnCr-LDH	Coprecipitation Hydrothermal	Xe lamp 150 W $\lambda > 420$ nm	1	AgNO ₃ (0.01 M)	-	$1022 \mu\text{mol g}^{-1} \text{h}^{-1}$	55% at 450 nm	194
MgFe-MMO/g- C ₃ N ₄	Coprecipitation Calcination	300 W Xe lamp $\lambda > 420$ nm	0.3	10% TEOA	$1.26 \text{ mmol g}^{-1} \text{h}^{-1}$	-	6.9% at 420 nm	144
ZnCr-LDH/g-C ₃ N ₄	Coprecipitation	300 W Xe lamp $\lambda > 420$ nm	0.125	10% TEOA	$186.97 \mu\text{mol g}^{-1} \text{h}^{-1}$	-	-	210
ZnCr-LDH/g-C ₃ N ₄	-	300 W Xe lamp $\lambda > 420$ nm	-	10% TEOA	$155.7 \mu\text{mol g}^{-1} \text{h}^{-1}$	-	-	215
NiAl LDH/g-C ₃ N ₄	Hydrothermal	300 mW cm ² Quartz Tungsten Halogen lamp	0.3	10% TEOA	$3170 \mu\text{mol g}^{-1} \text{h}^{-1}$	-	-	197
CoAl-LDH/g-C ₃ N ₄	Coprecipitation Hydrothermal	300 W Xe lamp Optical filter AM 1.5	0.5	10% TEOA	$680.13 \mu\text{mol g}^{-1} \text{h}^{-1}$	-	-	211
CdS/MgAl-LDH	-	Lamp UV light (254 nm -4.4mW)	0.125	50% MeOH	$1100 \mu\text{mol}$	-	-	199

CdS/NiFe-LDH	Microemulsion systems	300 W Xe lamp	1	10% MeOH	469 $\mu\text{mol g}^{-1} \text{h}^{-1}$	-	-	216
CdS/NiFe-LDH Nanorods	Liquid laser ablation	150 W Xe lamp Simulated sunlight	0.06	20% $\text{C}_3\text{H}_6\text{O}_3$	72 $\text{mmol g}^{-1} \text{h}^{-1}$	-	18.2% at 425 nm	217
NiCo-LDH/P-CdS	Coprecipitation Hydrothermal	300W Xe lamp $\lambda \geq 420 \text{ nm}$	0.5	10% $\text{C}_3\text{H}_6\text{O}_3$	8.665 $\text{mmol g}^{-1} \text{h}^{-1}$	-	14.0% at 420 nm	218
Ni(OH) ₂ &Ce(OH) ₃ @P-CdS	Coprecipitation Hydrothermal	-	0.4	10% lactic acid ($\text{C}_3\text{H}_6\text{O}_3$)	738.13 μmol	-	-	219
NH ₂ -MIL-125(Ti)/ZnCr-LDH	Coprecipitation	300 W Xe lamp $\lambda > 420 \text{ nm}$	0.6	0.01 M TEOA	127.6 $\text{mmol g}^{-1} \text{h}^{-1}$	-	-	220
CdS/MCTMPs	-	150 W Xe lamp Solar simulator	0.06	20% $\text{C}_3\text{H}_6\text{O}_3$	136.77 $\mu\text{mol mg}^{-1} \text{h}^{-1}$	-	40.6% at 425 nm	221
Cu ₂ O/ZnCr-LDH	Hydrothermal	300 W Xe lamp $\lambda > 420 \text{ nm}$	1	Pure water	0.90 $\mu\text{mol h}^{-1}$	0.44 $\mu\text{mol h}^{-1}$	~0.2%	222
Cu ₂ O/ZnCr-LDH	-	300 W Xe lamp $\lambda > 420 \text{ nm}$	1	Pure water	3.42 $\mu\text{mol h}^{-1}$	1.63 $\mu\text{mol h}^{-1}$	0.76% at 420 nm	223
Co(OH) ₂ /ZnCr-LDH	Coprecipitation	125 W Hg lamp $\lambda > 400 \text{ nm}$	1	10% MeOH AgNO ₃ (0.05 M)	27875 $\mu\text{mol g}^{-1} \text{h}^{-1}$	14000 $\mu\text{mol g}^{-1} \text{h}^{-1}$	13.12% 6.25%	224
LaFeO ₃ /ZnCr-LDH	Coprecipitation	visible light irradiation	-	MeOH	963 $\mu\text{mol h}^{-1}$	-	5.94%	225

CeO ₂ /MgAl-LDH	Coprecipitation	125 W Hg Lamp $\lambda \geq 420$ nm	1	10% MeOH	990.0 $\mu\text{mol } 2 \text{ h}^{-1}$	-	-	226
Bi ₂ O ₃ NPs/ZnCr-LDH	Coprecipitation Calcination	Solar simulator (Vis 380-780 nm)	0.83	AgNO ₃ (0.01 M)	-	1470 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	-	227
TiO ₂ /ZnAl-MMO-LDH	Coprecipitation	400-Wmetal halide lamp $\lambda \geq 400$ nm	0.2	AgNO ₃ (0.01 M)	-	371 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	84% at 400 nm	228
ZnS-ZnO/ZnAl-LDH	Coprecipitation	Mercury lamp (UV Pen-Ray)	0.5	50% MeOH	1599 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	-	37.9%	229
ZnSQDs/MnZnAl-LDH	Coprecipitation	300 W Xe lamp $\lambda > 420$ nm	0.5	AgNO ₃ (0.01 M)	12.64 $\mu\text{mol h}^{-1}$	-	-	230
ZnSQDs/CoZnAl-LDH	Hydrothermal				10.56 $\mu\text{mol h}^{-1}$	-	-	
MoS ₂ /NiFe-LDH	Coprecipitation Exfoliation Hydrothermal	125 W Hg lamp $\lambda > 400$ nm	1	10% MeOH	550.9 $\mu\text{mol h}^{-1}$	-	-	200
CoAl-LDH/r-GO	Solvothermal method	300 W Xenon lamp λ ≥ 420 nm	-	CH ₃ CN, TEOA, H ₂ O (3/1/1, v/v/v ratio)	1571.84 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	-	0.98% at 450 nm	203
ZnCr ₂ O ₄ @ZnO/g-C ₃ N ₄	Coprecipitation Calcination	125 W Vis lamp $\lambda \geq 400$ nm	1	10% MeOH AgNO ₃ (0.05 M)	847 $\mu\text{mol h}^{-1}$	454 $\mu\text{mol h}^{-1}$	28.01% 15.0%	198

BiVO ₄ /MgAl-LDH/CdS	Coprecipitation Hydrothermal	UV: 125 W Hg Vis: 150 W Xe lamp	1	Na ₂ S/Na ₂ SO ₃ (1 M) AgNO ₃ (0.05 M)	17350 μmol g ⁻¹ h ⁻¹	33000 μmol g ⁻¹ h ⁻¹	7.22% for HER & 13.73% for OER	231
NiFe-LDH/N-rGO/ g-C ₃ N ₄	Coprecipitation Hydrothermal Exfoliation	125 W Hg lamp λ > 400 nm	1	10% MeOH	2508 μmol g ⁻¹ 2h ⁻¹	-	-	232
r-GO/LTO/NiFe-LDH	Coprecipitation	Simulated solar irradiation, AM 1.5 (100 mW cm ⁻²)	0.5	10% TEOA	532.2 μmol g ⁻¹ h ⁻¹	-	-	233
Ag@Ag ₃ VO ₄ /ZnCr-LDH	Coprecipitation	150 W Hg lamp λ > 400 nm	1	AgNO ₃ (0.05 M)	-	14250 μmol g ⁻¹ h ⁻¹	-	208
WO _{3-x} /Ag/ZnCr-LDH	Coprecipitation	150 W Xe lamp λ ≥ 420 nm	1	10% MeOH	29 375 μmol g ⁻¹ h ⁻¹	-	9.41%	234
CoAl-LDH/CaFe ₂ O ₄ /Au	Coprecipitation Sol-gel	150 W Xe lamp λ > 420 nm	1	10% MeOH AgNO ₃ (0.01 M)	379.1 μmol h ⁻¹	205.5 μmol h ⁻¹	-	235
MgAl-LDH/NiS	Hydrothermal	300 W Xe lamp λ > 420 nm	1	25% MeOH	35.8 μmol h ⁻¹	-	-	185
NiCo-LDH/g-C ₃ N ₄	<i>In-situ</i> growth	300 W Xe lamp UV-vis	0.5	AgNO ₃ (0.01 M)	-	26.7 μmol h ⁻¹	-	167

Ni _x Co _{1-x} O@C/CdS	-	300 W Xe lamp $\lambda > 420$ nm	0.5	10% MeOH	56 mmol g ⁻¹ h ⁻¹	-	-	236
---	---	-------------------------------------	-----	----------	---	---	---	-----

2.3. Graphene-derivatives

GR is a 2D carbon allotrope material with a hexagonal structure that provides it with unprecedented electrical conductivity and carrier mobility, as well as excellent mechanical flexibility and high specific surface area. GR and its derivatives have been widely investigated for photocatalytic applications due to their intrinsic ability to extract and transport charges from optical semiconductors. An overview concerning the synthesis, properties and photocatalytic water splitting applications of GRDs will be summarised in this section. Further, a list of some studies examples on GCN/GRDs-based photocatalysts for water splitting are presented in **Table 3**.

2.3.1 Properties and synthesis

GR is a single atom thick sheet of sp^2 hybridised carbon atoms covalently bound to three others through a carbon–carbon bond (with a fixed length of 0.142 nm), resulting in a hexagonal ring-like structure (**Figure 18**).²³⁷⁻²³⁹ The thickness of a GR sheet is *ca.* 0.34 nm, and its sheet size ranges from few nanometres to several centimetres, depending on the synthesis process. GR edges can present armchair or zigzag motifs (**Figure 18**), with the two edge groups leading to different electrical and magnetic properties.²³⁷⁻²³⁹ Single-layered GR is a zero bandgap semiconductor due to the electronic band overlap; it has high carrier mobility ($\sim 20\,000\text{ cm}^2\text{ V}^{-1}\text{ S}^{-1}$) with an exceptional charge transfer ability, owed to its electrical conductivity ($\sim 10^8\text{ S m}^{-1}$). Its electrical, optical, and mechanical properties combined with its 2D structure and high specific surface area (theoretical value of $\sim 2630\text{ m}^2\text{ g}^{-1}$) make single-layered GR an efficient material for enhancing charge extraction and transport and easily combine with other semiconductors and conjugated polymers to form electronic bridges.^{202, 237-240} Single-layered GR possesses high optical transparency (97.7%) in the visible light region with little reflectance ($< 0.1\%$). However, this transparency can be reduced by increasing the number of layers, originating a multi-layered GR that is an attractive conductor with photo-responsive capacity.^{202, 237-240} Considering its ease of modification, GR is deemed as the building block for all graphite-derivatives such as fullerene, graphene quantum dots, carbon nanotubes, graphene nanoribbons, and the topologically similar graphanes and graphynes.²⁴⁰⁻²⁴³ GRDs such as graphene oxide (GO), rGO and few-layer graphene (FLG), together with the mentioned graphite-derivatives, possess similar electrochemical properties to GR but with semiconducting abilities (*i.e.*, with an intrinsic bandgap), rendering them interesting materials for photocatalytic applications.²⁴²⁻²⁴⁶ Moreover, GCN can be considered as an N-substituted

GRDs by some authors^{53, 247} since it shows a planar structure composed of aromatically-conjugated carbon and nitrogen atoms in the polymeric matrix.

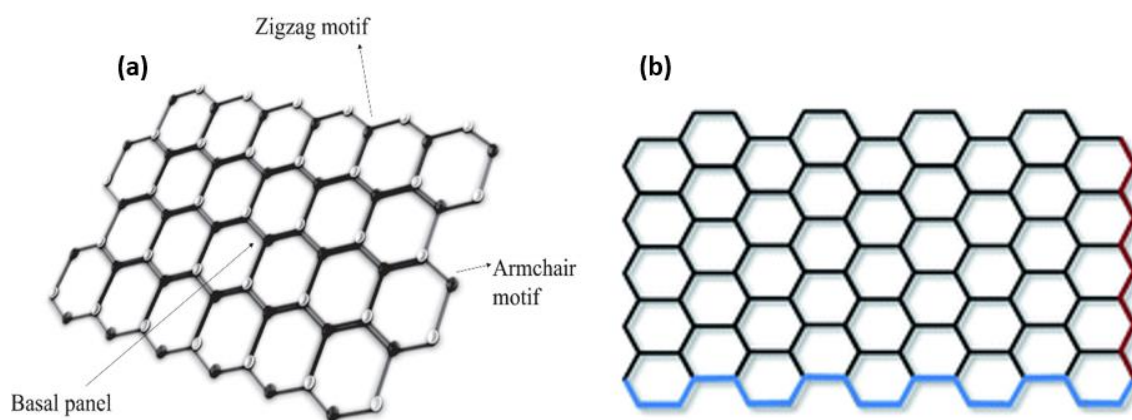


Figure 18. a) Structure of pristine GR; b) Armchair (blue) and zigzag (red) edges in monolayer GR. Reprinted from Ref.^{240, 248}

Several attempts were made to synthesise GR, but only in 2004, ground-breaking research by Geim and Novoselov resulted in the preparation of a single sheet of GR using a scotch tape process on top of a silicon wafer.³⁹ Since then, extensive progress has been achieved on fabricating GR and GRDs by different approaches. GR can be obtained through top-down or bottom-up techniques, which are depicted in **Figure 19**.^{202, 242, 245} Briefly, in top-down approaches, the starting material is graphite which is afterwards exfoliated by mechanical, oxidative-reduction or liquid-phase treatments to generate pristine GR. In comparison, bottom-up approaches rely on different processes to generate GR from molecular precursor building blocks, such as chemical vapour deposition (CVD), or epitaxial growth, to name a few.

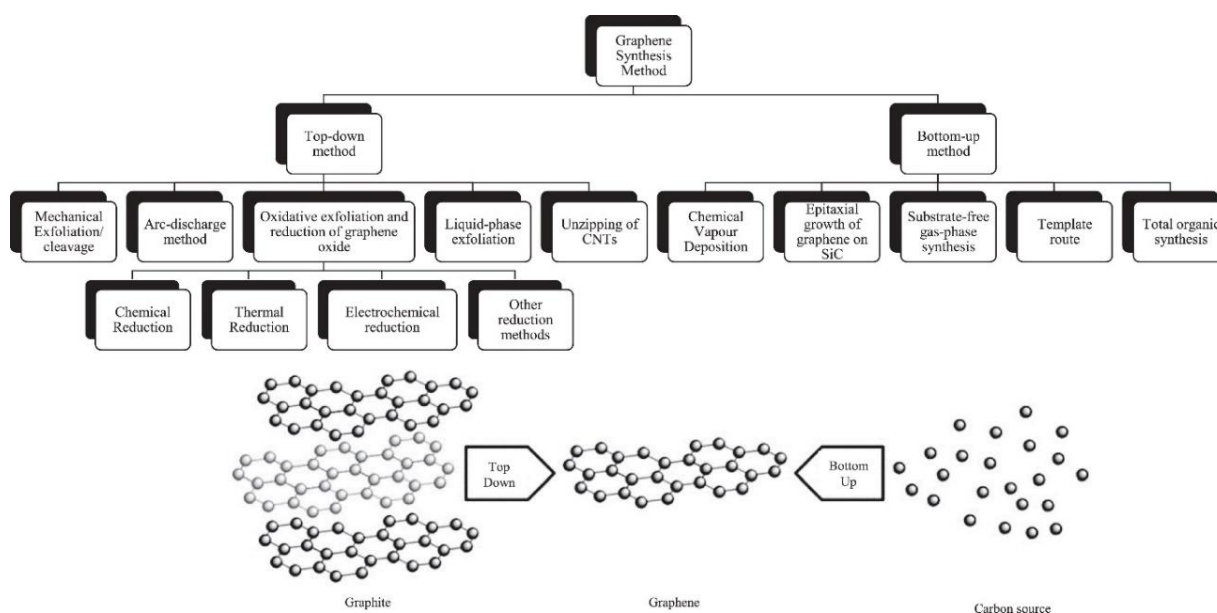


Figure 19. Synthesis methods of GR. Adapted from Ref.²⁴⁰

The mechanical exfoliation method is one of the most common approaches used in the synthesis of thin flakes of GR on pre-selected substrates.^{240, 249, 250} It consists of a rapid peeling process of graphite using advanced equipment and techniques with ultra-sharp single-crystal diamond wedges.^{240, 251, 252} In this approach, GR is isolated from the graphite crystal by means of repeatedly placing-removing using adhesive tape. Then, multi-layers of GR are cleaved into single layers and flakes. Usually, solvents like acetone are used to separate GR from the tape.²⁵³ In addition, mechanical cleaving requires an external force of up to 300 nN mm^{-2} to remove a single atomic layer from graphite.^{249, 250} Despite the relative ease of application and rapid processing of graphite, this method is limited by its low yield of GR.^{240, 250}

Oxidative exfoliation–reduction is based on two subsequent steps using graphite as initial material. First, an oxidation reaction to obtain GO *via* a concentrated acid solution, such as H_2SO_4 , followed by mechanical, chemical or physical exfoliation to produce single layer GO sheets. Then, the GO is converted to GR using strong reductants, such as hydrazine (N_2H_4), which restores the aromatic single-layer carbon lattice.^{242, 254} Another technique includes the reduction of GO through sonication to synthesise GR, wherein the addition of hydrogen occurs using alkenes together with nitrogen gas extrusion and sodium borohydride (NaBH_4) is used as the reducing agent.²⁵⁵

Liquid-phase exfoliation is another widely used method to fabricate single- or multi-layer GR.^{240, 256, 257} This technique was first introduced in 2008²⁵⁸ and consisted of three major steps: (i) dispersion of graphite in a suitable solvent, (ii) exfoliation and (iii) final product purification.²⁵⁹ Graphite contains several layers of GR bound by Van der Waals forces which

can be overcome if the used solvent has a surface tension in the range 40–50 mJ/m². Hernandez *et al.*²⁶⁰ studied liquid-phase exfoliation of GR over 40 types of solvents. The compiled information may be used to yield high concentrations of GR using relatively small volumes of solvent as well as to choose more cost-effective, less toxic, and more reliable solvents. Besides solvent selection, sonication modulation is a critical parameter for providing sufficient cavitation effects during graphite exfoliation to produce single-layered GR. However, it is important to note that some studies report sonication as a cause of defects on the edges and basal planes of GR.²⁶¹

Besides these techniques, electrochemical exfoliation, microwave-assisted exfoliation and microwave-irradiation strategies were also reported to produce GR or FLG with a high productivity and large size materials.²⁶²⁻²⁶⁵

The CVD method has been proven to produce a large area of GR layers.^{240, 243, 246, 266, 267} This technique is a substrate-based process that involves the diffusion of hydrocarbon precursor gases into the surface of transition metal catalysts at a certain growth temperature, followed by the precipitation of carbon out of the bulk metal-to-metal surface upon cooling.^{240, 243, 246, 267} Typically, Ni, Cu and Co films are used as substrates and methane as the feeding gas. The deposition step is carried out in a CVD chamber under vacuum conditions and at selected temperatures ranging from 650 to 1000 °C.^{240, 246, 267, 268} After cooling of the substrate, the solubility of the carbon on the substrate reduces, and a thin film of carbon precipitates forms GR sheets. The GR layer thickness is determined by the cooling rate and the amount of carbon dissolved in the substrate.²⁶⁷ Nonetheless, many process parameters such as gas flow, transition metal catalyst selection, type of precursor, temperature, growth time and gas pressure have significant impacts on the quality of the obtained GR, such as the number of layers, grain size, and doping effect.^{243, 246, 267}

Epitaxial growth is another substrate-based method, in which a single-layer GR is grown on silicon carbide (SiC) substrate using very high temperatures (typically above 1100 °C).^{240, 250, 267} This high-thermal treatment of SiC under vacuum and/or inert conditions result in the sublimation of silicon atoms and formation of GR sheets through a reorganisation and “graphitisation” of the carbon-enriched surface.^{240, 242, 250, 267, 269} The dimensions of the formed GR nanosheets are mostly determined by the size of SiC crystals. However, epitaxial growth leads to low yield and lack of homogeneity, limiting its utilisation.^{240, 242, 267}

Succinctly, GR and GRDs can be prepared by different approaches. From the abovementioned techniques, the most promising and with higher know-how is the CVD method, since it benefits from high yields of GR or GRDs with thin layers with large areas.

The exceptional electrochemical characteristics of GR and GRDs make them a good choice for assisting composite construction, as effectively separate charge carriers and increase the surface area. In addition, the formation of an interface between GRDs and semiconductors can facilitate the transfer of photoexcited e^-/h^+ pairs to the GRDs conductive texture, and thus improve the photocatalytic performance.²⁰² Therefore, there have been different methods developed to design GRDs/semiconductor composites. Among these, hydrothermal, solvothermal, coprecipitation, sol-gel and *in-situ* thermal treatment processes can be found.²⁰² A short overview of the employment of GR and GRDs-based semiconductors and the various approaches carried out to improve the photocatalytic activity towards water splitting will be summarised in the following section.

2.3.2 Graphene-derivatives for photocatalytic water splitting

The conductive and electrochemical properties of GRDs make them a suitable candidate for photocatalytic applications. It was reported that graphite oxide (GrO), GO and rGO behave as semiconductors, in contrast to the ideal GR.²⁴⁴ Moreover, GrO usually behaves as a p-type semiconductor, and its bandgap has been determined to be between 2.4 and 4.3 eV.²⁴⁴ Yeh *et al.*²⁴⁴ reported that GrO exhibits photocatalytic activity towards H_2 generation affording a rate of $2833 \mu\text{mol h}^{-1}$ in the presence of methanol as an electron donor and $47 \mu\text{mol h}^{-1}$ in the absence of sacrificial agents. The same group reported the preparation of various GrO photocatalysts with various oxygen contents and investigated the photocatalytic behaviour towards water splitting.²⁷⁰ The authors revealed that a gradual increase in oxygen resulted in a decrease of the VB maximum of GrO. Thus, O_2 evolution was more easily observed with the GrO with the highest oxidation potential, while the less oxygenated GrO did not show any activity. The GrO with the highest oxygen content had a sufficiently positive VB potential for water oxidation, and H_2 generation was identified in all cases. However, the extremely oxidised GrO possessed a large bandgap, which slowed light absorption into deep UV and resulted in lower H_2 evolution than the GrO with the lowest oxidation level but the smallest bandgap.²⁷⁰ In another study using GRDs, Latorre-Sánchez *et al.*²⁷¹ synthesised P-doped GR through pyrolysis of phosphate derived from natural alginate that contained $H_2PO_4^-$ anions which allowed for a defective GR with oxygen and phosphorous insertions. The obtained P-doped GR produced H_2 from water by a methanol mixture with a rate of $12 \mu\text{mol h}^{-1} \text{ g}^{-1}$ under UV-Vis illumination, which was higher than the non-doped GR. Moreover, the authors studied the activity using TEOA as sacrificial agent and Pt as cocatalyst and observed that the activity was increased to a rate of $282 \mu\text{mol h}^{-1} \text{ g}^{-1}$. Similarly, Chai and co-workers²⁷² reported the preparation of

N-doped rGO and B-doped rGO *via* pyrolysis of GO in the presence of urea and boron anhydride, respectively. The photocatalytic activity towards H₂ production of these doped GRDs, in the presence of 0.1 M Na₂S/Na₂SO₃ aqueous solutions and irradiated with visible light, was about 65 $\mu\text{mol h}^{-1} \text{g}^{-1}$ with both doped photocatalysts, which was 2.6 and 5.3 times higher than the non-doped GO and rGO, respectively. Yeh *et al.*²⁷³ synthesised N-doped GO quantum dots (QDs) by treating GO in NH₃ at 500 °C, followed by oxidation using the Hummers' method.²⁷⁴ The authors demonstrated through EIS that the material behaves as both a p- and n-type semiconductor. Thus, both n and p domains serve as interfacial junctions where charge separation can occur. The bandgap of the N doped-GO QDs was found to be 2.2 eV. In the presence of only water and under visible light irradiation, the H₂ and O₂ evolution amounts were 5 μmol and 3 μmol , respectively.

Oliva and co-workers²⁷⁵ used a casting process to prepare flexible GR composites, which were then grown with Ni(OH)₂ nanoparticles (NPs) using a wet chemical method. These NPs showed spherical shapes and were uniformly dispersed on the GR surface. The obtained Ni(OH)₂ NPs supported on the GR films presented a photocatalytic activity for H₂ evolution upon UV light irradiation of 330 $\mu\text{mol g}^{-1}$, while the GR film alone produced 90 $\mu\text{mol g}^{-1}$. Moreover, it was observed that the GR surface was oxidised during the photocatalytic reaction, resulting in oxygenated groups that acted as active sites in the photogeneration of e⁻/h⁺ pairs and contributed to the overall H₂ generation. In a similar manner, rGO decorated with Ni NPs (Ni-rGO) was synthesised *via* a one-pot reduction using GO and Ni salt as precursors. A synergistic effect between the rGO defects and Ni NPs were found to be responsible for enhanced photocatalytic H₂ production. Using 6 wt.% Ni loading, the photocatalytic activity over the Ni-rGO in an aqueous solution containing TEOA and visible light irradiation was 94 $\mu\text{mol h}^{-1}$, with a QY of 30.3% at 470 nm. In another study, Chen *et al.*²⁷⁶ used a hydrothermal approach to prepare ammonia-modified N-doped GO QDs. The N-doped GO QDs underwent an ammonia treatment to convert certain pyridinic/pyrrolic groups into amino/amide groups. The N-doped GO QDs photocatalyst was latterly modified with Pt NPs as cocatalyst and achieved an H₂ generation rate of 12 $\mu\text{mol h}^{-1}$, which correspond to AQY of 21% at 400 nm.

In addition, to be used as a photocatalyst, GRDs have also shown to play the role of conductive materials to improve the activity of other semiconductors such as GCN, MoS₂ and TiO₂. For instance, MoS₂ nanoplatelets were grown on rGO sheets by one-step pyrolysis at 900 °C under Ar flow with alginate films or powders containing variable amounts of (NH₄)₂MoS₄, as reported by Latorre-Sánchez *et al.*²⁷⁷. The dispersion of MoS₂ on the rGO surface resulted in a strong interaction between the two-layered materials. The photocatalytic reactions under visible light

irradiation and using TEOA as sacrificial agent showed an H_2 production rate around $1.25 \text{ mmol h}^{-1} \text{ g}^{-1}$ over 10%rGO/MoS₂ catalyst, thus being 2.5 times higher than pristine MoS₂. Yuan *et al.*¹⁰⁷ reported a successful strategy to construct an rGO/GCN/MoS₂ heterostructure through a hydrothermal technique. The obtained photocatalyst exhibited an enhanced absorption of visible light and surface area compared to bare GCN. The rGO/GCN/MoS₂ photocatalyst with rGO (0.5%) and MoS₂ (1.2%) reached a high H_2 production rate of $317 \text{ } \mu\text{mol h}^{-1} \text{ g}^{-1}$ and a QY of 3.4% at 420 nm. The enhanced activity was ascribed to the intimate 2D nanojunctions exhibited in rGO/GCN/MoS₂ photocatalysts, which can efficiently suppress charge recombination and accelerate the charge transfer, as demonstrated by photoluminescence and transient photocurrent studies. In another study, Xiang *et al.*²⁷⁸ reported the role of GR/MoS₂ as cocatalyst in the heterojunction TiO₂/rGO/MoS₂. The GR/MoS₂ contributed to suppress charge recombination, enhance the interfacial charge transfer, and provided a large number of active catalytic sites, thus leading to a significant increase in performance towards H_2 generation. The composites yielded an H_2 production rate of $165.3 \text{ } \mu\text{mol h}^{-1}$ (correspond to an AQE of 9.7% at 365 nm), which was 39 and 4 times higher than TiO₂ and TiO₂/MoS₂, respectively.

Further progress was made by Xue *et al.*²⁷⁹, who reported the synthesis of a Cd_{0.5}Zn_{0.5}S/rGO/GCN photocatalyst by a two-step. The Cd_{0.5}Zn_{0.5}S and rGO particles were well distributed on the GCN surface according to the SEM results, and the Cd_{0.5}Zn_{0.5}S were well dispersed on the surface of rGO. This ternary composite shows a maximum photocatalytic H_2 generation rate of $39.2 \text{ mmol h}^{-1} \text{ g}^{-1}$ under visible light with a QE of 37.9% at 420 nm, which was about 48.4-fold superior to bare GCN. The enhanced photoactivity was due to the presence of rGO material which acts as a mediator carrier between the two semiconductors, and to the synergistic effect between the materials.

In another work, Rahman *et al.*²⁸⁰ constructed a ternary heterostructure by soft grafting GCN and GO into an amorphous carbon nitride (ACN) substrate. A redox junction was formed due to the band alignment of GCN, ACN and GO, thus facilitating the separation of photogenerated e^-/h^+ pairs and increasing the photoactivity. Moreover, the obtained composite exhibited a larger surface area than that of pure ACN or GCN/ACN due to the presence of GO. The photocatalyst exhibited an H_2 generation rate of $251 \text{ } \mu\text{mol h}^{-1}$ and an AQE of 6.3% at 420 nm when using 3 wt.% of Pt cocatalyst and TEOA as a sacrificial agent under visible light irradiation. The enhanced photoactivity was attributed to the presence of GO as an electron acceptor and to the synergistic effect between the materials.

More recently, Zhao *et al.*²⁸¹ constructed a ternary B-doped GCN dots (BCNDs)/GCN/GO photocatalyst through a hydrothermal method. The obtained BCNDs/rGO/GCN photocatalyst showed a high H₂ evolution of 741.4 $\mu\text{mol h}^{-1} \text{g}^{-1}$ under visible irradiation and an AQE of 19% at 420 nm, which was 11.0, 2.4 and 2.3 times higher than that of GCN, GCN/rGO and BCNDs/GCN, respectively. The increased photoactivity was assigned to the synergistic effect between the three compounds, enhanced visible light absorption, higher surface area and restrained charge carrier recombination.

Zhang *et al.*²⁸² investigated the photocatalytic activity of TiO₂/GR sheets under UV-Vis light irradiation. The highest H₂ evolution rate was 5.4 $\mu\text{mol h}^{-1}$, obtained with the composites containing 2 wt.% of GR. The enhanced activity was ascribed to the high GR electron conductivity and suppressed recombination of photogenerated e^-/h^+ . In another example based on a TiO₂ semiconductor, Fan and co-workers²⁸³ compared the H₂ production efficiency from TiO₂-rGO composites prepared through UV-assisted photocatalytic reduction, using hydrazine reduction and hydrothermal synthesis. The composites prepared by the hydrothermal process achieved the highest H₂ generation. When the mass ratio was 1.0/0.2 for TiO₂/rGO, the rate was 74 mmol h^{-1} , higher than that of pure TiO₂ (6.8 mmol h^{-1}). The composites even demonstrated catalytic H₂ evolution in pure water without the use of sacrificial agents, showing enormous prospects for future materials. The hydrothermal approach provided the most intimate interaction between the titanate moiety and rGO, enabling the composites to fully take advantage of the electron acceptor and transfer ability of GR.

In sum, the interesting physicochemical properties of GR and GRDs, such as their high carrier mobility and large surface area, make them appealing for photocatalytic applications. The role of these conductive materials as electron sinks and in preventing e^-/h^+ pair recombination in semiconducting systems has been widely elucidated. The combination with other semiconductors has proven very effective for photocatalytic water splitting reactions. Therefore, in this Thesis, different type of FLG as GRDs family were prepared by the CVD method and assembled with GCN semiconductor to build heterostructures for photocatalytic water splitting.

Table 3. Some reported H₂ generation of several GCN/GRDs based heterostructures.

Photocatalyst	Light Source	Sacrificial reagent	H ₂ generation ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	AQY (%)	Ref.
GCN/GO	300 W Xe lamp, $\lambda > 400 \text{ nm}$	Methanol	451	2.6%	108
GCN/GO	300 W Xe lamp, $\lambda > 420 \text{ nm}$	TEOA	251	6.3 at 420 nm	280
C ₆₀ /GR/GCN	LEDs, $\lambda > 420 \text{ nm}$	TEOA	545	4.28 at 420 nm	284
Doped GR-QDs/ZnNb ₂ O ₆ /GCN	300 W Xe lamp, $\lambda > 420 \text{ nm}$	Methanol	341	-	285
GR-QDs/Mn-N-TiO ₂ /GCN	300 W Xe lamp, $\lambda = 320\text{-}780 \text{ nm}$	-	870	-	286
GCN/GR/MoS ₂	300 W Xe lamp, $\lambda > 420 \text{ nm}$	TEOA	317	3.4 at 420 nm	107
GCN/rGO/BCNDs*	300 W Xe lamp, $\lambda > 420 \text{ nm}$	TEOA	744	19 at 420 nm	281
GCN.QDs/GO	300 W Xe lamp, $\lambda = 350\text{-}870 \text{ nm}$	Ethanol	1231	13 at 420 nm	287
GCN/GO	300 W Xe lamp, $\lambda > 400 \text{ nm}$	TEA	225	-	288
GCN/GR/RCF*	300 W Xe lamp, $\lambda \geq 420 \text{ nm}$	TEOA	412	-	289
GCN/GR/Co	300 W Xe lamp, $\lambda \geq 420 \text{ nm}$	TEOA	892	0.67 at 420 nm	290

*RCF = recycled carbon fibre

Chapter 3

Characterisation techniques

In this chapter, the overall characterisation techniques used throughout this Thesis are listed with a brief description. The list includes scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), physisorption measurements, UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), steady-state and time-resolved fluorescence, zeta potential analysis, and electrochemical techniques, such as linear sweep voltammetry (LSV).

3.1 Electron microscopy

Electron microscopy is a powerful technique that provides direct visualisation of materials at different length scales, with resolutions ranging from micro- to nanometres. In this technique, a beam of electrons is used to create an image of the specimen.^{291, 292} Different electron microscopy techniques exist nowadays, with the most used ones being scanning and transmission electron microscopy (SEM and TEM, respectively). As the names suggest, the main difference between the two microscopies is the analytical methodology: SEM operates through a scanning approach, while TEM works in a transmission mode. Another difference between them is that SEM focuses on the surface of the sample and allows for surface composition, while TEM observes beyond the surface. Generally, TEM achieves a much higher resolution than SEM.²⁹¹⁻²⁹⁴

Both methods were used in this dissertation to investigate the morphology and the structure of the prepared materials.

3.1.1 Scanning electron microscopy

SEM produces images by bombarding the specimen with a focused electron beam scanned across the sample in a rastering manner, with an electron acceleration voltage between 1 eV and 30 eV.²⁹¹⁻²⁹³ These highly energetic electrons dissipate their energy by interacting with the sample, providing different morphological information. The recorded signals are composed of secondary electrons (SE), backscattered electrons (BSE), X-rays useful for EDX analysis, cathodoluminescence and Auger electrons (AE) (**Figure 20**). These signals carry information about the morphology, topography, and composition of the sample.²⁹¹⁻²⁹³

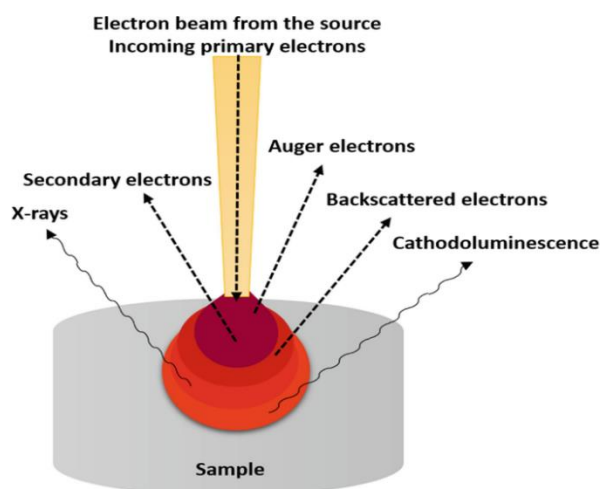


Figure 20. Schematic of different signals produced by interactions of an electron beam with the sample. Each signal comes from a different depth of the sample. Reprinted from ref.²⁹⁵

In this Thesis, three different SEM apparatus were used. Chapter 4 (*FLG/GCN heterojunctions for H₂ generation*) used a Hitachi S4100 instrument with an electron beam accelerating voltage of 30 kV (University of Aveiro). In chapter 5 part 1 (*NiCeAl-LDH/GCNN hybrids for photocatalytic H₂ generation*) was used an FEI Quanta 400FEG ESEM/EDAX Genesis X4M instrument (Centro de Materiais da Universidade do Porto – CEMUP, University of Porto), and in chapter 5 part 2 (*CuAl-LDH/GCNN hybrids for photocatalytic H₂ and O₂ evolution*) was used an FEI 2 Quanta 250 FEG at 200 keV with an electron beam acceleration voltage of 2 kV (Institute of Materials Chemistry, Vienna University of Technology).

3.1.1.2 Energy-dispersive X-ray spectroscopy

EDX (or sometimes known as EDS) is a technique used for elemental analysis of a sample, usually performed in conjugation with SEM. This technique is based on the interaction of the electrons (alternatively X-rays) with a sample and provides information about the atomic composition of the sample's surface.

3.1.2 Transmission electron microscopy

TEM provides information relative to beam energies ranging between 100 to 400 keV (in contrast to SEM from 1 to 30 keV) and uses the signals captured from transmitted electrons (**Figure 20**). The sample thickness critical as it improves signal resolution and the visibility of the obtained imagery. The specimen must be thick enough to absorb electrons but thin enough for electrons to pass through (range of 100 nm). When the electrons are transmitted through the sample, they are distributed or dispersed at various angles by the sample, depending on the chemical composition and thickness of the material. Hence, different phases, atomic composition, structural defects, and others, can be detected.^{291, 294, 296}

In this Thesis, two different TEM apparatus were employed to characterise the materials. The samples were prepared in an ethanolic solution (alternatively sonicated for 5 min for material dispersion), added dropwise on specific grids and dried. In chapter 4 (*FLG/GCN heterojunctions for H₂ generation*) was used a Jeol JEM-2200FS equipment operated at 200 kV acceleration voltage (University of Aveiro). In chapter 5, part 2 (*CuAl-LDH/GCNN hybrids for photocatalytic H₂ and O₂ evolution*), the samples were measured on an FEI Tecnai F20 equipment with a field emission gun in bright field mode using a 200 kV acceleration voltage (Institute of Materials Chemistry, Vienna University of Technology).

3.2 X-ray methods

The determination of chemical and crystalline structure are indispensable features for identifying and characterising materials. X-rays are highly energetic electromagnetic radiation with a wavelength (λ) varying between 0.01 and 10 nm. This makes it appropriate to collect information at the atomic scale as the interatomic spacing lies in the same order of magnitude.^{297, 298} When an X-ray beam interacts with the sample, two processes can occur: (i) scattering of the incident beam and (ii) absorption of X-ray photons that allow the electrons to be ejected. These two phenomena are used respectively for X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).^{297, 298}

3.2.1 X-ray diffraction

X-ray diffraction (XRD) is a powerful technique useful for determining the crystallographic structure of a material. XRD is based on the elastic interaction between the monochromatic X-rays and the ordered atomic structure of the solid sample.^{297, 299} XRD provides details on the crystals structure, arrangement of atoms, size of crystals and symmetry. In a standard powder diffraction experiment, a parallel beam of X-rays is scattered by a periodic crystalline structure resulting in a different direction length of $2\Delta l$ for incident X-rays (1 and 2) and reflected by two parallel lattice planes of crystalline materials (**Figure 21**).^{297, 299} The crystal parameters are determined by the interplanar spacing of the atoms. These values can be determined by Bragg's law diffraction, Eq. (7):

$$2 d \sin(\theta) = n \lambda \quad (7)$$

where d is the inter-planar spacing, θ is the angle at which both the incident (1 and 2) and the outgoing (1' and 2') beams scatter concerning the atomic planes, n present a positive integer and λ the wavelength of the incoming beam.^{297, 299} In order to have constructive interference of the scattered beams, the condition required to achieve a diffractogram, the discrepancy in the path length of the scattered beams has to accomplish the Bragg condition, $2d\sin\theta$. Otherwise, disruptive interference can occur, and lower intensities or no signal can be observed.^{297, 299}

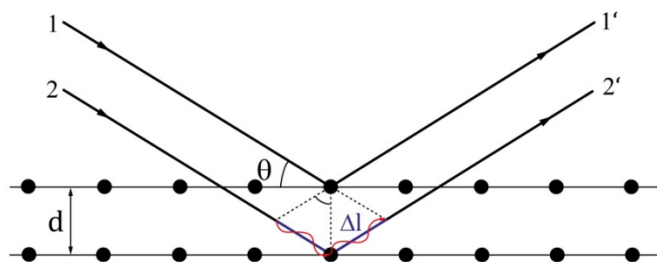


Figure 21. Bragg diffraction scheme. Black circles represent atoms of two parallel periodic lattice planes with a distance between them equal to d . Ingoing (1 and 2) and outgoing (1' and 2') parallel X-ray beams possess a difference in path length of $2\Delta l$ after the scattering. Reprinted from ref.²⁹⁷

In this Thesis, in both chapter 4 and chapter 5 part 1, the XRD patterns were recorded on a PANalytical X'Pert MPD apparatus equipped with an X'Celerator detector and secondary monochromator ($\text{CuK}\alpha = 0.154 \text{ nm}$, 40 kV, 30 mA; data recorded at a 0.0178 step size, 100 s/step) (University of Aveiro). In chapter 5 part 2, XRD analysis was performed using an XPERT II: PANalytical XPert Pro MPD Q-Q diffractometer and a X'Celerator (2.1°) detector with the signals being acquired with a Bragg-Brentano Q/Q-diffractometer geometry ranging from 10° to 70° degrees and data being recorded after irradiation with a Cu X-ray source (8.04 keV, 1.5406 Å) (Institute of Materials Chemistry, Vienna University of Technology).

3.2.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a commonly used surface chemistry analysis technique that operates under ultra-high vacuum. After X-ray irradiation of the sample's surface, electrons are ejected from valence and core energy levels. The kinetic energies of the ejected photoelectrons are not only characteristic of the atoms from which they are emitted but can also provide information on the chemical states of those atoms.^{298, 300} Each atom in the sample has specific binding energy according to their inner-shell electrons. To promote electron excitation, the energy of the incident X-ray photons must be larger than the critical energy known as the surface work function. At the same time, the excited electrons need to overcome the binding energy. Hence, the kinetic energy of an ejected electron will be equal to the energy of the incident X-rays minus the work function and the binding energy of the electron as shown by Eq. (8).^{298, 300}

$$E_K = E_p - (E_B + \phi) \quad (8)$$

Where E_k is the kinetic energy of photoexcited electrons, E_p states to X-ray photons energy, E_B is the bonding energy, and ϕ is the surface work function of the instrument detector. Thus, the elemental identity, chemical state, and quantity of a detected element can be determined from the binding energy and intensity of a photoelectron peak.

In chapter 5 part 2 (*CuAl-LDH/GCNN hybrids for photocatalytic H_2 and O_2 evolution*), the XPS measurements were carried out on a custom-built SPECS XPS-spectrometer equipped with a monochromatic Al- K_α X-ray source (μ 350) and a hemispherical WAL-150 analyser (acceptance angle: 60°) (Institute of Materials Chemistry, Vienna University of Technology). Pass energies of 100 eV and 30 eV and energy resolutions of 1 eV and 100 meV were used for survey and detail spectra, respectively (excitation energy: 1486.6 eV, beam energy and spot size: 70 W onto 400 μ m, angle: 51° to sample surface normal, base pressure: 5×10^{-10} mbar, pressure during measurements: 2×10^{-9} mbar). In addition, a broad-spot low energy electron source (SPECS FG 22 flood gun, 8–12 eV/15–30 μ A) was used for charge compensation in some samples to reduce charging effects. In both cases, CasaXPS was utilised for data analysis.

3.3 Attenuated total reflectance - Fourier transform infrared spectroscopy

FTIR is an effective method for identifying the chemical structure as well as the presence or absence of different functional groups in a given sample. An infrared (IR) spectrum is obtained by passing IR radiation through a sample and determining what fraction of the incident radiation is absorbed in a particular wavenumber or frequency. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration or bending of a part of a sample. Moreover, chemical bonds in different environments will absorb varying intensities and at varying frequencies. Thus, IR spectroscopy involves gathering absorption information and analysing it in the form of a spectrum.^{301, 302}

ATR is an FTIR sampling method that enables the measurement of the sample directly in the solid or liquid state without further treatment. The phenomenon used here is the total internal reflection which generates an evanescent wave in the measured sample.³⁰¹

In this Thesis, the IR spectra were recorded on a JASCO Fourier Transform Infrared spectrometer (FT/IR-6800). Each spectrum was collected in ATR mode at room temperature in 600–4000 cm^{-1} (256 scans; 4 cm^{-1} resolution). The spectra were analysed using JASCO Spectra Manager™ II cross-platform software.

3.4 Surface area measurements

Physisorption experiment involves physical adsorption of a specific gas over the material's surface (including filling pores and cavities) and determining the total surface area, pore size distribution and pore volume. Many principles that provide mathematical models of the adsorption to derive the necessary information from the physisorption experiment, such as the Langmuir theory.³⁰³ However, the most helpful model is the Brunauer-Emmett-Teller theory (BET).^{304, 305} The BET model is an extension of the principle of monolayer molecular adsorption to multilayer adsorption where many molecules can adsorb on top of each other at each adsorption site. Assuming that the gas molecules will adsorb to the solid forming infinite layers, these layers do not interact with each other.^{304, 305} BET theory permits the measurement of specific surface area (S_{BET}) of the sample, as well as the type and shape of a physisorption isotherm, giving information on the porosity, pore volume and pore size distribution for macro ($d > 50$ nm), meso ($2 \text{ nm} < d < 50$ nm) and microporous ($d < 2$ nm) materials.³⁰⁴ Moreover, there are essentially six types of isotherms, as shown in **Figure 22**, identified by IUPAC.³⁰⁴ Each type is observed in practice, but by far, the most common are types I, II and IV. Type I is the characteristic example of a microporous material, while type II is given by a nonporous or merely macroporous material and type IV is an example of a predominantly mesoporous material.³⁰⁴

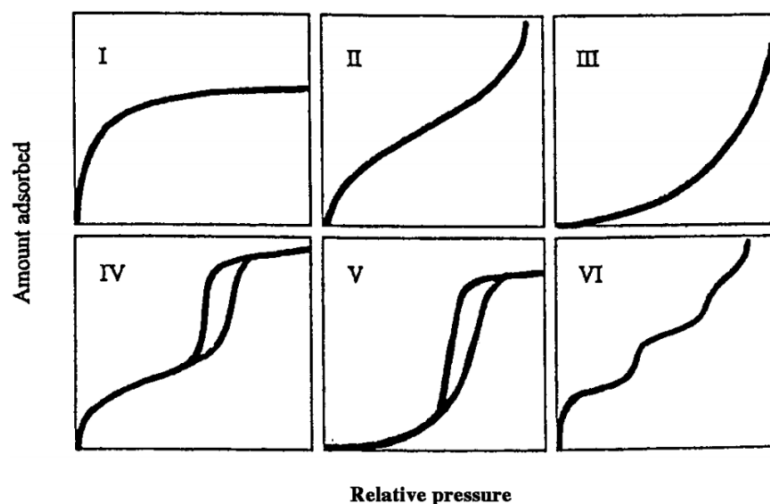


Figure 22. IUPAC classification of physisorption isotherm types. Reprinted from ref.³⁰⁴

In this Thesis, in chapter 4 (*FLG/GCN heterojunctions for H_2 generation*) and chapter 5 part 1 (*NiCeAl-LDH/GCNC hybrids for photocatalytic H_2 generation*), the physisorption measurements were carried out on a Quantachrome Nova 4200e apparatus equipment at

–196 °C (LSRE-LCM, University of Porto). Before the measurements, the samples were degassed at 120 °C for 3 h. Then, in chapter 5 part 2 (*CuAl-LDH/GCNN hybrids for photocatalytic H_2 and O_2 evolution*), the measurements were carried out on a Micromeritics ASAP 2020 at –196 °C (Institute of Materials Chemistry, Vienna University of Technology).

3.5 Optical spectroscopy

3.5.1 UV-Vis diffuse reflectance spectroscopy

The UV-Vis diffuse reflectance spectroscopy (DRS) is a technique that provides information about the electronic properties of the materials based on the absorptive and light scattering properties of the sample, allowing to calculate of the optical bandgap energy of semiconductors. In DRS, a beam of light is incident upon a solid sample surface. Due to particle packaging some of these incident photons are directly reflected back to the sample surface (**Figure 23**, left), while others can penetrate to a certain sample depth while undergoing several reflection/absorption steps.³⁰⁶⁻³⁰⁸ After these steps, these photons leave the sample and reflected back diffusely with an angle different from the initial incident, as shown in **Figure 23** (right). This diffuse reflected light can be collected and analysed to provide information on the optical absorption properties of the studied sample.³⁰⁶⁻³⁰⁸

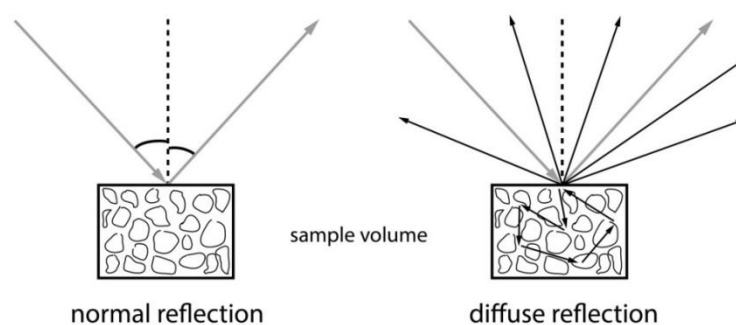


Figure 23. Light scattering at smooth surfaces: normal or regular (grey) and diffuse (black) reflection. Adapted from ref.³⁰⁸

Therefore, a typical reflectance spectrum is obtained in reflection (%) vs wavelength (λ , nm). Further, converting the spectrum to equivalent absorption units is possible through the Kubelka-Munk (KM) theory.³⁰⁶⁻³⁰⁹ This theory was first developed to explain the phenomena of light travel through a solid specimen; however, it can be applied to the DRS data using the KM equation – Eq. (9).³⁰⁶⁻³⁰⁹

$$\frac{K}{S} = \frac{(1 - R_{\infty})^2}{2 R_{\infty}} = F(R_{\infty}) \quad (9)$$

Where K represents the absorption coefficient, S represents the scattering coefficient of the sample, R_{∞} is the reflection of the sample when it is infinitely thick, and $F(R_{\infty})$ is usually termed remission KM function. In this method, the KM function is plotted against the wavelength.³⁰⁶⁻³⁰⁹

The UV-Vis spectra once, converted to the KM units, can then be used to calculate the E_g using the Tauc plot method and according to Eq. (10).³¹⁰

$$(\alpha h\nu)^{1/n} = K(h\nu - E_g) \quad (10)$$

Where α , h , ν , K and E_g are the absorption coefficient, Planck constant, light frequency, proportionality constant, and bandgap energy. The exponent n is determined by the optical transition of a semiconductor ($n = 1/2$ for direct transition and $n = 2$ for indirect transition). Thus, the value of E_g of the samples could be estimated from plotting $(\alpha h\nu)^{1/n}$ vs photon energy.³¹⁰

In this Thesis, the UV-Vis DRS spectra were recorded using a JASCO V-560 spectrophotometer equipped with an integrating sphere attachment (JASCO ISV-469).

3.5.2 Photoluminescence spectroscopy

Photoluminescence (PL) is a process by which a material absorbs photons, promoting electrons to leap into higher electronic energy states and then radiating photons, returning to a lower energy state. When these electrons return to their equilibrium states, the excess energy is released and emits light (*i.e.*, luminescence). This process is relevant to the study of photocatalytic systems since fluorescence occurs when electrons in the conduction band recombine with holes in the valence band. The steady-state studies of PL intensity can then be used to compare recombination rates of different photocatalyst materials.^{311, 312}

Time-resolved photoluminescence (TRPL) (or time-correlated-single-photon counting (TCSPC)) is like typical PL (steady-state PL spectroscopy) and gives information detailing the lifetimes of photogenerated species. There is a continuous excitation from a light source in steady-state, while TRPL spectroscopy is dependent on pulsed excitation and measures photoluminescence at certain time intervals after the excitation pulse. The PL emission intensity over time is then fitted to an exponential decay model to determine the lifetimes of photogenerated electron/hole pairs.^{311, 312}

In chapter 4 (*FLG/GCN heterojunctions for H_2 generation*) and chapter 5 part 1 (*NiCeAl-LDH/GCNN hybrids for photocatalytic H_2 generation*), the solid steady-state PL measurements were carried out using a JASCO (FP 82000) fluorescence spectrometer with a 150 W Xenon lamp as light source, using both excitation and emission bandwidth fixed at 2.5 nm. In chapter 5 part 2 (*CuAl-LDH/GCNN hybrids for photocatalytic H_2 and O_2 evolution*), a PicoQuant FluoTime 300 spectrophotometer with Xe arc lamp (ozone free with 300W power) as the source of light was used. The excitation wavelength and emission detection range depending on the selected material (Institute of Materials Chemistry, Vienna University of Technology).

In chapter 5, part 1 (*NiCeAl-LDH/GCNN hybrids for photocatalytic H_2 generation*), the fluorescence decays were measured in de-aerated aqueous solutions using the time-correlated single-photon timing technique. The samples were excited at 335 nm using a frequency-doubled laser of Rhodamine 6G (Coherent701-2). The fluorescence decays were measured with an emission polarizer set at the magic angle at 433 nm using a Jobin–Yvon HR320 monochromator and a Hamamatsu R-2809U microchannel plate. The instrument response function (IRF) was recorded as excitation light scattered by a Ludox dispersion (silica, colloidal water solution, Aldrich, Milwaukee, WI). The data was acquired in a multichannel analyzer with a time window of 1024 channels using a time-scale of 24.4 ps/channel (University of Aveiro). Typically, 50000 and 20 000 counts were acquired in the peak channels of the IRF and sample decay curves, respectively. The fluorescence decay parameters (normalized amplitudes, A , and lifetimes, t) were determined using the TRFA Data Processing Package (version 1.4) of the Scientific Software Technologies Center (Belarusian State University, Belarus) by fitting the fluorescence intensity decays, $I(t)$, to a sum of n exponentials, described in Eq. (11):

$$I(t) = \sum_{i=1}^n A_i e^{(-t/\tau_i)} \quad (11)$$

The fits tabulated represent the minimum set of adjustable parameters that satisfy the usual statistical criteria, namely a reduced χ^2 value <1.3 and a random distribution of weighted residuals. The intensity-weighted average lifetime, τ_{av} , was calculated by using Eq. (12):

$$\tau_{av} = \sum_{i=1}^n A_i \tau_i^2 / \sum_{i=1}^n A_i \tau_i \quad (12)$$

In chapter 5, part 2 (*CuAl-LDH/GCNN hybrids for photocatalytic H_2 and O_2 evolution*), the fluorescence lifetimes measurements were carried out using a PicoQuant FluoTime 300 spectrophotometer, using for excitation a picosecond-pulsed diode laser with a wavelength of 375 nm. The PL decay for the samples was then measured at the maximum emission wavelength of 451 nm. Finally, the exponential fitting of the acquired data was performed using EasyTau 2 software. The samples were prepared by dispersing 0.02 g L⁻¹ of the material in distilled water,

followed by bubbling with argon for 15 minutes before measurement, then they were measured using operation mode. Data were fitted using EasyTau2 software (Institute of Materials Chemistry, Vienna University of Technology).

3.6 Electrochemical techniques

3.6.1 Mott-Schottky method

Electrochemical impedance spectroscopy (EIS) is often used to derive the flat band potential (V_{fb}) from the Mott-Schottky (Eq.13):

$$\frac{1}{C^2} = \frac{2}{\epsilon \epsilon_0 A^2 e N_D} \left(V - V_{fb} - \frac{k_B T}{e} \right) \quad (13)$$

where C is the double layer capacitance, ϵ is the dielectric constant of the semiconductor, ϵ_0 is the electric permittivity in vacuum, A is the interface area, e is the electron charge, N_D is the number of donors, V_{fb} is the flat band potential, k_B is the Boltzmann's constant, T is the absolute temperature, V is the applied voltage.^{313, 314}

The flat band potential V_{fb} could thus be determined from the interception of the Mott-Schottky plot with the x axis (*i.e.*, $1/C^2$ vs V axis), while N_D value could be also calculated from the slope. A series of EIS measurements at different V results in a Mott-Schottky plot.³¹³ In an n-type semiconductor, the flat band potential is closely related to the conduction band whereas in a p-type semiconductor the flat band corresponds roughly to the valence band.³¹⁵

In chapter 4 (*FLG/GCN heterojunctions for H_2 generation*), the Mott-Schottky plots ($1/C^2$ against V) were obtained from EIS measurements performed at different applied voltages V using a three-electrode workstation (Autolab PGSTAT302N, Metrohm AG), as described elsewhere.³¹⁶ The working electrode was prepared on F-doped SnO_2 -coated glass (FTO glass). 5 mg powder sample was mixed with 50 μ L of Nafion solution 5 wt%, 250 μ L isopropanol and 1 mL of deionized water. The slurry was then spread onto FTO glass with a fixed area using Kapton tape. After air drying, the electrode was annealed at 150 °C for 30 min in air to improve adhesion. The frequency range for electrochemical impedance spectroscopy (EIS) measurements was 0.1 Hz – 100 kHz, and the magnitude of the modulation signal was 10 mV. All the measurements were performed at an applied potential range of -0.4 $V_{Ag/AgCl}$ to 0.6 $V_{Ag/AgCl}$ V under dark conditions. The EIS spectra were fitted to a resistance-capacitance (RC) electrical analogue circuit by means of the ZView software for plotting Mott-Schottky plots. The on/off photocurrent response plots were measured in ambient conditions and illuminated

under simulated solar light ($100 \text{ mW}\cdot\text{cm}^{-2}$) by a 150 W Xe lamp (Newport) equipped with an AM1.5 G filter (Newport), and the light beam was calibrated with a c-Si photodiode (Newport, USA). The transient photocurrent measurements were carried at an applied potential of $0.2 \text{ V}_{\text{Ag/AgCl}}$ during 1000 s with pulses of 60 s light on followed by 60 s light off.

3.6.2 Linear sweep voltammetry

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) are the most widely used electroanalytical techniques to study redox processes.³¹⁷⁻³¹⁹ In LSV, the potential is ramped from an initial to a final value at a constant scan rate while the corresponding current is monitored. A linear sweep voltammogram is then a plot of the measured current vs the applied potential.³¹⁸

In LSV, the working electrode potential is changed linearly with time, as shown in **Figure 24a**, beginning with a potential where no electrode reaction occurs and progressing to a potential where analyte reduction (more negative values) or oxidation (more positive values) occurs so that the instantaneously applied potential can be given by Eq. (14),

$$E_t = E_i \pm vt \quad (14)$$

Where E_t represents the electrode potential at time t , E_i represents the starting potential, and v is the scan (or sweep) rate, *i.e.*, the absolute value of the constant rate of potential change, dE/dt . The sign is determined by the potential scan path (positive for anodic sweeps and negative for cathodic sweeps).^{318, 320} Throughout the experiment, the current is measured, and the resulting current-potential curve (I/E curve or voltammogram) has the usual form display in **Figure 24b**, where I_p stands for the peak current (*i.e.*, the maximum current value), E_p is the peak potential (*i.e.*, the potential correspondent to I_p), and $E_{p/2}$ is the half-peak potential (the potential at which $I_p = I_p/2$).^{318, 320}

The peak position on the potential scale (E_p), which is related to the redox process's formal potential and to its reversibility degree (conditioning also the peak shape $E_p - E_{p/2}$) provides details about the nature of the analyte involved. Peak height (I_p) gives information on the analyte concentration, number of electrons involved in the electrochemical phase, and the possible presence of coupled chemical reactions.^{318, 320}

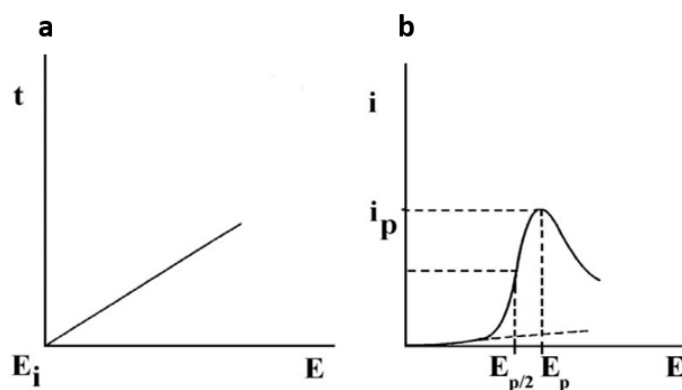


Figure 24. a) Potential waveforms for linear sweep voltammetry and b) its corresponding voltammogram. Reprinted from ref.³¹⁸

In chapter 5, part 2 (*CuAl-LDH/GCNN hybrids for photocatalytic H_2 and O_2 evolution*), the photoelectrochemical studies (LSV) were performed using electrochemical workstation Autolab PGSTAT302N potentiostat-galvanostat under illumination (40 mW cm^{-2}). The current-voltage was measured by using a conventional three-electrode cell setup composed of a working electrode (WE), a platinum wire and Ag/AgCl (1M KCl) electrodes as the counter electrode (CE) and reference electrode (RE), respectively. The electrolyte solution composed of aqueous Na_2SO_4 (0.1 M) was deaerated through sparging the solution with N_2 for at least 1 h. The WE were prepared on Fluorine-doped tin oxide coated glass slides (FTO glass; $1 \text{ cm} \times 1 \text{ cm}$). A solution containing a mixture of 5 mg of the catalyst powder, 50 μL of Nafion solution 5wt.%, 250 μL of isopropanol and 1 mL of deionized water was prepared and left under continuous stirring. The slurry was then spread onto FTO glass and dried in air, followed by heating at 150°C for 30 min in air (Institute of Materials Chemistry, Vienna University of Technology).

3.7. Zeta potential

Zeta potential measures the magnitude of the electrostatic or charge repulsion/attraction forces between particles and is one of the fundamental parameters known to affect the stability of materials.³²¹ From a theoretical viewpoint, zeta potential is the electric potential at the interfacial double layer of a dispersed particle or droplet vs a point in the continuous phase away from the interface (**Figure 25**). In other words, zeta potential is the potential difference between the mobile dispersion medium and the stationary layer of the dispersion medium attached to the dispersed particle.³²¹⁻³²³ Its measurement brings detailed insight into the causes of dispersion, aggregation or flocculation, and can be applied to improve the formulation of dispersions, emulsions and suspensions. The zeta potential is affected by various factors, including surface

properties (*i.e.*, charge, roughness, chemical heterogeneity), pH and temperature, and solution structure and concentration.³²¹⁻³²³ Zeta potential values are typically in the range of +100 to –100 mV. Zeta potential of NPs with values $> +25$ mV or < -25 mV usually have a high degree of stability.^{322, 323}

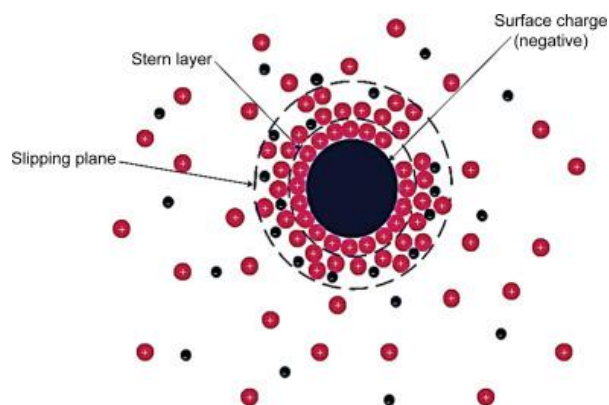


Figure 25. Illustration of zeta potential showing the surface charge, the Stern layer, and the slipping layer.³²³

In chapter 5, part 2 (*CuAl-LDH/GCNN hybrids for photocatalytic H_2 and O_2 evolution*), the zeta potential was measured using Litesizer 500 equipment (Institute of Materials Chemistry, Vienna University of Technology). For this, 1 mg of the materials were dispersed in 10 mL of water by sonication, followed by magnetic stirring for a certain time at room temperature.

Chapter 4

FLG/g-C₃N₄ hybrids for photocatalytic H₂ generation

Although graphitic carbon nitride (GCN) is considered a shining star material for several photocatalytic applications, a high degree of charge carriers' recombination and low surface area restrict its practical application for photocatalytic water splitting. Therefore, the work presented in this chapter consists of the modification of bulk GCN through building a heterostructure photocatalyst using another carbon-based 2D material, few-layer graphene (FLG) material.

The FLG was prepared by catalytic chemical vapour deposition (c-CVD) and assembled by calcination with GCN. The impact of loading and morphology of FLG on the activity of GCN has been evaluated. The FLG/GCN materials exhibited different textural, optical, and electronic properties compared to their original counterparts.

The photocatalytic performance of all materials was tested towards H₂ generation, using eco-efficient visible-LED as an irradiation source. The reusability of the best material was also studied.

This chapter is based on the following research manuscript:

Hanane Boumeriame, Eliana S. Da Silva, Bruno F. Machado, Nuno M. M. Moura, Philippe Serp, Tarik Chafik, Joaquim L. Faria. "Graphitic carbon nitride doped with few-layer graphene: an efficient 2D/2D heterostructure to separate charge carriers for improved LED-visible-light photocatalytic hydrogen generation". (Under review, May 2021, *Appl. Catal. B-Environ*)

4.1 Introduction

Graphene (GR) based materials present good chemical and electrochemical stability, as discussed in chapter 2. Therefore, owing to their excellent properties, a GR-based layered material appears to be a good candidate for coupling with GCN, originating heterojunctions with increased contact area for effective charge separation across the interface.

Single-layer GR presents a strong tendency to restack due to the π - π interactions. Consequently, few-layer graphene (FLG) is preferred for the synthesis of catalysts, as it can be produced in high yield by c-CVD with high order quality, exceptional electronic properties and reasonable price (~50 €/kg), compared to single-layer GR.³²⁴⁻³²⁷ However, and although FLG presents interesting characteristics for photocatalytic applications,^{326, 328, 329} it has not yet received wide attention as a photocatalyst for H₂ generation, heightening the interest in exploring this theme. Herein, in this work, FLG/GCN nanomaterials were prepared, characterised, and investigated for H₂ generation through photocatalytic water splitting using visible light-LED in the presence of sacrificial agent and cocatalyst.

4.2 Experimental section

4.2.1 Materials

Dicyandiamide (DCN, 99%), ethylenediaminetetraacetic acid (EDTA, $\geq 98\%$), L-ascorbic acid (99%), and chloroplatinic acid hydrate (H₂PtCl₆.xH₂O, 99.9%) were purchased from Sigma-Aldrich and used without further purification. Nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98%) was purchased from Alfa Aesar and methanol from Fischer Chemical. Ultrapure water was obtained from a Millipore Milli-Q system ($\geq 18 \text{ M}\Omega \text{ cm}^{-1}$) and used throughout all assays. EDTA aqueous solution (0.2 M) was prepared in NaOH (0.5 M).

4.2.2 Catalyst preparation

Synthesis of few-layer graphene

FLG materials were produced by c-CVD using a nickel ferrite (NiFe₂O₄) catalyst. This catalyst was prepared using a previously reported citrate-nitrate gel combustion method by replacing the cobalt(II) nitrate precursor (necessary to prepare CoFe₂O₄) with nickel(II) nitrate.³²⁵ The combustion and calcination steps were carried out in a muffle furnace at 200 °C for 2 h and 400 °C for 5 h, respectively. In a typical synthesis, 1 g of NiFe₂O₄ catalyst was inserted in a vertical fluidized-bed reactor and reduced *in-situ* under Ar/H₂ (3:1) flow until a temperature of 650 °C was reached (*ca.* 1 h, corresponding to a 10 °C min⁻¹ heating ramp). Ethylene

(30 cm³ min⁻¹) was then introduced for either 10 or 60 min, after which the reaction products were cooled under Ar. The yield of the reactions was calculated using the parameter ζ (in grams of purified carbon per gram of catalyst, g_C/g_{cat}). The carbon deposits containing reduced catalysts were immersed overnight in 35% HCl at *ca.* 20 °C to dissolve the catalyst. The carbon powder obtained was washed with deionized water and dried at 120 °C in air. The obtained materials were denoted as FLG_y, where y represents the reaction time (10 or 60 min).

Synthesis of FLG/GCN heterostructures

FLG/GCN heterostructures were prepared by thermal treatment. Different amounts of FLG₁₀ and FLG₆₀ (0.5, 1, 2 and 3 wt.%) were manually added to the GCN precursor, DCN, placed in closed crucibles inside a muffle furnace, heated, and treated under static air at 450 °C for 2 h with a heating ramp of 2 °C min⁻¹, followed by heating to 550 °C for 4 h. The obtained materials were ground into powder, washed with water to remove any unreacted precursor, dried overnight at 60 °C, and ground again into powder for further use. The materials were labelled xFLG_y/GCN, where x represents the amount of FLG_y (0.5, 1, 2, and 3 wt.%). Bulk GCN, used as reference material, was synthesised by the same thermal procedure without adding FLG_y.

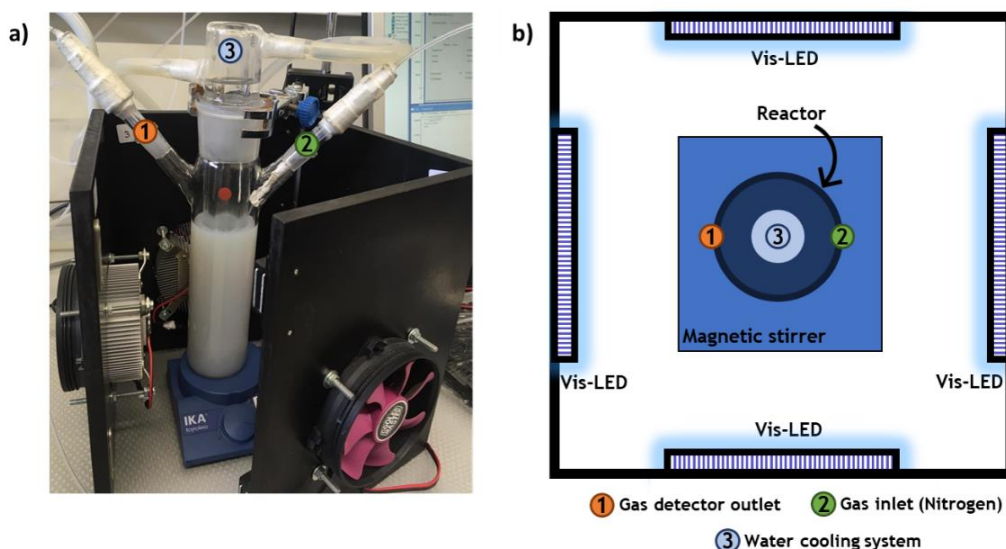
Synthesis of platinum nanoparticles

A colloidal solution of platinum (Pt) nanoparticles was prepared according to a previous procedure.^{330, 331} Typically, an aqueous solution of the chloroplatinic acid hydrate (60 mg in 20 mL of water) was added dropwise to a methanol solution containing L-ascorbic acid (600 mg in 180 mL of methanol). The mixture was heated with constant stirring under reflux for 3 h. After cooling, the suspension was centrifuged and washed several times with methanol. Finally, the solid was re-dispersed in a given volume of water.

4.2.3 Photocatalytic tests

The photocatalytic runs were performed in a system composed of four LED with maximum emission at 420 nm, symmetrically located 3 cm around a cylindrical glass photo-reactor (**Scheme 3**). The average nominal irradiance of each LED was 880 W m⁻², determined using a spectroradiometer (OceanOptics USB2000+). In a typical experiment, 0.15 g L⁻¹ of the catalyst was dispersed in an aqueous solution (100 mL) containing EDTA (10% v/v) as sacrificial electron donor and Pt nanoparticles (3 wt.%) as cocatalyst. Before irradiation, the suspension was stirred in an ultrasonic bath for 10 min, and the reaction system was continuously stirred

and bubbled with nitrogen for 30 min to ensure total removal of dissolved oxygen. The amount of H₂ produced was measured for 3 h using an online GC (Inficon Micro GC 3000) equipped with a 5Å molecular sieve column and a micro-TCD detector using argon as carrier gas. The best performing catalyst was tested over multiple cycles. After each run, the reactor was open to the air and left under dark for 30 min. Then it was closed again, bubbled with nitrogen to remove the air, and irradiated. This procedure was repeated over four consecutive cycles without adding additional Pt or EDTA before new irradiation.



Scheme 3. a) Image and b) schematic representation of the photocatalytic setup used during photocatalytic reactions.

4.3. Results and discussion

Several xFLG_y/GCN heterostructures have been synthesized *in-situ* by direct polymerization of dicyandiamide in the presence of different amounts of FLG_y and investigated for visible-LED photocatalytic H₂ production from water. The loading (wt.%) and type (morphology) of FLG (produced from ethylene for 10 or 60 minutes) were tested to ascertain its influence on the photocatalytic properties of bulk GCN. Based on preliminary photocatalytic experiments for H₂ production, the best performing materials, 2FLG₁₀/GCN and 2FLG₆₀/GCN, were fully characterised and compared with bulk GCN to establish a structure-activity correlation.

4.3.1 Characterisation of the photocatalysts

The optical properties of the materials were assessed by UV-Vis diffuse reflectance absorption spectroscopy. The UV-Vis DRS of GCN and xFLG_y/GCN heterostructures are given in

Figure 26. GCN presents an absorption wavelength maximum at around 370 nm attributed to the characteristic π - π^* transitions owing to the heterocyclic aromatic system,^{65, 331-333} and an absorption edge in the visible region around 460 nm. In contrast, FLG is a gapless semiconductor (**Figure 26**).²⁴⁶ The heterostructures showed the same UV absorption band as GCN but an enhanced light-harvesting capability in the visible region of the spectra between 460 and 800 nm, owing to the presence of FLG.

Moreover, this new absorption feature in the visible region increases with increasing FLG content. This is in line with observations reported in literature^{108, 280} and the colour variation of the materials, which changed from yellow (GCN) to dark-sea-green for the 2FLG₁₀/GCN and 2FLG₆₀/GCN heterostructures, respectively (**Figure 26**). Furthermore, all the materials showed a slight redshift of the absorption edge with the increase of FLG loading, which is more evident for the heterostructures with FLG₆₀ (**Figure 26b**). This is probably due to π - π stacking interactions between the sp^2 lattices of GCN and the sp^2 lattices of FLG.^{108, 334}

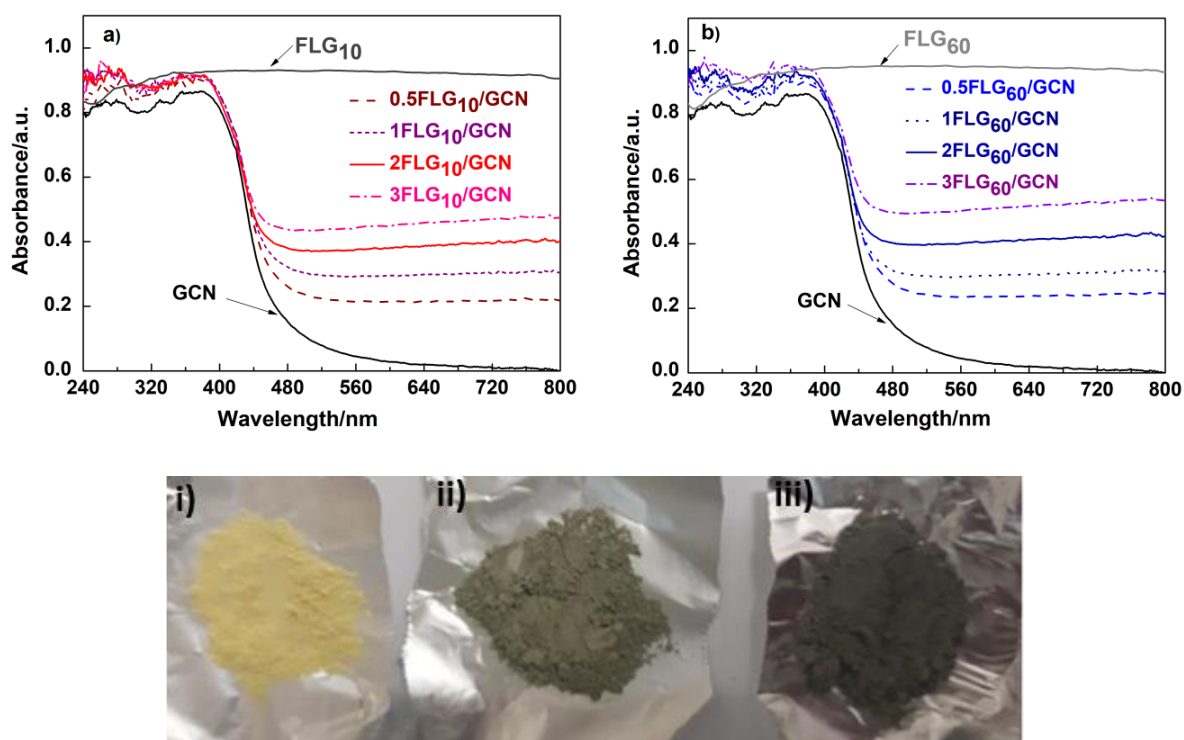


Figure 26. Upper row: UV-Vis DRS of a) GCN, FLG₁₀ and xFLG₁₀/GCN; and b) GCN, FLG₆₀ and xFLG₆₀/GCN composites. Lower row: visual aspect of the colours of the materials i) GCN, ii) 2FLG₁₀/GCN, and iii) 2FLG₆₀/GCN, respectively.

The bandgap energy of the materials was calculated using the Tauc-plot method,³³⁵ through the intercept of the tangents of the plots of $(\alpha h\nu)^{1/2}$ vs photon energy (**Table 4**). The bandgap energy of GCN is estimated to be 2.65 eV, whereas all the heterostructures exhibited band gaps with lower energy values. The narrowing band gap and enhanced visible light absorption of the heterostructures could be due to the hybridisation with FLG, providing more photogenerated electrons and holes.

Table 4. Optical (bandgap energy) and textural (surface area, pore volume, and size) properties of the prepared materials.

Samples	E_g (eV)	S_{BET} area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)
GCN	2.65	7	0.08	3.6
FLG ₁₀	–	29	0.22	4.6
FLG ₆₀	–	23	0.17	4.6
0.5FLG ₁₀ /GCN	2.62	13	0.12	3.6
1FLG ₁₀ /GCN	2.61	17	0.12	3.6
2FLG ₁₀ /GCN	2.55	26	0.13	3.6
3FLG ₁₀ /GCN	2.54	31	0.17	3.6
0.5FLG ₆₀ /GCN	2.61	12	0.11	3.6
1FLG ₆₀ /GCN	2.60	13	0.12	3.6
1FLG ₆₀ /GCN	2.60	13	0.12	3.6
2FLG ₆₀ /GCN	2.55	14	0.09	3.6
3FLG ₆₀ /GCN	2.52	19	0.13	4.6

The textural properties of the materials were studied by N₂ adsorption-desorption isotherms measurements at –196 °C, as these play a significant role in photocatalytic reactions.³³¹ S_{BET} , pore volume, and pore size of all samples are summarised in **Table 4**, while the N₂ isotherms profile of GCN, 2FLG₁₀/GCN, and 2FLG₆₀/GCN are given in (**Figure 27**). The GCN isotherm is classified as Type II with H3-type hysteresis loop,³⁰⁴ resulting from physisorption of the gas

on a mostly macroporous adsorbent, and confirms the presence of mesopores (3-5 nm) and macropores (65-70 nm), similar trends are observed for all the heterostructures.

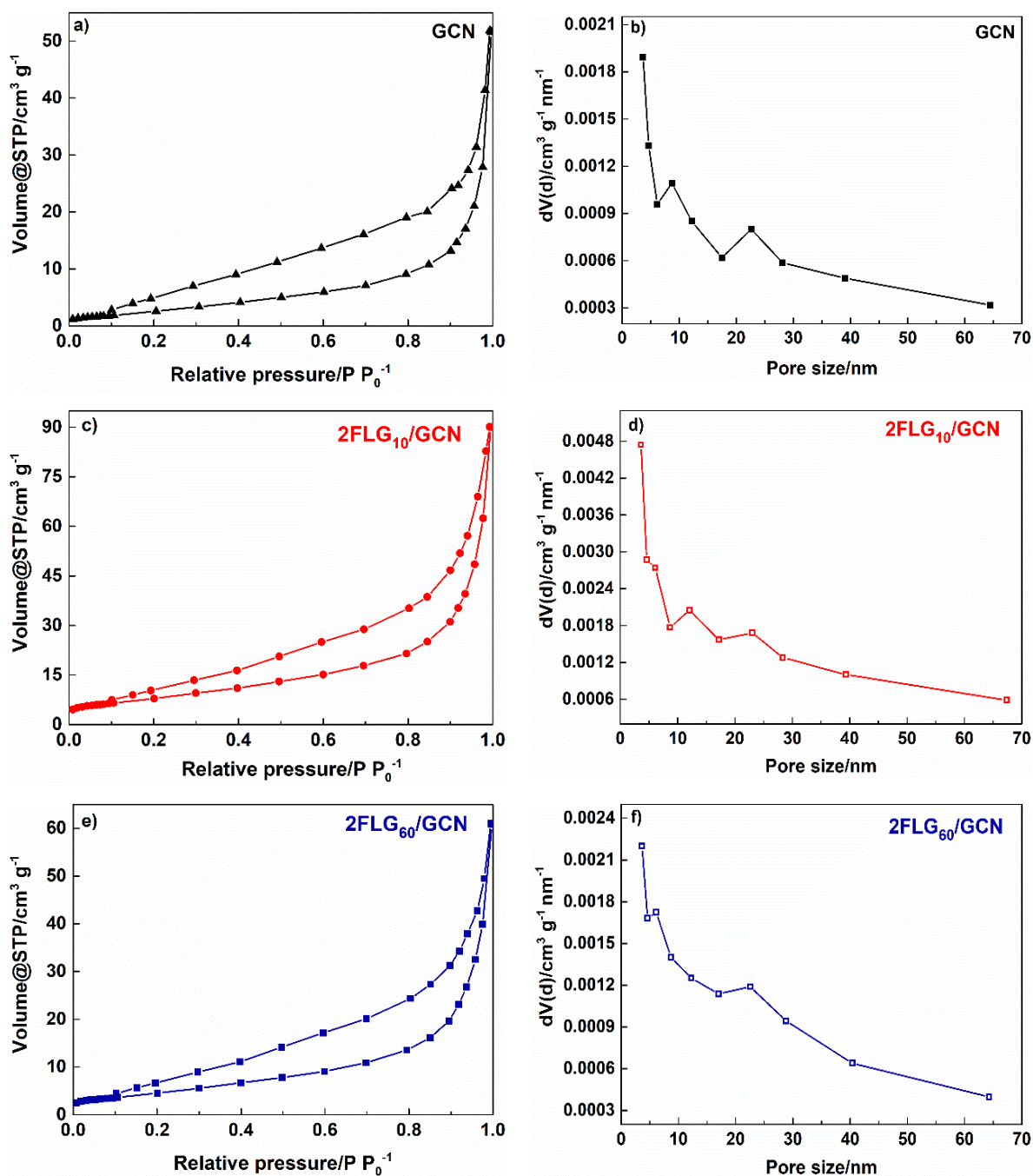


Figure 27. N_2 adsorption-desorption isotherms at $-196^\circ C$ and BJH pore size distribution curves of a, b) GCN; c, d) 2FLG₁₀/GCN and e, f) 2FLG₆₀/GCN.

As listed in **Table 4**, GCN presents a specific surface area of $7 m^2 g^{-1}$, in line with values previously reported for this material.^{331, 333} All the xFLG_y/GCN heterostructures present higher

values, owing to the presence of FLG. It is interesting to observe that the S_{BET} of all the heterostructures increases with increasing FLG loading. Also, the heterostructures prepared with FLG₁₀ display a higher surface area than those prepared with FLG₆₀. This is probably due to the higher surface area of FLG₁₀ ($S_{\text{BET}} = 29 \text{ m}^2 \text{ g}^{-1}$) compared to FLG₆₀ ($S_{\text{BET}} = 22 \text{ m}^2 \text{ g}^{-1}$), also in line with the SEM and TEM images, as discussed below. A larger surface area of the heterostructures can provide more active sites and reduce the charge carrier's migration path, which could improve photocatalytic activity.^{332, 336} Furthermore, the increase in the surface area for 2FLG₁₀/GCN was accompanied by an increase in pore volume. This can enhance light-harvesting, provide additional diffusion channels and increase the number of exposed active sites, significantly improving the mass transfer and shortening the diffusion of the photogenerated charge carriers across the carbon nitride plane.^{108, 333, 337}

SEM and TEM analyses were performed to study the morphology of the prepared materials. GCN presents a typical agglomerated layered morphology (**Figure 28a,b**) resulting from the stacking of GCN layers,^{65, 88, 333, 338, 339} according to its low S_{BET} (**Table 4**). SEM images of FLG₁₀ (**Figure 28c**) show agglomerates made up of flakes of uniform diameter (200-300 nm) tending to curl up at the edges (wrinkles).³⁴⁰ The TEM images of these flakes (**Figure 28d**) show stacked crystalline layers of graphene. Due to a more extended growth period, FLG₆₀ (**Figure 28e, f**) presents flakes that are thicker than those obtained after only 10 min (FLG₁₀; **Figure 28c, d**), which is in accordance with its lower S_{BET} compared to FLG₁₀ (**Table 4**). These observations are in line with previous studies.^{324, 325, 341} The morphology of the heterostructures 2FLG₁₀/GCN (**Figure 28g, h**) and 2FLG₆₀/GCN (**Figure 28i, j**) reveals a layered structure, similar to the one of GCN. Nonetheless, the typical flakes of FLG were observed on the surface and edges of the GCN structure (indicated by the arrows), forming a tight 2D/2D junction, suggesting an effective interaction between both materials. The TEM image of 2FLG₆₀/GCN composite (**Figure 28j**) shows more flakes than 2FLG₁₀/GCN (**Figure 28h**), which may explain a lower surface area than 2FLG₁₀/GCN. Furthermore, and due to the FLG structure, it is possible that these uniform flakes on the surface of GCN could enhance the photocatalytic efficiency towards H₂ generation due to the interaction and interfacial contact between both components.

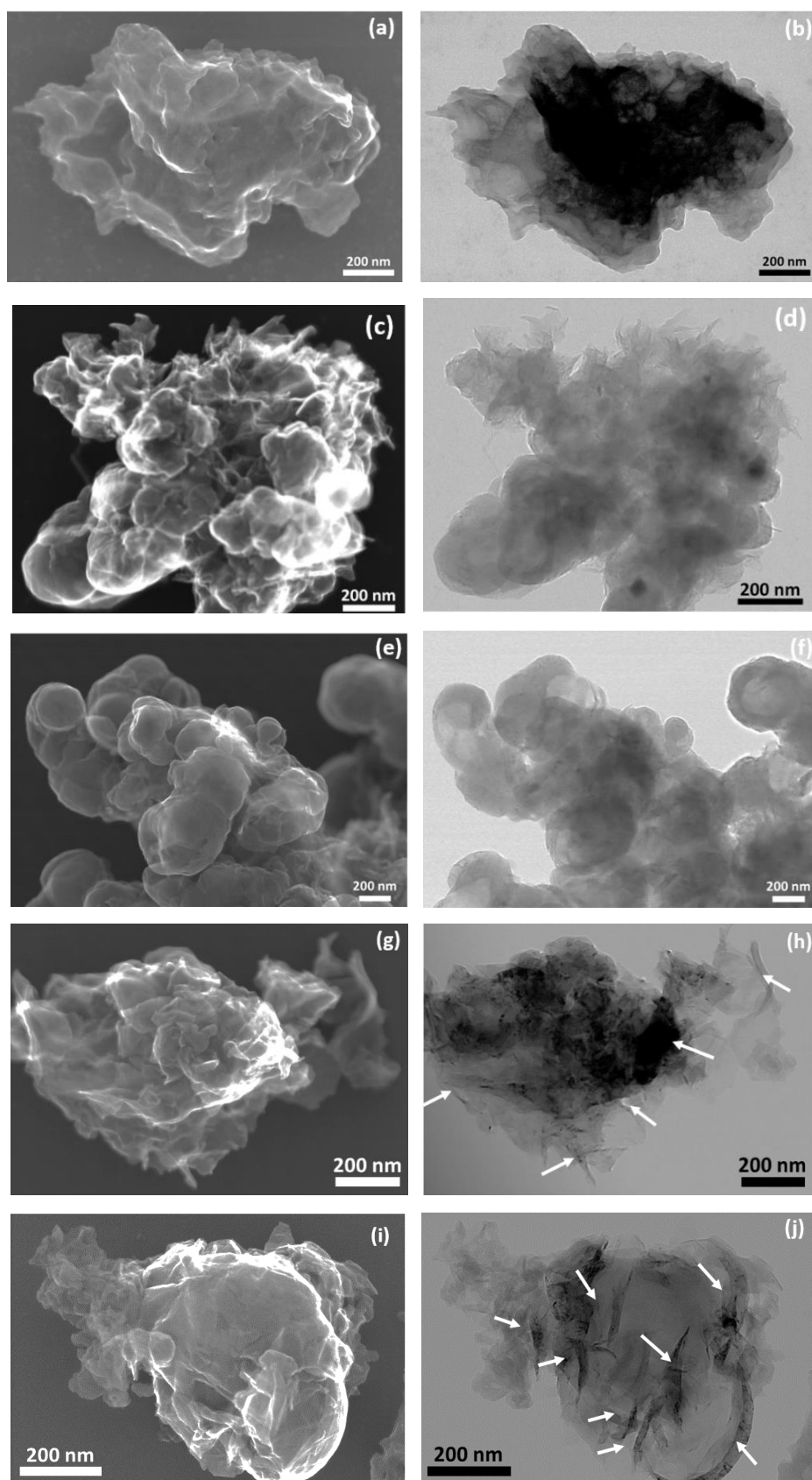


Figure 28. SEM (left) and TEM (right) images of (a, b) GCN, (c, d) FLG₁₀, (e, f) FLG₆₀, (g, h) 2FLG₁₀/GCN and (i, j) 2FLG₆₀/GCN. See text for arrow meaning.

The crystal structures of GCN, FLG_y, and the best performing heterostructures, 2FLG₁₀/GCN and 2FLG₆₀/GCN, were analysed using powder XRD (**Figure 29**). FLG₁₀ and FLG₆₀ (**Figure 29a**) showed a narrow peak at around $2\theta = 26.33^\circ$ corresponding to an interlayer distance of 0.3381 nm, and smaller peaks at 42.72° , 43.59° and 54.31° , corresponding to (002), (100), (101) and (004) reflections of graphene materials, respectively^{324-326, 342}. The GCN (**Figure 29b**) presents two distinct diffraction peaks located at 13.10° (100) and 27.40° ($d_{002} = 0.3251$ nm), attributed to the in-plane repeated tri-s-triazine unit and to the interlayer-staking of the conjugated aromatic GCN system, respectively.^{65, 333, 343} As for the heterostructures (**Figure 29b**), these present the characteristic peaks of pure GCN in addition to the expected signal of few-layer graphene, a shoulder near 26.33° (**Figure 29b**, inset), indicating that the basic structure of GCN was preserved. The (002) diffraction peak clearly deconvolutes in two components, one at lower angles ascribed to FLG_y in the composite and another at higher angles attributed to GCN (**Figure 29c, d**).

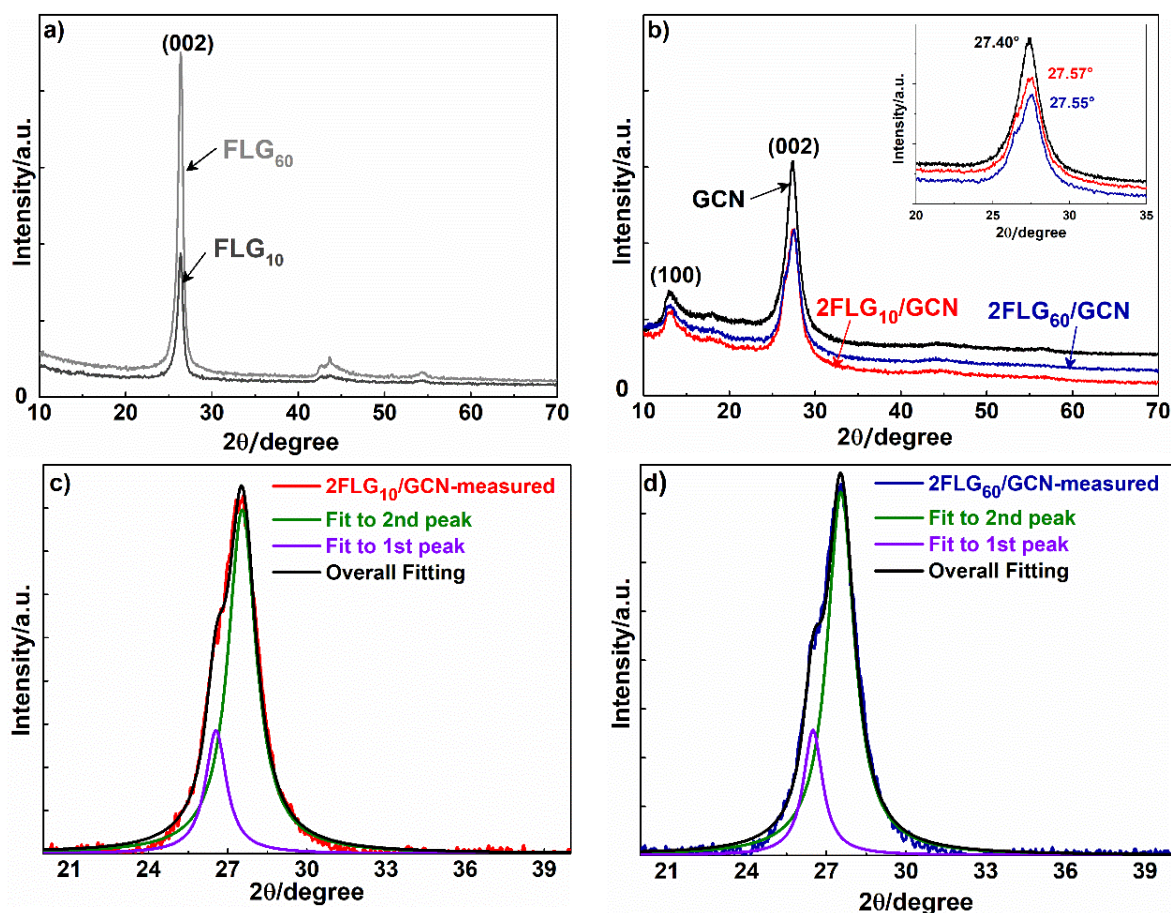


Figure 29. X-ray diffraction patterns of a) FLG₁₀, FLG₆₀, and of b) GCN, 2FLG₁₀/GCN, and 2FLG₆₀/GCN (inset: magnification of the (002) peaks of FLG and GCN); c and d) Deconvolution of the (002) peaks of both composites presented in b).

The (002) peaks of both materials were fitted using Gaussian and Lorentzian functions; all XRD data such as FWHM (°), 2θ (°), d_{002} (nm) and L_c (nm) are summarised in **Table 5**. The interlayer distance and the crystallite properties of FLG_y and GCN (d_{002} and L_{c002}) were determined based on the XRD using Scherrer's equation.³⁴⁴ Moreover, as perceptible in **Figure 29b**, the (002) peak of GCN in the composites was shifted to higher angles compared to pristine GCN, increasing from 27.40° in GCN to 27.57° and 27.55° in 2FLG₁₀/GCN and 2FLG₆₀/GCN, respectively. The same trends were observed for the FLG_y peaks in the composites, as depicted in **Table 5**. According to Bragg's law, this corresponds to a decrease in $d_{(002)}$ spacing of the tri-s-triazine building units and the FLG_y in the composites compared to the individual components.^{325, 333, 345} Since the interlayers are in closer contact, the charge transfer along the heterostructure interface will be favoured, contributing to enhancing the catalytic activity. Concerning the crystallite size (**Table 5**), FLG₁₀ presents a smaller value of L_c than FLG₆₀, which is also reflected in the composites (2FLG₁₀/GCN presents lower values than 2FLG₆₀/GCN). As known, smaller crystallites will lead to a shorter diffusion time of the charge carriers from the bulk to the surface of the catalyst, thus decreasing recombination and enhancing the photocatalytic activity.

Table 5. Structural parameters of the materials for the (002) peak obtained from the XRD data. FWHM is the full width at half-maximum of the peak, d_{002} is the interlayer distance, L_c is the crystallite size, and 2θ is the diffraction angle.

Catalyst	2θ (°) (002)	FWHM (°)	d_{002} (nm)	Crystallite size L_c (002) (nm)
FLG ₁₀	26.32	0.6620	0.3382	12.2
FLG ₆₀	26.34	0.6410	0.3379	12.6
GCN	27.40	1.3903	0.3251	5.8
2FLG ₁₀ /GCN	26.55 (FLG ₁₀)	0.9663	0.3353	8.3 (FLG ₁₀)
	27.57 (GCN)	1.2947	0.3231	6.2 (GCN)
2FLG ₆₀ /GCN	26.49 (FLG ₆₀)	0.8830	0.3360	9.1 (FLG ₆₀)
	27.55 (GCN)	1.2520	0.3234	6.5 (GCN)

To evaluate the electronic interactions between GCN and FLG_y in the heterostructures, FTIR spectra of GCN, 2FLG₁₀/GCN, and 2FLG₆₀/GCN were recorded (**Figure 30**). The tri-s-triazine

(heptazine) structure of GCN was confirmed by the typical bending vibration modes of the triazine units located at 803 cm⁻¹ and the stretching modes of g-C₃N₄ heterocycles in the 1200-1650 cm⁻¹ region.^{65, 88, 108, 331, 333} The intense band located around 1231 cm⁻¹ can be ascribed to the presence of C–N–C bonds, while the band at 1310 cm⁻¹ corresponds to the stretching vibrations of the connected units of N–(C)₃.³³¹ The bands at 1450, 1545 and 1620 cm⁻¹ were attributed to the stretching vibration modes of heptazine-derived repeating units. The wideband at 2890-3400 cm⁻¹ was attributed to –NH_x and –OH resulting from uncondensed amine groups on the surface (–NH or –NH₂) of GCN and adsorbed water molecules.^{331, 346, 347} In what concerns the heterostructures, both materials show similar infrared spectra related to carbon nitride skeletal vibration, indicating that the heterostructures kept the same framework as bulk GCN, as evidenced by the XRD patterns.

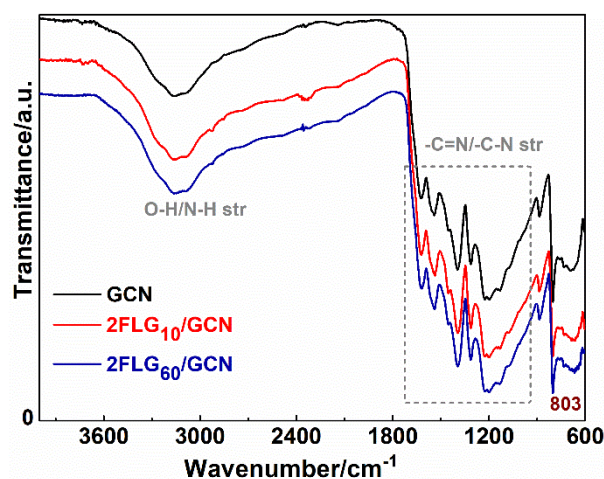


Figure 30. FTIR spectra of GCN, 2FLG₁₀/GCN and 2FLG₆₀/GCN.

Raman spectroscopy was used to study the properties of the FLG-based materials (FLG₁₀, FLG₆₀) and the best composite, 2FLG₁₀/GCN (**Figure 31**). The Raman spectrum of GCN was not possible to obtain using the laser excitation at 532 nm due to the high fluorescence signal of the material. However, our group has previously measured its spectrum using laser excitation at 1064 nm³³³, in which two prominent peaks were observed at 1232 and 1560 cm⁻¹ and ascribed to the D and G bands, respectively, characteristic of *sp*² and *sp*³ carbon-based materials. As shown in Fig. 5, all three samples present D, G and 2D (also called G') bands, typical of graphene-based materials³⁴⁸. In addition to these bands, the 2FLG₁₀/GCN composite presents a small D' shoulder band at around 1612 cm⁻¹, probably related to the disorder of FLG₁₀ edge carbons in the composite³⁴⁹. FLG₁₀ and FLG₆₀ show the typical D band at 1346

and 1343 cm⁻¹, respectively, considered to be the defect-induced vibration peak of graphene, attributed to structural defects on its edges,³⁵⁰ while the G peak at 1575 cm⁻¹ and 1568 cm⁻¹ (for FLG₁₀ and FLG₆₀, respectively), is characteristic of sp² carbon hybridisation³⁵¹. As observed, the D peak of FLG₆₀ is weaker than that of FLG₁₀, suggesting the presence of fewer defects, following the observations made using the SEM/TEM images. The 2D peak at 2600-2710 cm⁻¹ is ascribed to the second overtone of D peak and exhibits a strong frequency dependence on the excitation laser energy and the number of layers,³⁵² as the latter affects the shape width and position of the 2D peak.

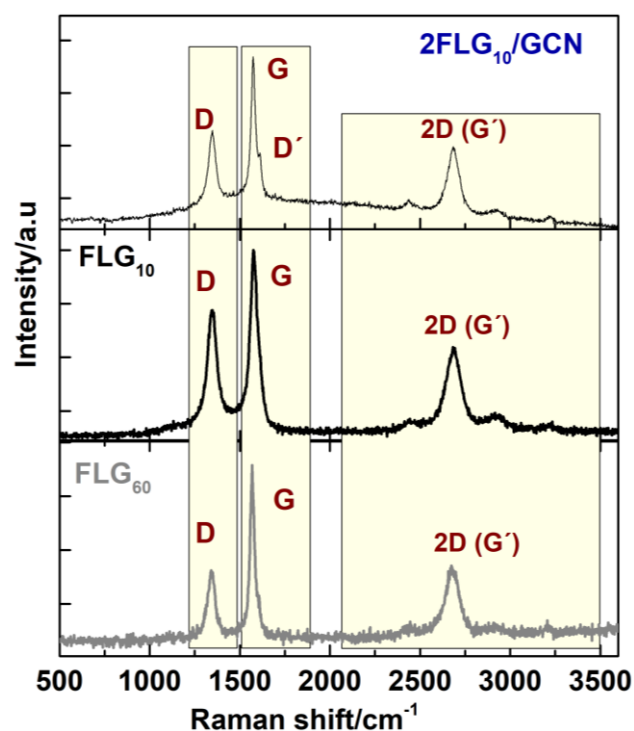


Figure 31. Raman spectra of 2FLG₁₀/GCN, FLG₁₀ and FLG₆₀.

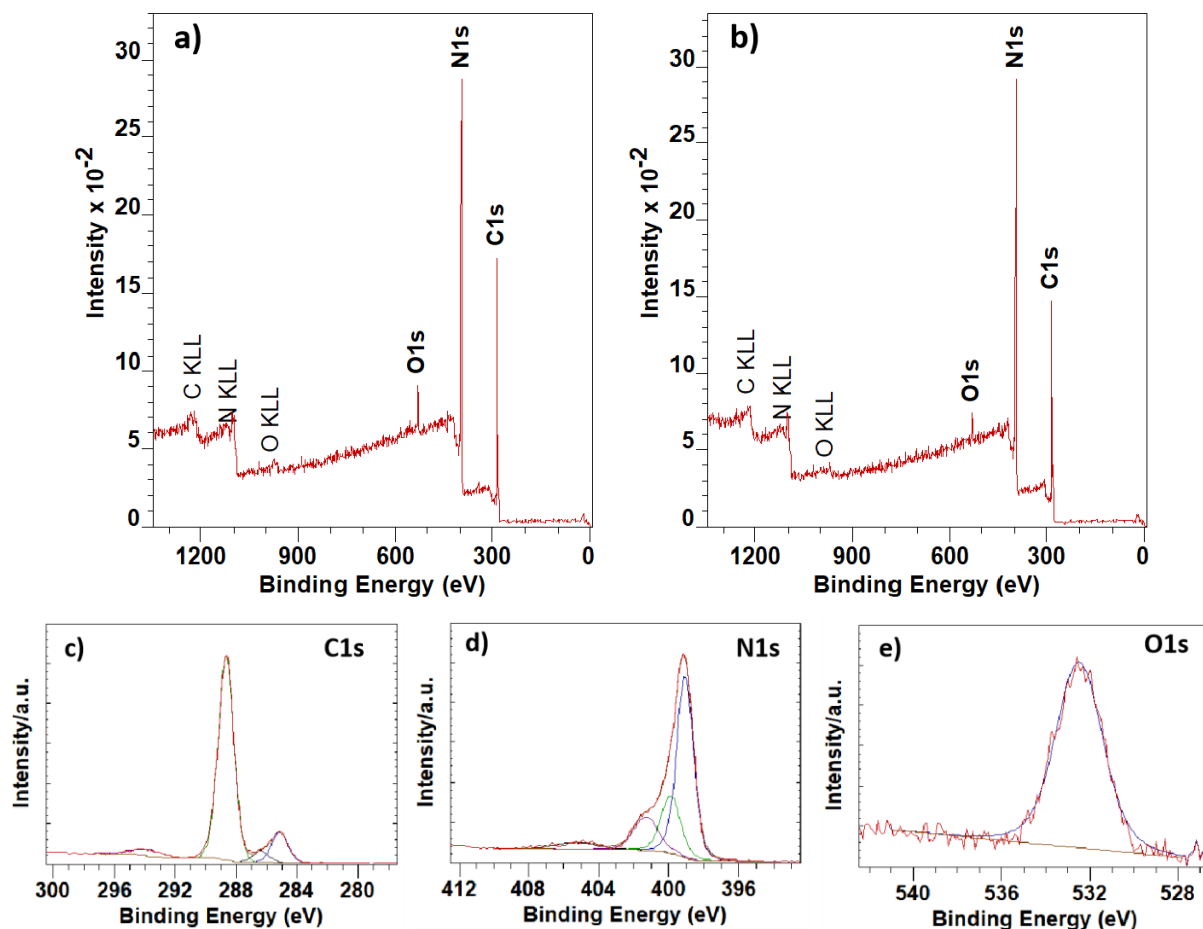
The intensity ratio between D and G peaks (I_D/I_G) is indicative of the degree of crystallinity (or graphitization) of the carbon material³⁵¹, in which a higher I_D/I_G ratio indicates the presence of more defects in that material.³⁵³ Therefore, we calculated the ratio peak intensities of the three materials (**Table 5**), being that the I_D/I_G ratios of FLG₁₀, FLG₆₀ and 2FLG₁₀/GCN presents values of 0.68, 0.42 and 0.52, respectively. This suggests that among the two FLG materials, FLG₁₀ presents a higher number of defects. Furthermore, compared to pristine FLG₁₀, 2FLG₁₀/GCN presents a decrease in the intensity ratio, probably owing to new sp² regions due to the interactions with carbon nitride, along with an upper-shift (2 cm⁻¹) and a down-shift

(3 cm⁻¹) of the D and G bands, respectively, suggesting possible charge transfer interactions between both materials.^{354, 355}

Table 6. Peak position (cm⁻¹) and ratio peak intensities (I_D/I_G) of the materials FLG₁₀, FLG₆₀ and 2FLG₁₀/GCN obtained by Raman spectroscopy.

Catalyst	D peak (cm ⁻¹)	G peak (cm ⁻¹)	I_D/I_G	2D peak (cm ⁻¹)
FLG ₁₀	1346	1575	0.68	2686
FLG ₆₀	1343	1568	0.42	2675
2FLG ₁₀ /GCN	1348	1572	0.52	2686

XPS analyses of pristine GCN and the composite 2FLG₁₀/GCN were performed to study the surface chemical states and obtain information on the interactions of both materials (**Figure 32**). As expected, the XPS survey spectra of the catalysts (**Figure 32a,b**) shows only the presence of C, O and N.



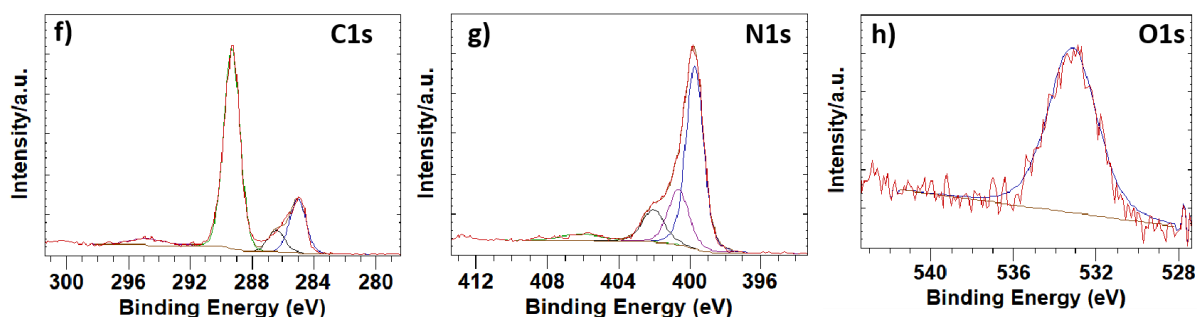


Figure 32. Survey spectra of a) GCN and b) 2FLG₁₀/GCN. High-resolution XPS spectra of C1s, N1s and O1s for GCN (c, d, e) and 2FLG₁₀/GCN (f, g, h) materials.

The C1s spectrum of GCN (**Figure 32c**) presents four peaks with binding energies going from 285.0 eV to 293.9 eV, as indicated in **Table 7**. These peaks are attributed to the C(–N)₃ planar trigonal carbon geometry, the *sp*³-bonded carbon atoms characteristic of g-C₃N₄ defects such as amino groups (C–NH₂), the tertiary carbon (–N–C=N–) in the lattice of GCN and the π electron delocalization in C₃N₄ heterocycles, respectively.³³¹ The N1s spectrum of GCN (**Figure 32d**) is deconvoluted into four peaks (**Table 7**). The most abundant peak at 399.0 eV is ascribed to the *sp*²-bonded N in the triazine rings (C–N=C), followed by a peak with a binding energy of 399.8 eV attributed to the tertiary nitrogen in N–(C)₃ units, reflecting the polymerisation of dicyandiamide into GCN. The other two peaks with binding energies at 401.2 and 405.3 eV correspond to C–NH_x (amino functional groups) and charging effects or π excitations, respectively. A residual O1s peak (**Figure 32e**) at 532.4 eV can be attributed to adsorbed H₂O, CO₂ and O₂ onto the GCN surface during the polymerisation process.³³¹ Concerning 2FLG₁₀/GCN (**Figure 32f,g**), it is possible to observe that the C1s and N1s spectra present the same four binding peaks as GCN. However, the peaks show a shift to higher energy values (**Table 7**), thus implying the occurrence of electronic interactions between both materials at the interface and a decrease in electronic intensity of N atoms.³⁵⁶

Table 7. Peak position (eV) and relative composition (at.%) of the materials obtained by XPS analysis.

Catalyst		C1s				N1s				O1s
GCN	eV	285.0	286.1	288.6	293.9	399.0	399.8	401.2	405.3	532.4
	at.%	12.0	4.35	79.1	4.43	59.0	24.1	15.8	5.41	100
2FLG ₁₀ /GCN	eV	285.0	286.4	289.3	294.9	339.7	400.6	402.0	406.5	533.1
	at.%	17.4	7.11	67.7	5.12	54.6	21.6	13.9	5.32	100

A limiting factor in photocatalysis is the electron/hole recombination process. Therefore, PL spectroscopy was used to reveal the efficiency of electron/hole charge migration, transfer, and separation, which are key parameters in determining photocatalytic performance.^{280, 331, 333} Consequently, the emission spectra of GCN and the heterostructures were obtained upon excitation at 370 nm at room temperature (**Figure 33**). GCN presents a typical PL pattern of a semiconductor with a strong and wide fluorescence emission band with a maximum at 460 nm, reflecting important charge recombination caused by the conjugated system of GCN.^{331-333, 339} However, and although the PL spectra of xFLG_y/GCN heterostructures present profiles similar to GCN, a drastic quenching of the fluorescence intensity at the maximum wavelength of emission was observed, along with a blueshift (**Figure 33**), indicating an efficient suppression of GCN charge carriers recombination.

Nevertheless, it is possible to notice that the evolution of the PL intensity of the xFLG₁₀/GCN series is slightly different from that of xFLG₆₀/GCN, where the PL intensity of 2 and 3 wt.% FLG₁₀ reaches a plateau (**Figure 33a**). In contrast, the intensity of 2 and 3 wt.% FLG₆₀ continues to decrease (**Figure 33b**). This could be explained by the difference in the interlayer distance and crystallite properties of FLG_y, as shown in **Table 5**. It is possible to notice that both the individual FLG₁₀ material and the corresponding composite 2FLG₁₀/GCN present the smallest crystallite size (*L_c*) and interplanar distance (*d*₀₀₂) compared to FLG₆₀ and 2FLG₆₀/GCN. Smaller particles result in easier charge carriers diffusion and transfer from the bulk to the surface of the catalyst, thereby decreasing the opportunity of charge recombination.

Therefore, and owing to its 2D π -conjugated structure, good electron acceptance ability, and transport features,³⁵⁷ FLG efficiently facilitates the separation of the photoinduced electron/hole pairs of GCN, thus suppressing its direct recombination.^{108, 280, 328} These results find support on the work function of both materials, with values of 4.34 eV and 4.43 eV (related to vacuum), for g-C₃N₄³⁵⁸ and few-layer graphene,³⁵⁹ respectively. Thus, electrons flow from the CB of the material with a lower work function (GCN) to the CB of the material with a higher work function (FLG), and holes flow in the opposite direction until the Fermi level of both materials is aligned. This work function difference between both materials leads to charge distribution in the interface, preventing direct electron/holes recombination, probably forming an n-type like Schottky barrier.^{358, 359} In addition, it was possible to observe that the PL intensity of the heterostructure 2FLG₁₀/GCN was slightly reduced compared to that of 2FLG₆₀/GCN (**Figure 33c**), which might favour its photocatalytic performance for H₂ generation.

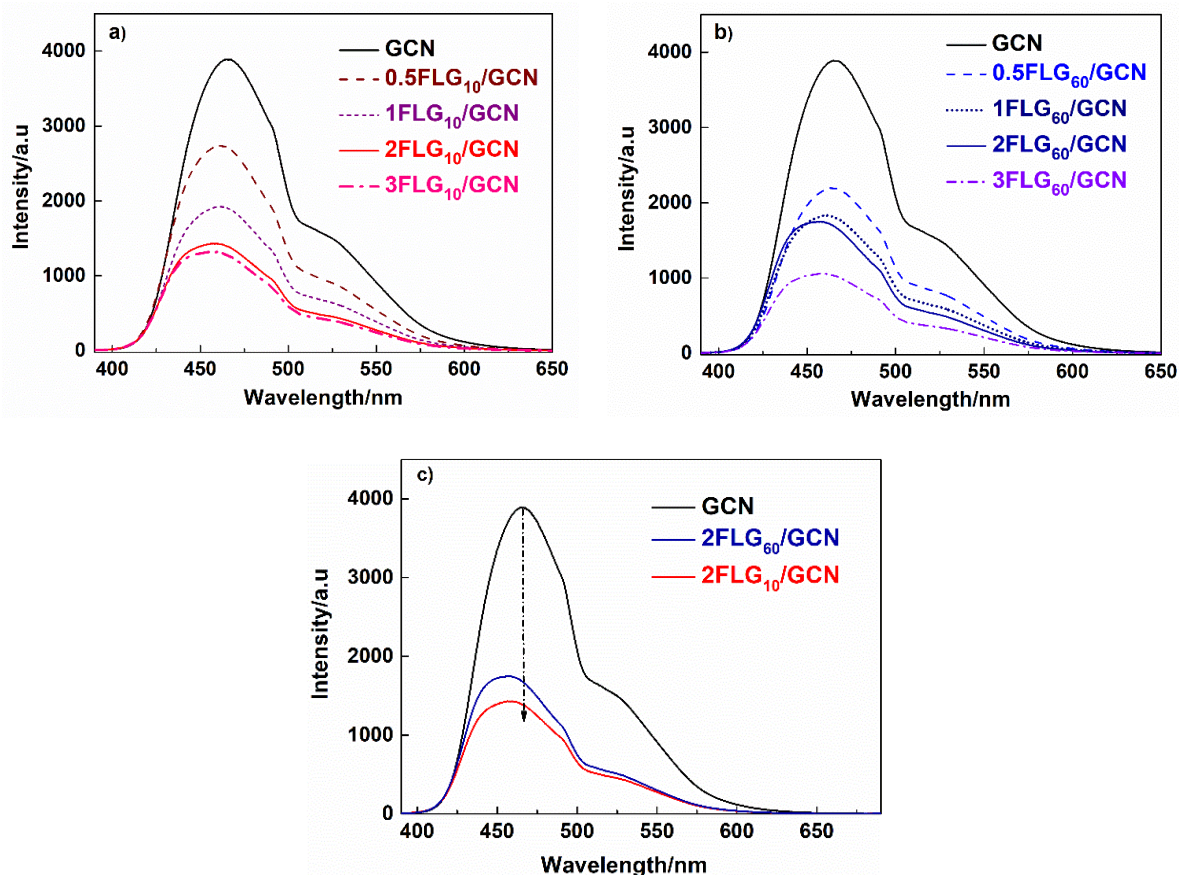


Figure 33. Steady-state PL emission spectra of GCN and a) xFLG₁₀/GCN, and b) xFLG₆₀/GCN, c) comparison of PL emission spectra of GCN, 2FLG₁₀/GCN, and 2FLG₆₀/GCN upon excitation at 370 nm.

4.3.2 Photocatalytic hydrogen generation

The photocatalytic activity of the materials was evaluated by assessing the amount of H_2 produced from water under visible-LED irradiation ($\lambda_{em} = 420$ nm) in the presence of EDTA as a sacrificial donor, and Pt as cocatalyst. Blank tests were performed in the absence of either light, catalyst, or sacrificial agent. Under these conditions, no H_2 generation was detected. The photocatalytic results show that all the materials can photochemically produce H_2 (**Figure 34a**); additionally, all the heterostructures displayed higher photocatalytic activity than the parent GCN. These results also indicate that both the FLG morphology and loading play a significant role in optimising the photocatalytic performance of GCN. After 3 h of irradiation, the H_2 evolved from bulk GCN was $333 \mu\text{mol g}^{-1} \text{h}^{-1}$, whereas, in the presence of even a tiny amount of FLG, 0.5 wt.%, the H_2 rate was improved to $874 \mu\text{mol g}^{-1} \text{h}^{-1}$. The photocatalytic activity was further enhanced by increasing the content of FLG_y, reaching the highest rate of hydrogen with 2 wt.% of FLG_y. The 2FLG₁₀/GCN and 2FLG₆₀/GCN materials showed a 4-times

(1275 $\mu\text{mol g}^{-1} \text{h}^{-1}$) and 3-times (1101 $\mu\text{mol g}^{-1} \text{h}^{-1}$) increase in photocatalytic H₂ generation compared to GCN, respectively. Furthermore, the continuous H₂ generation rate vs time for 2FLG₁₀/GCN hybrid was plotted and shown in **Figure 34c**. As presented in **Figure 34c**, the activity increased rapidly within the first minutes of illumination, and it continued to rise until it reaches a plateau rate. A steady rate in a plateau achieved after 100 min. The same profile was observed for all the prepared materials (data not shown). A comparison between the photocatalytic performance of our best material (2FLG₁₀/GCN) and other g-C₃N₄/graphene-based materials (**Table 3**; chapter 2) suggests that our material has an excellent response for H₂ generation. However, it is essential to keep in mind that experimental conditions and graphene type reported in this table are different from those used in that work.

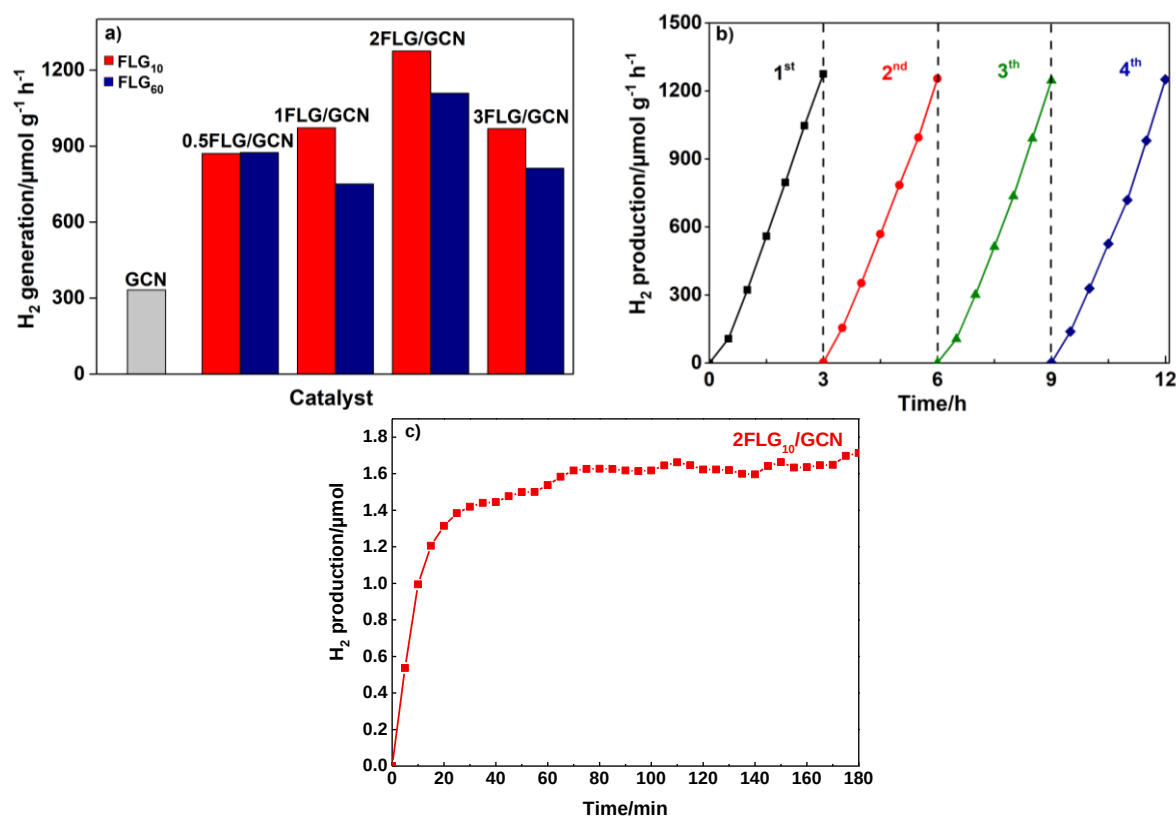


Figure 34. a) Rate of H₂ production over GCN, xFLG₁₀/GCN, and xFLG₆₀/GCN after 3 h of visible-LED irradiation in the presence of EDTA (10% vol) and Pt (3 wt.%). b) Variation in H₂ production of the catalyst 2FLG₁₀/GCN over four cycles of visible light irradiation (LED, $\lambda_{\text{em}} = 420 \text{ nm}$) in the presence of EDTA and Pt. c) HER profile run of 2FLG₁₀/GCN hybrid.

Additionally, it is possible to note that the photocatalytic activities of the heterostructures prepared with FLG₁₀ are slightly higher than those obtained with FLG₆₀, except for the 0.5 wt.%. This can be attributed to the lower recombination of the photogenerated electron/hole pairs in the 2FLG₁₀/GCN composite (**Figure 33**) and the higher surface area of FLG₁₀ (see

Table 4), which provided xFLG₁₀/GCN heterostructures with more active catalytic sites and channels for the photocatalytic hydrogen reaction. When the FLG_y content increased to 3 wt.%, a decrease in photocatalytic activity was observed, probably due to the shading effect caused by the large amount of black FLG_y.^{27, 107, 108} Nevertheless, both heterostructures containing 3 wt.% of FLG_y still result in higher hydrogen generation (800-900 $\mu\text{mol g}^{-1} \text{h}^{-1}$) than pristine GCN. The structure-activity of the materials GCN and xFLG_y/GCN can be inferred from the plots of the optical (PL) and surface (S_{BET}) parameters vs H₂ generation (**Figure 35**). The data concerning the material with 3wt.% was not considered due to a potential shading effect for this comparison. From the obtained data, it is possible to notice a reasonable linear correlation between these structural properties and activity, highlighting that a lower PL and higher surface area contribute to enhancing the photocatalytic activity of the 2FLG₁₀/GCN heterostructure.

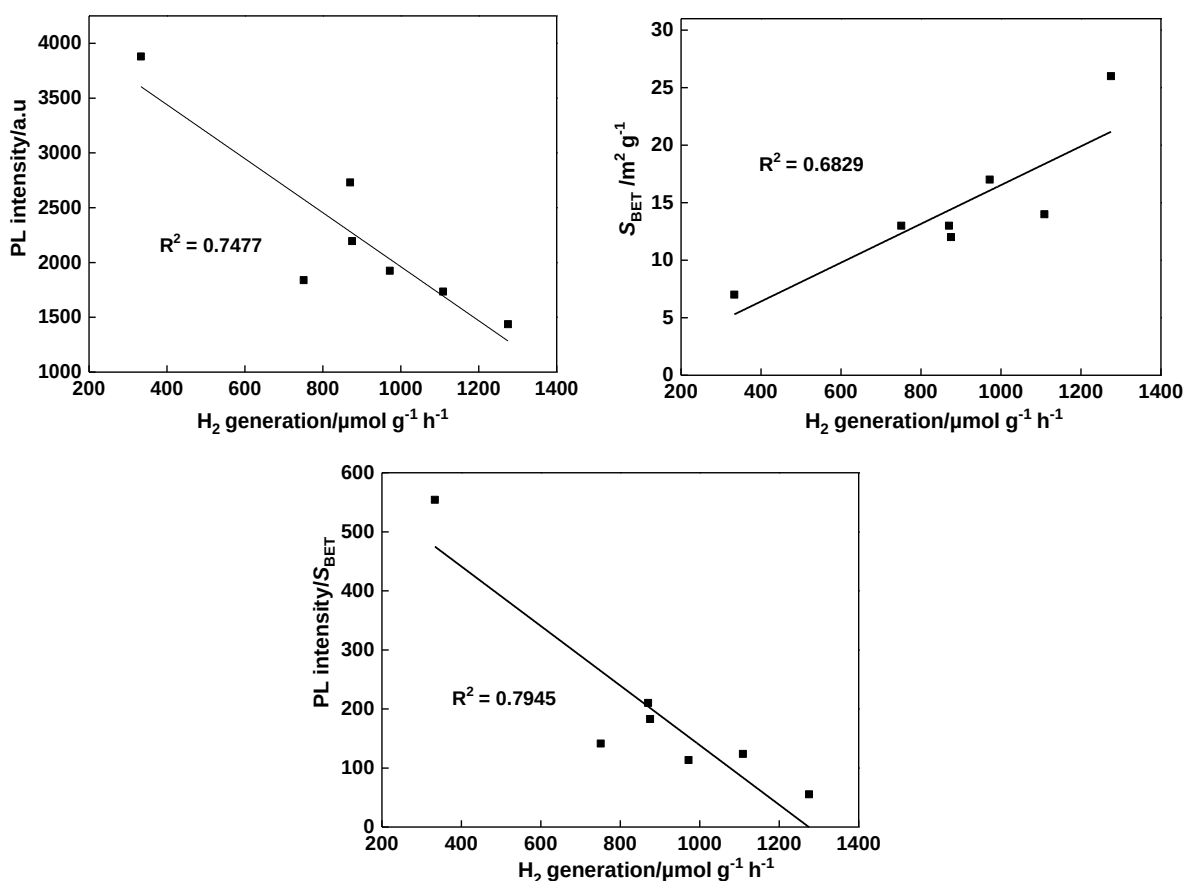


Figure 35. Correlation between the optical/surface parameters (PL, S_{BET} and PL/ S_{BET} ratio) and the photocatalytic activity for the materials GCN and xFLG_y/GCN (x = 0.5, 1 and 2 wt.%).

A physical mixture of 2 wt.% FLG₁₀ and GCN was trialled towards H₂ production under visible light, in the presence of EDTA and Pt, to test the occurrence of an efficient heterojunction on

the heterostructures. Under these conditions, 277 $\mu\text{mol g}^{-1} \text{h}^{-1}$ of H₂ was detected, a much smaller amount than that obtained with the equivalent heterostructure, which shows a 4-times enhancement. This lower photocatalytic performance of the physical mixture supports the formation of an effective heterojunction between GCN and FLG_y.³⁶⁰

Although the vibrational spectra do not show any significant difference in the intensity of the bands recorded for the different materials (**Figure 30**), may be due to the low amount of FLG present, the possibility of a covalent interaction between the FLG and the GCN cannot be excluded considered the relatively high temperature used for the synthesis of the heterostructures, and the smaller distances observed between both components (XRD). Indeed, covalently coupled hybrids of g-C₃N₄ with reduced graphene oxide have already been reported in the literature.³⁶¹

In addition, the photocatalytic stability of the best performing catalyst, 2FLG₁₀/GCN, was evaluated during four recycling tests under visible light irradiation (LED, $\lambda_{\text{em}} = 420 \text{ nm}$). Under these conditions, the material presented good stability with an almost constant H₂ produced during the complete 12 h of reaction (**Figure 34b**). That value is a good indication of the capability of these materials to sustain long-cycle usability.

4.3.3 Proposed photocatalytic mechanism

Electrochemical impedance spectroscopy (EIS) was used to gain further information on the electronic properties of the materials 2FLG₁₀/GCN and GCN. As displayed in **Figure 36a**, the Mott-Schottky (MS) plot shows positive slopes indicative of n-type behaviour.^{333, 362} Furthermore, from the MS plots it is possible to calculate the electron donor density of the materials (N_D), as the slopes are proportional to $1/N_D$. The N_D values determined for GCN ($\sim 7.71 \times 10^{20} \text{ cm}^{-3}$) and 2FLG₁₀/GCN ($\sim 4.11 \times 10^{21} \text{ cm}^{-3}$), respectively. The higher value of N_D obtained for 2FLG₁₀/GCN is useful to enhance the charge carrier mobility and improve the photocatalytic activity.^{333, 362} The flat-band potential (E_{fb}) was derived from the interception of the slope with X-axis, with values of -0.65 and -0.51 V vs NHE for GCN and 2FLG₁₀/GCN, respectively. For n-type materials, the E_{fb} is associated with the bottom of the conduction band (CB). It is then possible to calculate the valence band (VB) potentials of the materials through the combination of the CB potentials and the E_g values (**Table 4**). The VB values were determined to be +2.00 V and +2.04 V vs NHE, for GCN and 2FLG₁₀/GCN, respectively.

The transient photocurrent responses of both materials were also measured as this reflects the ability of a material to generate and transfer charge carriers under illumination. As shown in

Figure 36b, it is notorious that 2FLG₁₀/GCN produces a higher photocurrent density than GCN, as the former displays a larger difference (higher gap) between the recorded current response under dark and in light conditions. In fact, when the light was turned on, an approximately 20 % improvement on the current response was recorded for 2FLG₁₀/GCN compared to GCN. This demonstrate that 2FLG₁₀/GCN presents lower recombination of photoinduced e^-/h^+ pairs, also in accordance with PL data (**Figure 33**), and thus can contribute to explain the higher efficiency in H_2 production.

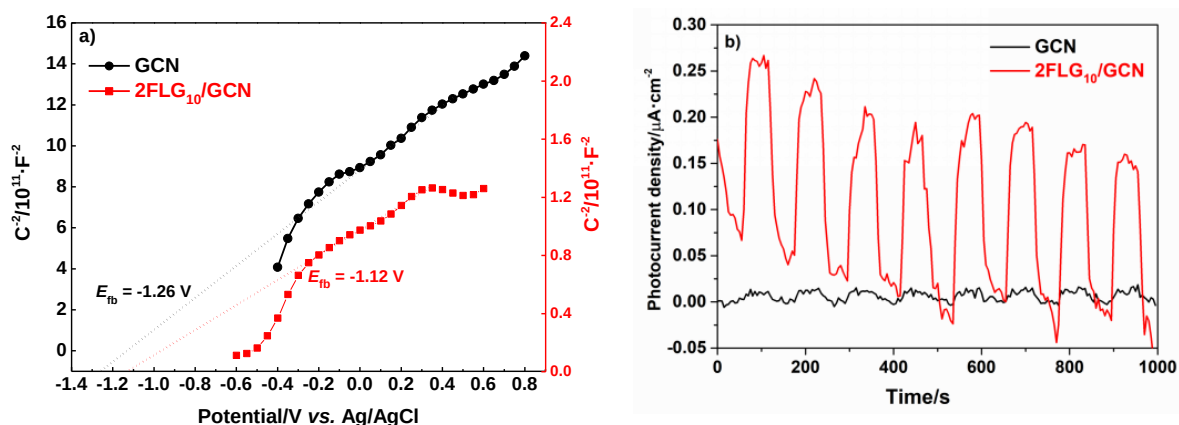


Figure 36. a) Mott-Schottky plots and b) transient photocurrent response (constant applied potential of 0.2 V vs Ag/AgCl, with 60 s simulated solar light ($100 \text{ mW} \cdot \text{cm}^{-2}$) on/off cycles during 1000 s for GCN and 2FLG₁₀/GCN materials.

Based on the results, a possible mechanism for electron transfer in 2FLG₁₀/GCN is proposed (**Figure 37**). Under visible light irradiation, both materials are able to absorb photons and generate electron-hole pairs. According to PL data, the electrons are transferred from the CB of GCN to the CB of FLG, thus decreasing the charge carrier recombination. Then, the photoexcited electrons migrate to the 2FLG₁₀/GCN surface and react with the Pt co-catalyst, which therefore react with water to generate H_2 . Meanwhile, the generated holes on the VB of 2FLG₁₀/GCN can be directly quenched by the hole scavenger, EDTA.

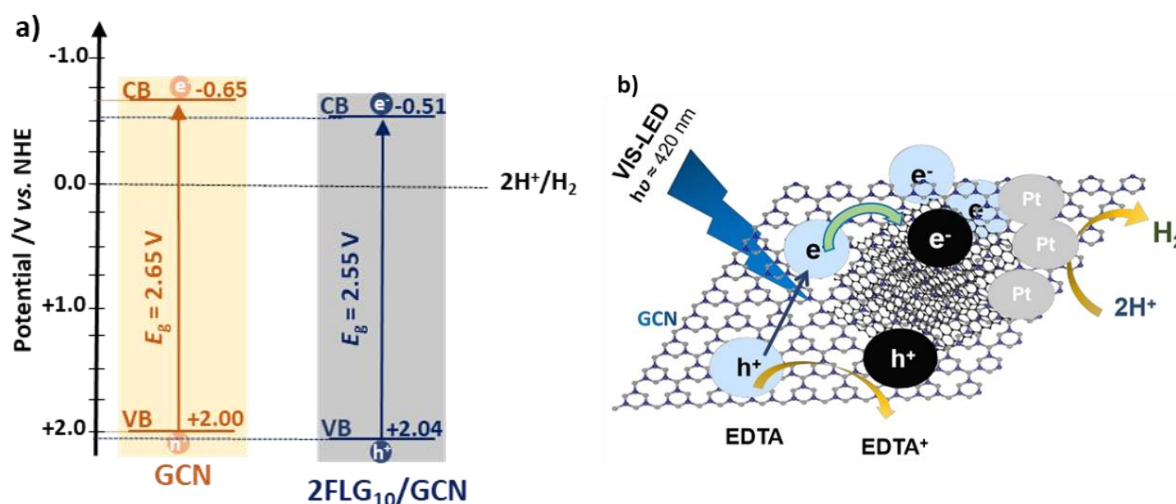


Figure 37. a) Band structure diagram of GCN and 2FLG₁₀/GCN materials, b) Proposed diagram of charge carrier transfer and H₂ production on 2FLG₁₀/GCN.

4.4. Conclusions

GCN and FLG (c-CVD) heterostructures can be easily prepared and used for visible-light photocatalytic hydrogen generation. In these heterostructures, FLG acts as a suitable acceptor of the electrons photogenerated from GCN and as conductive channels to separate the electron/hole pairs and accelerate charge transfer at the interface, hindering their recombination and primarily enhancing the visible light photocatalytic hydrogen activity of GCN.

Moreover, the loading and morphology of FLG directly influence the photocatalytic activity of the prepared materials. The optimal FLG content is found to be 2 wt.%, leading to a hydrogen production rate four times higher than that observed for GCN. Overall, the observed performance is comparable to other materials, with the advantage of having a resilient material prone to be used in long cycles. Such material will have many benefits in technical applications, *e.g.*, in the field of CO₂ direct photocatalytic methanation, using *in-situ* H₂ generation.

This study shows that the construction of metal-free FLG/GCN materials is an efficient strategy to improve the charge separation efficiency of bulk GCN and consequently increase its photocatalytic activity.

Chapter 5

LDH/g-C₃N₄ hybrids for photocatalytic water splitting

The research work presented in this chapter relies on engineering bulk GCN by thermally exfoliating it in order to obtain GCN nanosheets (GCNN) and couple it with novel synthesised 2D LDH materials in order to obtain 2D/2D hybrid materials with improved photocatalytic activity for hydrogen (HER) and oxygen (OER) from water, using highly eco-efficient irradiation sources.

This chapter is subdivided into two parts. Part 5.1 addresses the construction of 2D/2D heterostructures between the novel ternary NiCeAl-LDH and GCNN *via* impregnation, varying the loading amount of NiCeAl-LDH. The formed 2D/2D heterostructures were tested for HER under visible-LED irradiation using EDTA as sacrificial agent and Pt as cocatalyst. The reusability tests of the best material were also performed. Part 5.2 addresses the fabrication of 2D/2D heterostructures composed of novel CuAl-LDH and GCNN through an electrostatic co-assembly method. The hybrids materials were tested towards photocatalytic HER and OER under visible-LED irradiation. Different sacrificial agents were studied for HER reaction.

Part 5.1 is based on the following research manuscript:

Hanane Boumeriame, Ana Coutinho, Manuel Prieto, Luísa Andrade, Tânia Lopes, Adélio Mendes, Nuno M. M. Moura, Tarik Chafik, Eliana S. Da Silva, Joaquim L. Faria. “Enhanced visible-LED photocatalytic hydrogen generation from novel 2D/2D NiCeAl-LDH/g-C₃N₄ hybrids.” (To be submitted).

Part 5.2 is based on the following research manuscript:

Hanane Boumeriame, Eliana S. Da Silva, Dogukan H. Apaydin, Dominik Eder, Tarik Chafik, Alexey S. Cherevan, Joaquim L. Faria. “Novel 2D/2D CuAl-LDH/g-C₃N₄ nanohybrids for visible-light-driven photocatalytic H₂ and O₂ generation.” (To be submitted).

The research concerning Part 5.1 was partially carried out by a nine-month stay at the Institute of Materials Chemistry, the University of Vienna, under the co-supervision of Dr Alexey Cherevan and Prof. Dominik Eder.

5.1 NiCeAl-LDH/GCN hybrids for photocatalytic H₂ generation

5.1.1. Introduction

Bulk GCN photocatalyst has several shortcomings due to the fast recombination of e^-/h^+ pairs, limited visible light absorption and low surface area. Thermal exfoliation has acquired the most attention. It is a very efficient and rapid way to produce high-quality thin-layered GCN with enhanced surface area, overcoming one of the limitations of bulk GCN and increasing the material's photocatalytic activity.^{88, 94, 363} Furthermore, coupling nanosheets-like GCN with other semiconductors to construct 2D/2D heterostructures has also shown to be an effective strategy for enhancing photocatalytic performance.^{95, 364} This strategy is typically applied to facilitate interfacial charge separation and extraction at the space charge region formed due to the difference in Fermi levels of the two semiconductors. The photogenerated electrons and holes can move directionally and be spatially split by the inbuilt electric field,^{45, 365} which ultimately lowers their recombination rates and enhanced photocatalytic performance.

In recent years, using 2D layered double hydroxides (LDH) to design heterojunctions has received significant interest, owing to their tunable optical and electrochemical properties.³⁶⁵ Considering the advantages and drawbacks of both materials classes, as already explained in chapter 2, the design of LDH/GCN heterojunctions has been seen as a tool to overcome the drawbacks of both individual materials.³⁶⁵

This chapter reports the fabrication and characterisation of a novel-type photocatalyst heterostructure composed of ternary NiCeAl-LDH and GCN for photocatalytic H₂ generation *via* water splitting under vis-LED irradiation. In addition, the effect of the loading amount of NiCeAl-LDH on GCNN photoactivity was evaluated. This is the first report on the visible-LED photocatalytic activity for 2D/2D NiCeAl-LDH/GCN heterostructures towards H₂ generation.

5.1.2. Materials and methods

This section describes the materials, the main approaches used to synthesise both GCN and LDH materials, and the photocatalytic experiments. All the characterisation techniques employed in this chapter are given in chapter 3.

5.1.2.1 Materials

All the materials used for the syntheses were obtained from different commercial suppliers and used without further purification. Dicyandiamide (DCN, 99%), ethylenediaminetetraacetic acid (EDTA, $\geq 98\%$), L-ascorbic acid (99%), chloroplatinic acid hydrate (H₂PtCl₆·xH₂O, 99.9%), aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O, $\geq 98\%$) from Sigma-Aldrich. Cerium

nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\geq 95\%$) from Alfa Aesar. Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%) from EMSURE® ACS. Urea ($\text{CH}_4\text{N}_2\text{O}$, 99.5%) from ACROS. Ethanol and N,N'-dimethylformamide (DMF) from Fischer Chemical. Ultrapure water obtained from a Millipore Milli-Q system water purification system ($\geq 18 \text{ M}\Omega \text{ cm}^{-1}$) was implemented throughout all assays. EDTA aqueous solution (0.2 M) was prepared in NaOH (0.5 M).

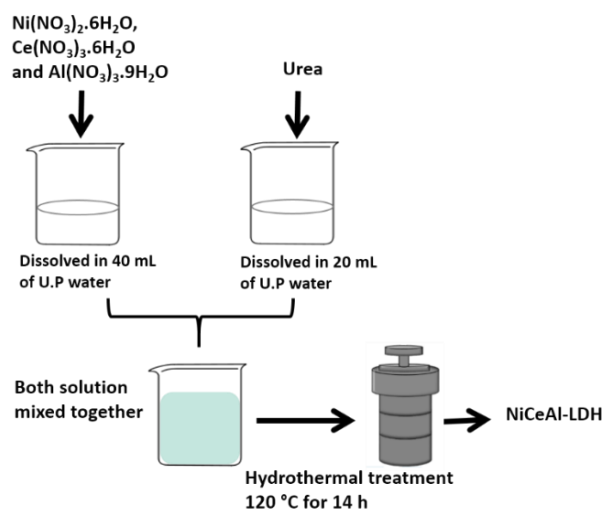
5.1.2.2 Catalyst preparation

Synthesis of graphitic carbon nitride nanosheets

Bulk GCN was synthesised through thermal decomposition of DCN as described in chapter 4. Then, the obtained bulk powder was homogeneously spread in an open crucible and thermally exfoliated under air at 500 °C for 2 h, generating nanosheets of GCN. This solid material was labelled as GCNN and presented a slightly lighter yellow colour than the initial bulk material.

Synthesis of NiCeAl-LDH

NiCeAl-LDH was synthesised by the one-step hydrothermal method. In a typical synthesis, 2.4 mmol of Ni (II) nitrate, 9.6 mmol Ce (III) nitrate and 4 mmol Al (III) nitrate were dissolved into 40 mL of ultrapure water, while a certain amount of urea was dissolved in another 20 mL of ultrapure water. Both solutions were mixed and stirred for a given time. Then, the solution was transferred into a Teflon lined stainless steel autoclave. The autoclave was sealed, put into an oven, and maintained at 120 °C for 14 h (**Scheme 4**). The light blue obtained precipitate was recovered by centrifugation followed by washing with deionised water and ethanol repeatedly and finally dried overnight at 60 °C.



Scheme 4. The synthesis process of NiCeAl-LDH.

Preparation of NiCeAl-LDH/GCNN heterostructure

GCNN ethanolic suspensions and NiCeAl-LDH in DMF suspensions (varying the weight ratio (wt.%)) were separately ultrasonicated for 30 min. The hybrids were prepared by mixing both dispersions under ultrasonic stirring for 30 min, followed by magnetic stirring for 6 h at room temperature. The hybrids were centrifuged, washed several times with water and ethanol, and finally dried overnight at 60 °C. The weight ratio of NiCeAl-LDH was 0, 0.5, 1, 1.5, 3, and 7 and the materials were labelled as xNiCeAl-LDH/GCNN, where x represents the wt.% of NiCeAl-LDH.

Synthesis of platinum nanoparticles

The Pt nanoparticles were synthesised as described in chapter 4, section 4.2.2.

5.1.2.3 Photocatalytic tests

The photocatalytic H₂ evolution reactions were performed under visible light irradiation using LEDs at maximum emission of 420 nm, symmetrically located at 3.0 cm around the reactor wall (**Scheme 3**, chapter 4, section 4.2.3). The average nominal irradiance of each LED was 880 W m⁻², determined using a spectroradiometer (OceanOptics USB2000+). A cylindrical glass reactor was employed in photocatalytic experiments. In a typical experiment, 0.3 g L⁻¹ of the catalyst was dispersed in an aqueous solution (100 mL) containing EDTA (15% vol.) as sacrificial electron donor and Pt (3.0 wt.%) as cocatalyst. Before irradiation, the suspension was stirred in an ultrasonic bath for 10 min. After that, the reactor was closed, continuously stirred and purged with nitrogen for 30 min to ensure total removal of dissolved oxygen, before irradiation. The amount of H₂ generated was measured during 3 h using an online gas chromatograph (Inficon Micro GC 3000) equipped with a mol sieve column and a micro-TCD detector using argon as carrier gas. Reuse tests were carried out for the best performing catalyst to evaluate its stability during four cycles. After each run, the reactor was first open to the air and left under dark for a given time, after which it was again closed, bubbled with nitrogen to remove the air and irradiated. This procedure was repeated for four continuous cycles without extra addition of Pt or EDTA between the cycles.

5.1.3. Results and discussion

Different loading amounts of NiCeAl-LDH were coupled with GCNN *via* impregnation to design 2D/2D xNiCeAl-LDH/GCN heterostructures. The materials were thoroughly characterised by several techniques and were investigated for the first time for photocatalytic H₂ generation through water splitting.

5.1.3.1 Materials characterisation

The chemical structure information of the materials was obtained by ATR-FTIR (**Figure 38**). The FTIR spectrum of pure NiCeAl-LDH (**Figure 38a**) shows vibration bands at 3460 cm⁻¹ and 1535 cm⁻¹ corresponding to the symmetric and asymmetric stretching vibrations of O–H and bending vibrations of water molecules that are positioned in the interlayer of the LDH, respectively.^{96, 97, 210, 366} The two bands located at 1385 and 1430 cm⁻¹ correspond to the vibrational modes of intercalated NO₃⁻ anions and the asymmetric stretching of O–NO₂, respectively.^{96, 97, 210, 366} The bands below 900 cm⁻¹ are related to the metal-oxygen (Ni–O, Ce–O, and Al–O) and metal–oxygen–metal (Ni–O–Ce, Ni–O–Al).^{96, 97} As for the GCCN (**Figure 38b**), it presents similar peak features of GCN (as discussed in chapter 4, **Figure 5**), indicating that the exfoliated nanosheets keep the same chemical structure as the bulk GCN. However, the peak at 803 cm⁻¹ for GCN was shifted to 807 cm⁻¹ for GCNN (**Figure 38b**), indicating that the vibrational modes of triazine units were modified. Moreover, a slight difference in the intensity of each peak was observed, which might be due to a higher amount of the specific functional groups or bonds in terms of volume.^{363, 367, 368} The FTIR spectra of xNiCeAl-LDH/GCNN heterostructures (**Figure 38c**) present similar infrared spectra related to GCNN skeletal vibration, probably due to the low amount of NiCeAl-LDH, thus indicating that the introduction of LDH did not change the base structure of GCNN.

Moreover, zeta-potential measurements of both NiCeAl-LDH and GCNN aqueous suspensions indicate a surface charge of +34 mV and –33 mV, respectively. This suggests that the individual components can be assembled *via* electrostatic interactions, resulting in hybrids with proximate interfacial contact.

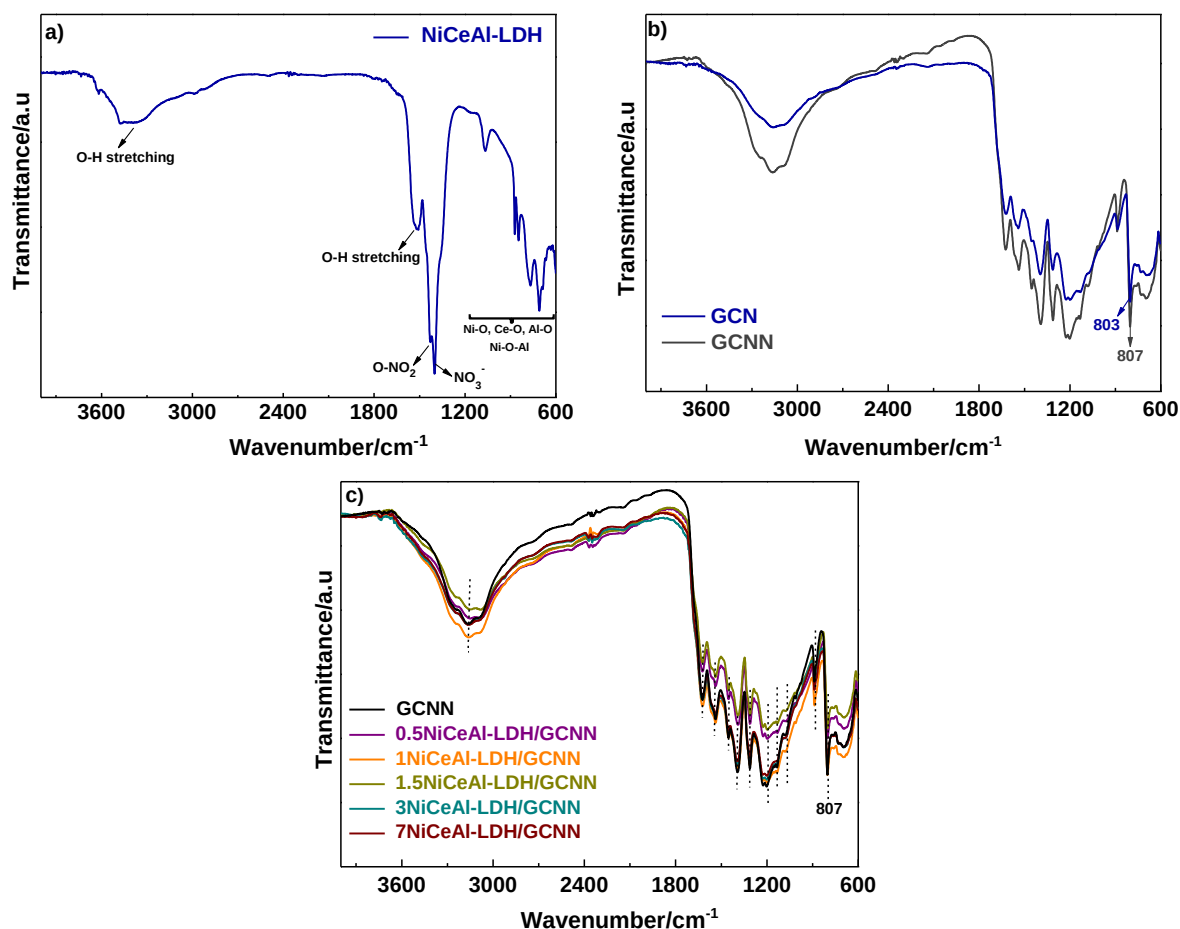


Figure 38. ATR-FTIR spectra of a) NiCeAl-LDH, b) GCN and GCNN, c) GCNN and xNiCeAl-LDH/GCNN materials.

In order to obtain information on the crystal structure of the materials, XRD measurements were performed. As shown in (**Figure 39a**), both GCN and GCNN present similar diffraction patterns consistent with the typical graphite-like hexagonal phase of g-C₃N₄ (as previously discussed in chapter 4, section 4.3.1), and no other impurity phase was detected. For GCNN, the peak at 27.7° ascribed to inter-layer stacking of the conjugated aromatic systems corresponds to the (002) plane. The peak located at 13.0° belongs to the (100) plane attributed to the in-plane structure repeating motif of tri-s-triazine units.^{333, 369, 370} Moreover, the (002) peak shifts from 27.4° for GCN to 27.7° for the GCNN, which indicates that the interlayer structure of GCN was modified, within the decreasing of the $d_{(002)}$ spacing.^{88, 363} Concerning the pristine NiCeAl-LDH (**Figure 39b**), this shows various reflections at 2θ values of 11.52°, 24.50°, 33.94°, 38.36°, 43.62°, 61.38°, and 63.10°, indexed to the (003), (006), (009), (015), (220), (110), and (113) planes, respectively, characteristic of LDH phases,^{97, 170, 197, 371} The diffraction peaks at 30.63°, 47.62° and 57.50° corresponding to (111), (220) and (331) planes can be attributed to the metal oxide-containing Ni and Ce.^{170, 226} In the case of xNiCeAl-

LDH/GCNN heterostructures, these present the typical diffraction peaks of GCNN, indicating that the basic structure of GCNN was preserved and also the presence of NiCeAl-LDH. The characteristic peaks became more visible as the amount (wt.%) of NiCeAl-LDH increases. These observations are in line with the SEM results discussed below.

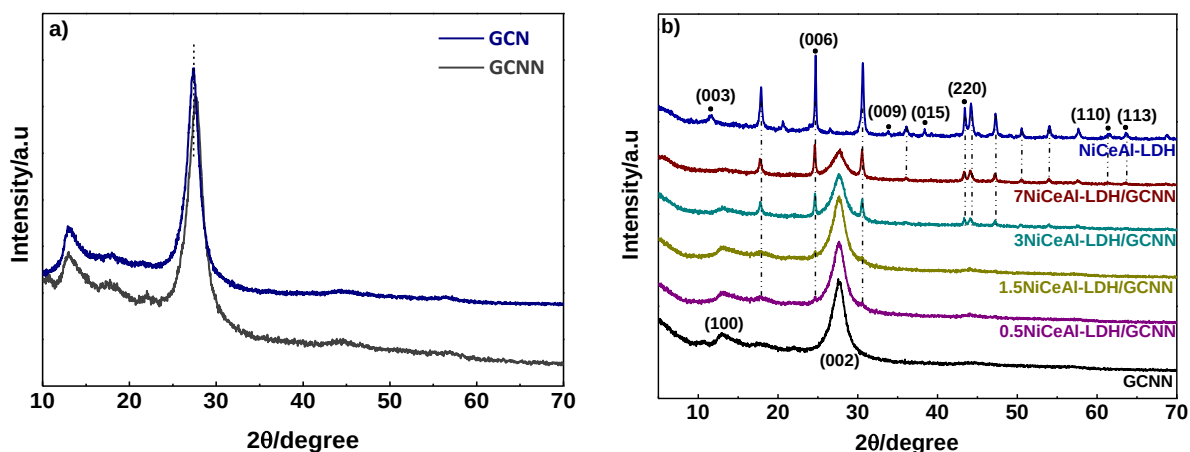


Figure 39. X-ray diffraction patterns of a) GCN and GCNN, b) GCNN, NiCeAl-LDH and xNiCeAl-LDH/GCNN materials.

The surface area and porous properties of the materials were evaluated through N₂ adsorption-desorption analysis at −196 °C. The specific surface area (S_{BET}), pore volume and pore size of the materials are given in **Table 8**, whereas the N₂ isotherms of NiCeAl-LDH, GCNN and 1.5NiCeAl-LDH/GCNN are shown in **Figure 40**. As displayed, all the materials exhibited a type II isotherm with a hysteresis loops type H3 which indicate the existence of meso- and macroporous structure owing to non-rigid aggregation of plate-like particles.³⁰⁴ As expected, the thermal exfoliation increased the S_{BET} of g-C₃N₄, going from 7 m² g^{−1} for bulk GCN (chapter 4, **Table 1**) to 155 m² g^{−1} for GCNN, which indicates the availability of more active catalytic sites in GCNN for photocatalytic reaction.^{90, 336} Concerning the NiCeAl-LDH, this possesses a surface area of 32 m² g^{−1} (**Table 8**). Moreover, it is observed that the amount of N₂ adsorbed volume decreases significantly from GCNN to the 1.5NiCeAl-LDH/GCNN hybrid, which matched with the surface area reduction (**Table 8**). The decreased S_{BET} could be due to the hybridisation mechanism between the positively charged NiCeAl-LDH and negatively charged GCNN, which might therefore occur in the interlayer spacing of GCNN. The pore volume and diameter also follow the same tendency, suggesting the formation of heterostructures.

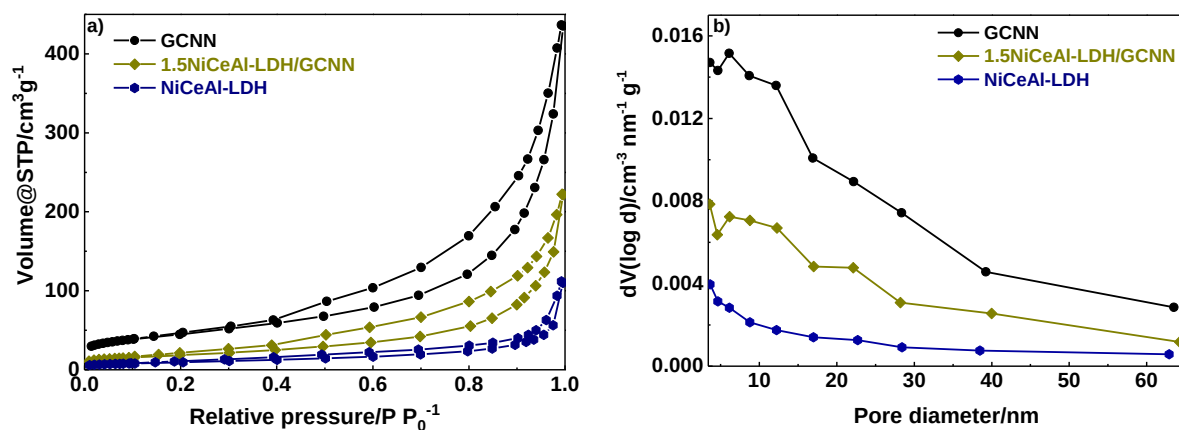


Figure 40. a) N₂ adsorption-desorption isotherms at -196 °C and b) the pore size distribution of GCNN, NiCeAl-LDH and 1.5NiCeAl-LDH/GCNN heterostructures.

Table 8. Textural properties of GCNN, NiCeAl-LDH and xNiCeAl-LDH/GCNN heterostructures determined by N₂ adsorption-desorption isotherms at -196 °C.

Materials	S_{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
GCNN	155	0.691	6.109
NiCeAl-LDH	32	0.166	3.643
1NiCeAl-LDH/GCNN	73	0.273	3.596
1.5NiCeAl-LDH/GCNN	74	0.346	3.594
3NiCeAl-LDH/GCNN	77	0.3618	3.618
7NiCeAl-LDH/GCNN	88	0.326	3.638

The morphological properties of GCNN, NiCeAl-LDH, 1.5NiCeAl-LDH/GCNN and 7.0NiCeAl-LDH/GCNN heterostructures were characterised by SEM analysis (**Figure 41**). GCNN presents many thin nanosheets layers arranged in irregular patterns (**Figure 41a**), which indicates the successful exfoliation of bulk GCN, **Figure 37a**, chapter 4, and in line with the literature.⁸⁸ The NiCeAl-LDH presents several clusters of flaky sheets (**Figure 41b**), which are arranged haphazardly. In the case of the hybrid 1.5NiCeAl-LDH/GCNN (**Figure 41c**), the clusters flaky sheets-like morphology of LDH were observed in the layers of GCNN, as indicated by the white arrows. As for 7NiCeAl-LDH/GCNN hybrid, the presence of LDH is visible by a large amount of small bright structures (**Figure 41d**). These results are well consistent with the XRD results discussed above.

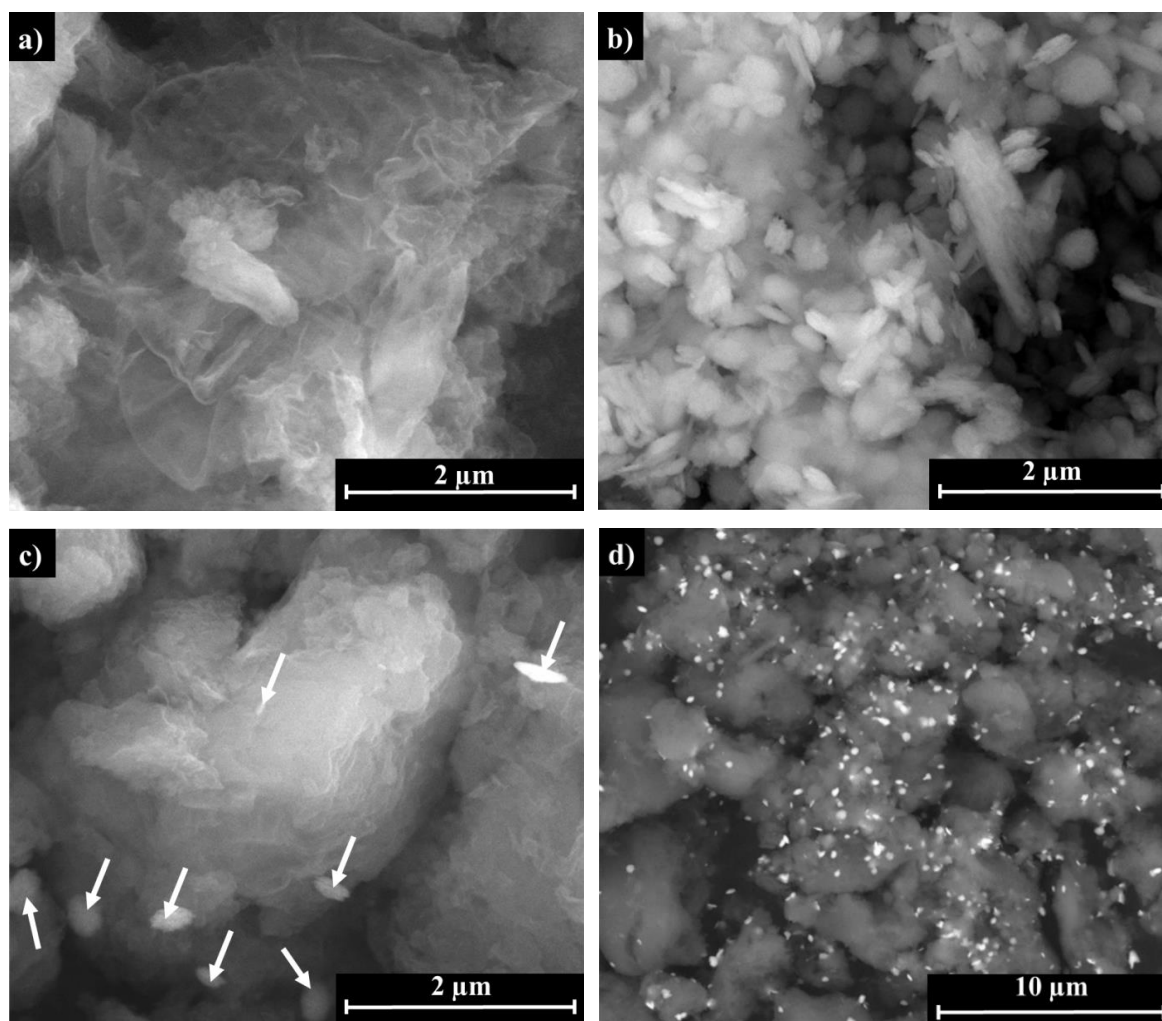


Figure 41. SEM images of a) GCNN, b) NiCeAl-LDH, c) 1.5NiCeAl-LDH/GCNN, and d) 7NiCeAl-LDH/GCNN materials.

The optical absorption properties of the materials were evaluated by UV-Vis DRS and PL. As shown in the UV-Vis DRS (**Figure 42a**), GCNN displays an intrinsic semiconductor-like absorption pattern in the blue region of the visible range with an absorption edge at around 457 nm, which is assigned to the characteristic π - π^* transitions owing to the heterocyclic aromatic system.^{65, 88, 333} After the thermal exfoliation, a blueshift in the band edge of GCNN compared to the bulk GCN was observed (**Figure 42a**), which might be due to the intrinsic electronic changes in the aromatic bonds (*e.g.*, transitions from n to π bonds).^{90, 372} Meanwhile, the NiCeAl-LDH exhibits two absorption bands (**Figure 42b**), one in the UV region and the second one in the visible region. More specifically, the wide absorption band in the region of 230-450 nm can be attributed to the ligand-to-metal charge transfer (LMCT) from the 2p orbitals of oxygen to the 3d orbitals of Ni^{2+} , while the small band at around 550-800 nm is

attributed to d-d transitions of the Ni²⁺ ions.^{96, 97, 170, 197, 366} The heterostructures exhibited a considerable absorption like GCNN but accompanied by a slight redshift in the absorption edges (**Figure 42c**). This might be attributed to electrostatic interactions between both materials. Furthermore, the slightly increased absorption capacity may result in more photogenerated charge carriers available for photocatalytic reactions, resulting in enhanced photocatalytic activity.

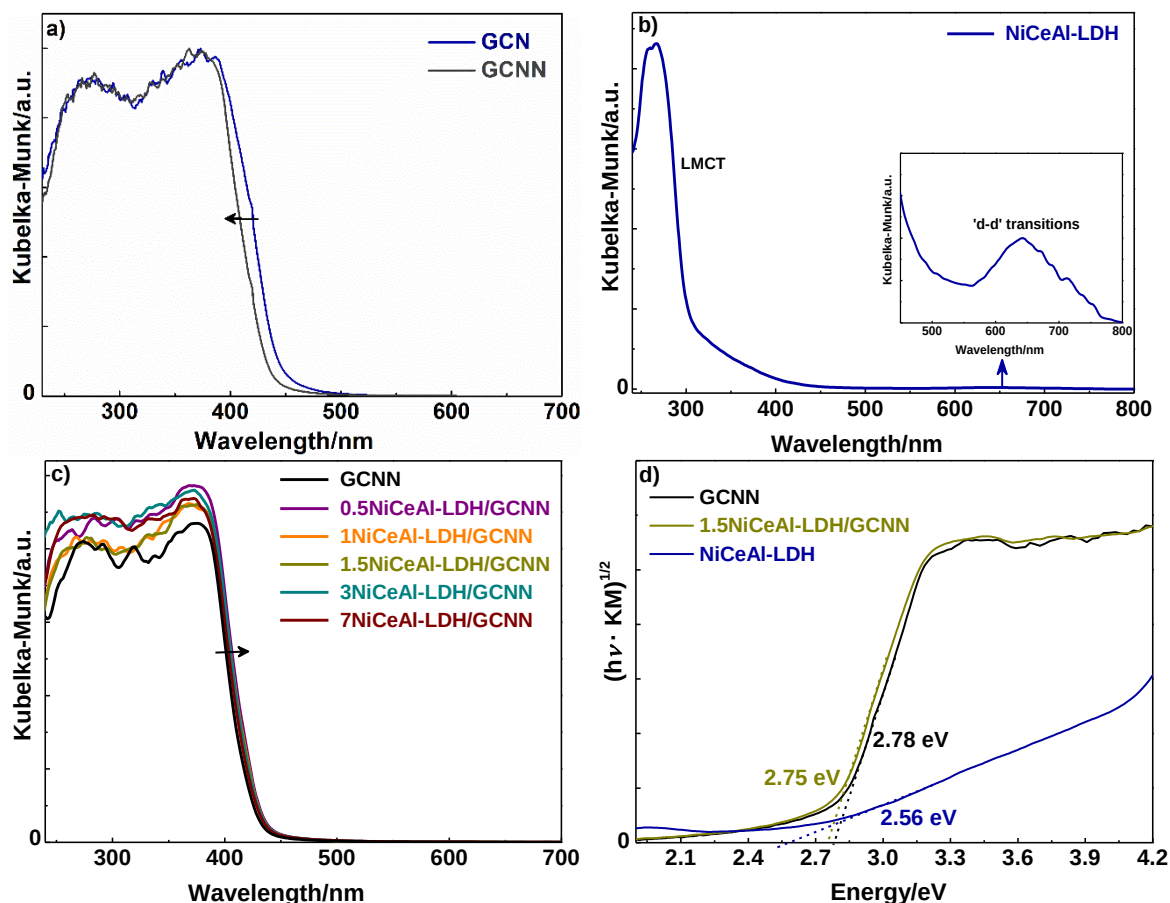


Figure 42. UV-Vis DRS of a) GCN and GCNN, b) NiCeAl-LDH, c) GCNN and xNiCeAl-LDH/GCNN hybrids, d) Tauc plot of GCNN, NiCeAl-LDH and 1.5NiCeAl-LDH/GCNN hybrids.

The bandgap energies (E_g) of the materials were estimated using the Tauc plot method (**Figure 42b**) via the intercept of the tangents of the $(\alpha h\nu)^{1/n}$ plots vs photon energy, calculated according to Eq. 10 (chapter 3).^{96, 366} The n value of 2 was applied corresponding to the indirect allowed transition model. The estimated bandgap energy of 1.5NiCeAl-LDH/GCNN heterostructure is 2.75 eV, slightly lower than GCNN ($E_g = 2.78$ eV). In bulk GCN, the bandgap energy was lower than the exfoliated material ($E_g = 2.65$ eV; **Table 4** in chapter 4), which is in

line with the blueshift observed in UV-Vis DRS. The bandgap of NiCeAl-LDH is found to be 2.56 eV, and the estimated bandgap values of the other heterostructures composed of 0.5, 1, 3 and 7 wt.% of NiCeAl-LDH/GCNN were found to be 2.69, 2.77, 2.76 and 2.76 eV, respectively. These results suggest a bandgap narrowing compared to GCNN, which may favour photocatalytic activity.

To evaluate the degree of charge separation and transportation in the prepared materials, photoluminescence (PL) measurements were performed at room temperature with excitation at 370 nm. As shown in **Figure 43a**, GCN presents an intense and broad fluorescence emission band with a maximum centred at 460 nm, which is usually related to the high charge carrier recombination caused by the π - π conjugated system of the polymeric GCN, as discussed in chapter 4.^{332, 333, 339} The exfoliated GCNN shows a fluorescence band with a blueshift in maximum emission wavelength as compared to GCN, centred at 440 nm. In addition, the PL intensity of this band is increased as compared to GCN, which could be ascribed to the quantum confinement effect, due to the separation and to the decreasing size of the material layers.^{88, 373, 374} Moreover, a second emission band at around 528 nm is observed, being assigned to the n - π^* emission of the electronic transitions involving lone pair on the edge of N atoms in the aromatic rings.³³³ The observed blueshift is consistent with the blueshift observed in the UV-Vis DRS.

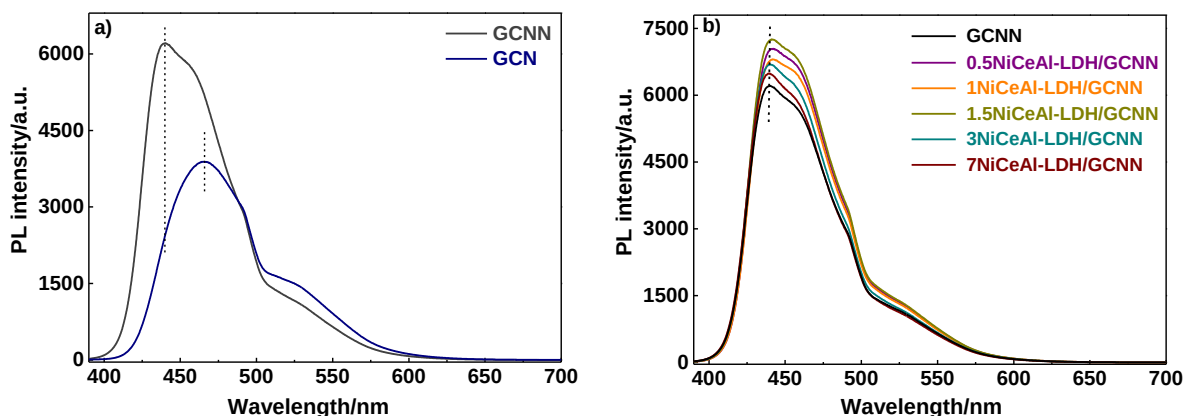


Figure 43. Solid steady-state PL spectra of a) GCN and GCNN, b) GCNN and xNiCeAl-LDH/GCNN materials.

As for the xNiCeAl-LDH/GCNN materials showed an increased PL intensity compared to the GCNN (**Figure 43b**), being the highest PL emission intensity measured for the 1.5NiCeAl-LDH/GCNN hybrid. The higher PL intensity might result from the electronic transition modes of the metals Ni, Ce and Al present in the NiCeAl-LDH. These metals may be

in some way leading to higher availability of electrons likely to participate in surface reduction reactions. Furthermore, a slight redshift of GCNN maximum emission was observed in the heterostructures, which is in line with the UV-Vis DRS results and the variation observed in energy bandgaps.

Time-resolved fluorescence measurements were further used to study the lifetimes of the charge carriers for GCNN and 1.5NiCeAl-LDH/GCNN materials. The obtained fluorescence lifetimes and their relative amplitudes are given in **Table 9**. Both materials present three components (A_1 , A_2 , A_3) with short lifetimes (< 4.0 ns), and a fourth component with longer lifetime ($\tau_4 > 10$ ns) and low amplitude ($A_4 < 5\%$). In all fourth exponential fitting, the lifetime of 1.5NiCeAl-LDH/GCNN was slightly lower than GCNN. The average fluorescence lifetime ($\tau_{av.}$) for 1.5NiCeAl-LDH/GCNN was slightly reduced compared to GCNN. The lower lifetime suggests more effective charge separation occurring on 1.5NiCeAl-LDH/GCNN, indicating that excited states can decay *via* a non-radiative path.^{211, 217, 333} Therefore, the excited states through charge transfer of electrons and holes re-localised to new localisation/surface states, which might facilitate charge generation and thus enhance the photocatalytic activity.^{333, 375}

Table 9. Fluorescence lifetimes (τ_i , $\tau_{av.}$), normalised amplitudes (A_i) and chi-square (χ^2) for GCNN and 1.5NiCeAl-LDH/GCNN materials ($\lambda_{ex} = 335$ nm; $\lambda_{em} = 433$ nm).

Materials	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	A_4	τ_4 (ns)	$\tau_{av.}$ (ns)	χ^2
GCNN	29.5	0.379	41.3	1.398	25.5	3.817	3.70	12.255	4.78	1.009
1.5NiCeAl-LDH/GCNN	23.8	0.252	40.4	1.082	30.9	3.274	4.90	10.938	4.74	1.023

5.1.3.2 Photocatalytic hydrogen generation

The photocatalytic activity of all materials was investigated towards H₂ generation under visible-LED emitting at 420 nm, in aqueous solutions containing EDTA as a sacrificial agent and Pt as cocatalyst (**Figure 44a**). Blank reactions were performed, and for all the materials, no H₂ was detected in the absence of either photocatalyst or light irradiation, supporting that the photocatalytic water splitting reactions are driven by light as well as the catalyst. As displayed in **Figure 44a**, the amount of H₂ produced by GCNN was 1050 $\mu\text{mol g}^{-1} \text{h}^{-1}$, about 3.2 times higher than bulk GCN (333 $\mu\text{mol g}^{-1} \text{h}^{-1}$). This enhanced photo-efficiency is mainly attributed to the increased surface area resulting from the separated and thin layers of GCNN, providing

more active sites to react at the surface of the catalyst. As for NiCeAl-LDH does not produce H_2 , probably due to the lack of absorption in this region. As for the hybrids, it is possible to see that the photoactivity of GCNN was further increased after assembling it with LDH. Although the photocatalytic performance depends on the LDH loading, with higher LDH loadings (3 and 7 wt.%), the photocatalytic activity was decreased, probably due to the shading effect.^{144, 210} The highest HER rate was obtained with the hybrid 1.5NiCeAl-LDH/GCNN, affording 2035 $\mu\text{mol g}^{-1} \text{h}^{-1}$, which was about 2 times higher than GCNN. The enhanced photocatalytic activity can thus be assigned to the improved visible light absorption, narrow bandgap, and synergistic effect established between both materials. The continuous H_2 production rate vs time of 1.5NiCeAl-LDH/GCNN catalyst (**Figure 44b**) indicated that activity increased quickly in the first minutes of irradiation. Then the activity continued to rise until a plateau rate achieved after almost 80 min.

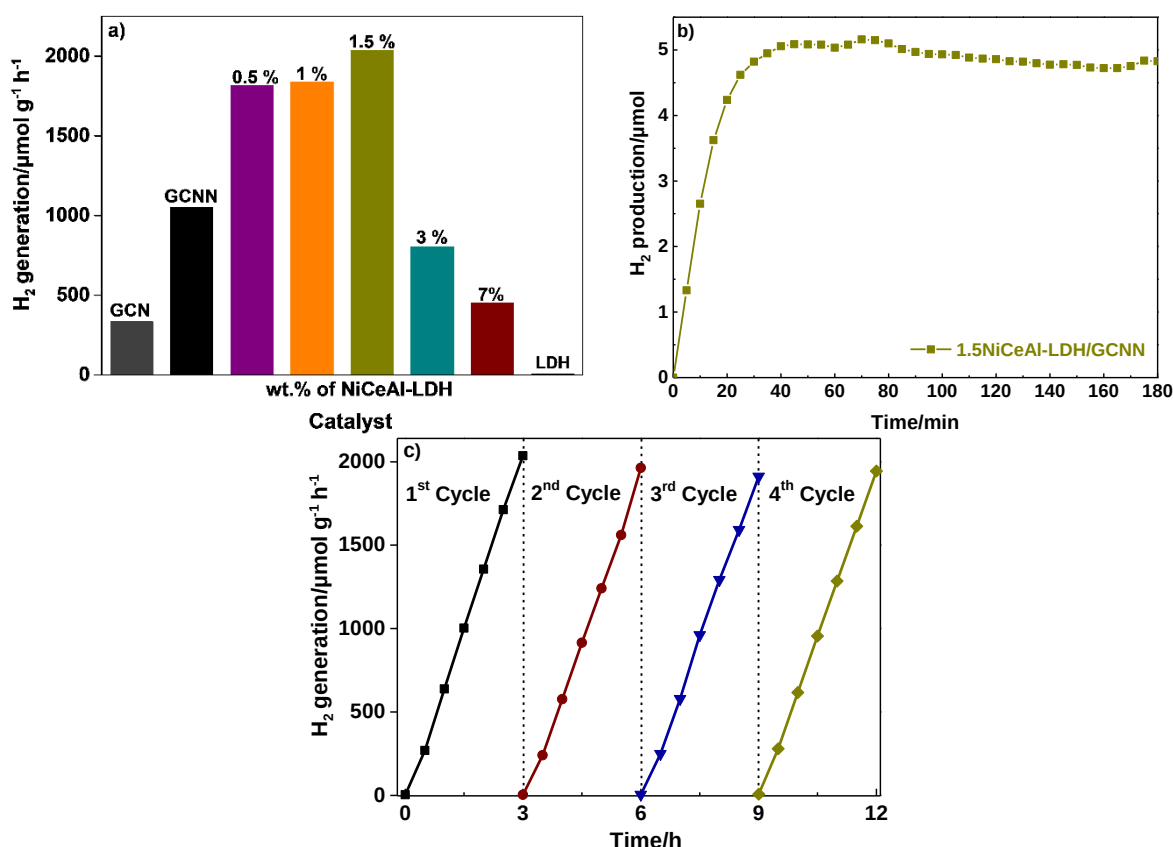


Figure 44. a) Photocatalytic H_2 production for GCN, GCNN, NiCeAl-LDH and xNiCeAl-LDH/GCNN composites under visible-LED irradiation, in the presence of EDTA and Pt. b) H_2 production profile for 1.5NiCeAl-LDH/GCNN catalyst after 3h of irradiation. c) Reusability test of 1.5NiCeAl-LDH/GCNN material for four cycles (3 h each).

The reusability and stability tests of the best-performing photocatalyst, 1.5NiCeAl-LDH/GCNN, were evaluated by reusing the photocatalyst four times under the same experimental conditions. As shown in **Figure 44c**, the hybrid shows high stability, with almost unchanged hydrogen produced during the 12 h of reaction.

5.1.4. Conclusions

2D/2D heterostructures of GCNN and NiCeAl-LDH were easily synthesised *via* electrostatic co-assembly of negatively charged GCNN and positively charged NiCeAl-LDH. The physicochemical techniques indicate the layered structure of both parent materials and suggest efficient interfacial contact. The formed heterostructure showed enhanced HER activity under visible light irradiation. The optimal NiCeAl-LDH loading is 1.5 wt.%, showing an H₂ rate 2-times higher than GCNN. Reusability tests of this material show high stability. This work provides a new insight to design heterostructure systems based on ternary LDH with exfoliated GCN as a high-performance photocatalyst for water splitting.

5.2. CuAl-LDH/GCN hybrids for photocatalytic H₂ and O₂ evolution

5.2.1. Introduction

The formation of LDH/GCN heterojunctions is gaining research interest as an alternative to overcome the limitations of the individual components, as mentioned above. Herein, we, for the first time, designed and synthesised 2D/2D CuAl-LDH/GCN heterostructures by coupling different wt.% of CuAl-LDH with exfoliated GCN through a simple electrostatic co-assembly impregnation method for photocatalytic water splitting. Furthermore, the photocatalytic H₂ generation under visible light irradiation was evaluated in the presence of a sacrificial agent but in the absence of cocatalyst. In addition, the O₂ formation was also assessed in these conditions, in the presence of TEOA and AgNO₃ as sacrificial agents.

5.2.2. Materials and Methods

5.2.2.1. Materials

All the materials used for the syntheses were obtained from different commercial suppliers and used without further purification. Dicyandiamide (DCN, 99%), aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O, ≥ 98%), N,N'-dimethylformamide (DMF, 98%), ethylenediaminetetraacetic acid (EDTA, ≥ 98%) and triethanolamine (TEOA, 99.8%) from Sigma-Aldrich. Copper nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99%) from EMSURE®. Urea (CH₄N₂O, 99.5%) from ACROS. Methanol (99.6%) from VWR. Deionised water (DI) and absolute ethanol from Chem-Lab NV. EDTA aqueous solution (0.2 M) was prepared in NaOH (0.5 M).

5.2.2.2. Catalyst preparation

Synthesis of graphitic carbon nitride nanosheets

The synthesis of GCN nanosheets was performed as described in section 5.1.2.2.

Synthesis of CuAl-LDH

The CuAl-LDH was obtained by a solvothermal method. Initially, a mixture of Cu (II) nitrate and Al (III) nitrate (molar ratio of 3:1) were suspended in 40 mL of ethanol. After, 1.5 M of aqueous urea solution was added to the metal mixture and continuously stirred for a given time. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 120 °C for 14 h. The obtained product was recovered by centrifugation, thoroughly and repeatedly washed with deionised water and ethanol, and then dried at 60 °C overnight. A light-blue colour powder was obtained.

Synthesis of CuAl-LDH/GCNN hybrids

To prepare CuAl-LDH/GCNN hybrids, a certain amount of GCNN and CuAl-LDH were separately dispersed in ethanol and DMF solutions, respectively, followed by ultrasonication for 30 min. Then, both solutions were mixed and sonicated further for another 30 min, followed by stirring for 6 hours at room temperature. Finally, the mixture solution was centrifuged, washed several times with water and ethanol, and dried at 60 °C overnight. The obtained products were denoted as xCuAl-LDH/GCNN, where x stands for the weight ratio of CuAl-LDH into GCNN (x = 0, 0.2, 1, 3, and 7 wt.%).

5.2.2.3. Photocatalytic experiments

Hydrogen evolution experiments were carried out in a 5 mL reactor equipped with a LED lamp light source emitting at 445 nm (Thorlabs) (**Figure 45**). In a single experiment, 0.5 g L⁻¹ of the catalyst containing 10% vol of TEOA as a sacrificial electron donor. The reactor was first purged with argon (flow rate of 100 mL min⁻¹, controlled with a mass flow controller from MCC-Instruments) to evacuate the system before starting the experiment properly. The temperature of the reactor was kept constant ($T = 15$ °C) through a water-cooling system (Lauda). The evolved H₂ gas was analysed with a GC-2030 (Shimadzu) instrument using a MICROPACKED-ST Column (ShinCarbon) and a Barrier discharge ionization detector (BID). The measurement was taken every hour. In addition, several blank experiments were performed under the same ambient conditions to confirm the evolution of H₂ gas without the photocatalyst. The quantum yield efficiency (QY) of the materials was calculated using Eq. (15):

$$\text{QY (\%)} = \frac{\text{Number of H}_2 \text{ molecules produced} \times 2}{\text{Number of incident light photons}} \times 100 \quad (15)$$

The oxygen evolution experiments were performed in a homemade side illumination closed reactor using the same light source and water-cooling system. The experiments were carried out using a 2 mL water solution containing 1 mg of a photocatalyst (dispersed *via* stirring) and AgNO₃ (0.01 M) as electron scavengers. The reactor was first purged with argon to remove the air, and the O₂ detection was started using a fibre-optic oxygen sensor (PyroScience) inserted in the reaction volume. Next, the suspension was stirred for 30 min in the dark to allow for O₂ signal stabilization followed by 1 h of visible-light illumination.

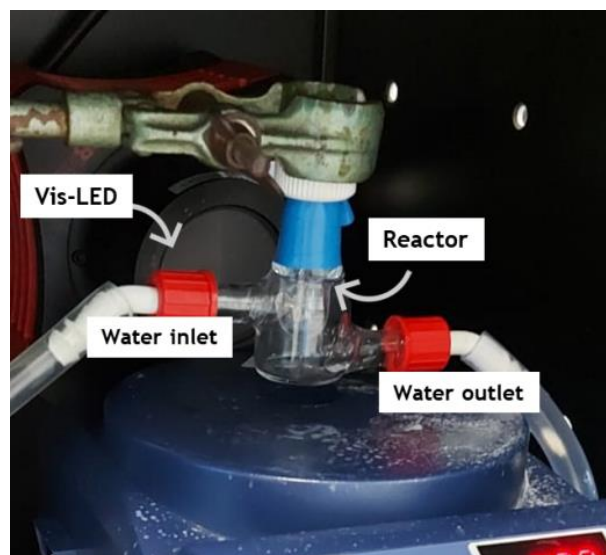


Figure 45. Photograph representation of the experimental setup used during photocatalytic HER reactions.

5.2.3. Results and discussion

5.2.3.1 Catalyst characterisation

The morphological properties of the individual and hybrid materials were first analysed by SEM and TEM, as shown in **Figure 46**. Pure CuAl-LDH seems to possess two primary morphologies: flower-like composed of irregular and randomly shaped layers, and slab-like resembling elongated multi-layered rods, being the latter dominant (**Figure 46a**). In addition, TEM images reveal the presence of thin layers (**Figure 46b**), indicative of the 2D nature of layered double hydroxides.³⁷⁶⁻³⁷⁸ As mentioned in part 5.1, the morphology of exfoliated GCNN shows a large number of thin 2D nanosheets arranged in irregular patterns (**Figure 46c, d**).

Zeta-potential measurements conducted for both CuAl-LDH and GCNN aqueous suspensions indicate a surface charge of +41.72 mV and –21.45 mV, respectively, at pH 7. These opposite charges of GCNN and CuAl-LDH indicate electrostatic interaction between both materials, which is beneficial for charge transfer. Therefore, it is expected that upon impregnation, the individual components are pulled together electrostatically, thus forming heterojunctions with proximate interfacial contact between them, favourable for charge transfer. TEM images of the 0.2CuAl-LDH/GCNN composite (**Figure 46f**) support the hypothesis that CuAl-LDH layers are indeed in close contact with GCNN sheets. EDX spectra further indicate the presence of Cu and Al elements in the hybrids (**Figure 47**). In the case of 7CuAl-LDH/GCNN, the slab-like morphology was also observed on the surface of GCNN (**Figure 46g, h**), in line with the XRD results discussed later.

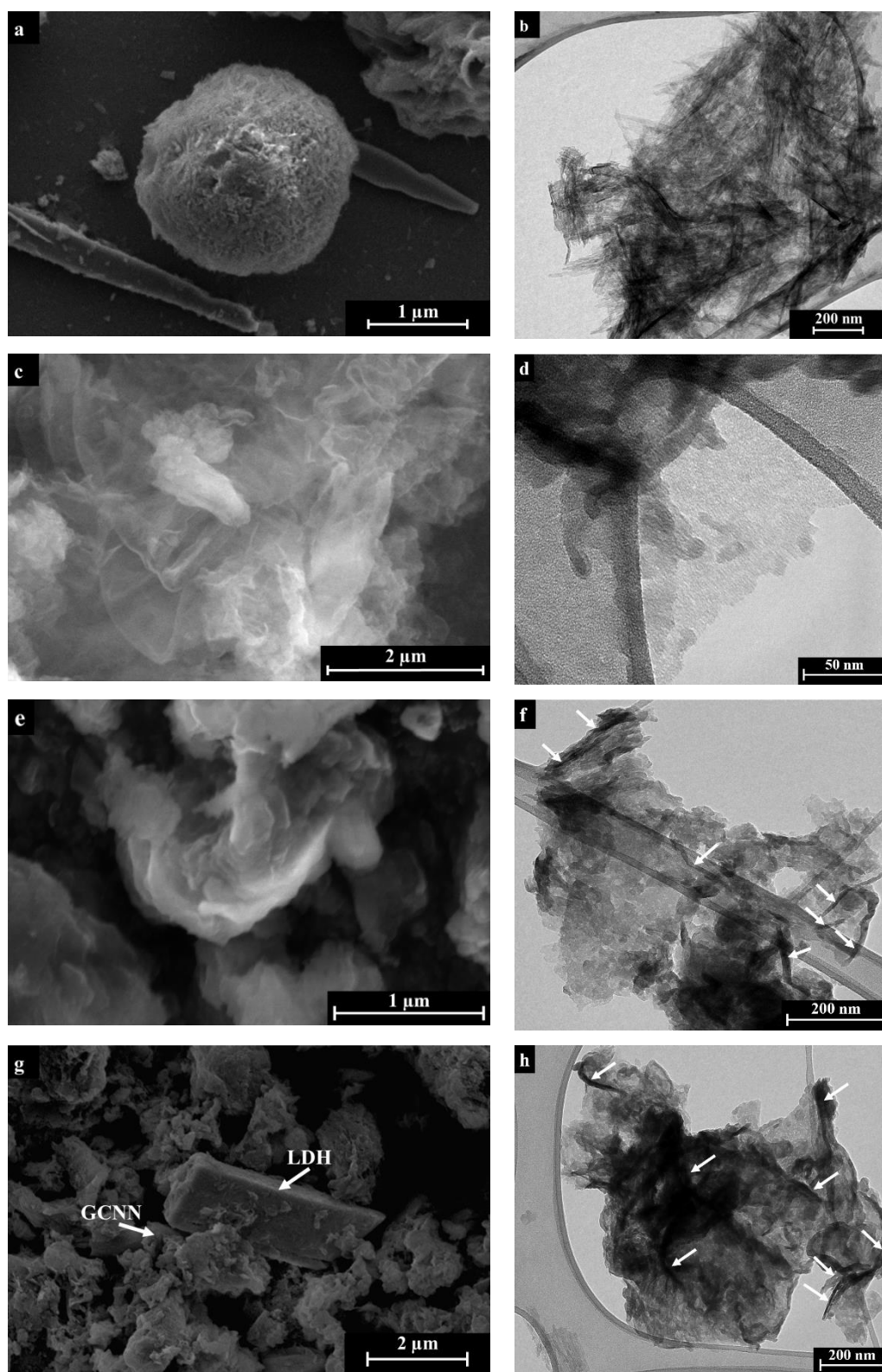


Figure 46. SEM (a, c, e, g) and TEM (b, d, f, h) images of CuAl-LDH, GCNN, 0.2CuAl-LDH/GCNN and 7CuAl-LDH/GCNN, respectively.

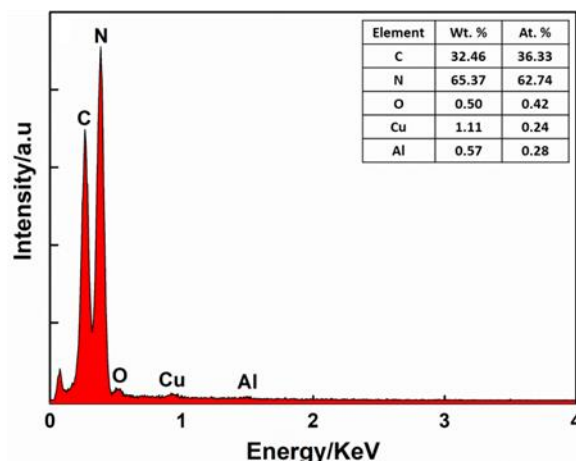


Figure 47. EDX spectrum of 7CuAl-LDH/GCNN hybrid.

The textural features of the samples were investigated through N₂ adsorption-desorption analysis at -196°C . The specific surface area, pore volume and pore size distribution values for GCNN, CuAl-LDH and xCuAl-LDH/GCNN are shown in **Table 10**. Overall, a decrease in the surface area values to around $100\text{ m}^2\text{ g}^{-1}$ was observed for the composites with higher ($\geq 1\text{ wt.}\%$) LDH contents compared to that of pristine GCNN ($150\text{ m}^2\text{ g}^{-1}$). However, the 0.2CuAl-LDH/GCNN hybrid is an exception as it exhibits a higher surface area ($222\text{ m}^2\text{ g}^{-1}$) and pore volume ($0.738\text{ cm}^3\text{ g}^{-1}$). The mechanism of the composite formation can explain these high values: apparently, intercalation of positively charged CuAl-LDH layers between the negatively charged GCNN sheets can restrict their re-stacking during the impregnation, which may result in the overall increase of the available surface. This also implies a potential synergy of the 0.2CuAl-LDH/GCNN heterojunction as it can have more active sites and thus promising photocatalytic performance.

Table 10. Textural properties (surface area, pore volume and size) and optical (bandgap energy) properties xCuAl-LDH/GCNN ($x = 0.2, 1, 3$ and 7) materials.

Materials	S_{BET} area ($\text{m}^2\text{ g}^{-1}$)	Micropore area ($\text{m}^2\text{ g}^{-1}$)	Pore volume ($\text{cm}^3\text{ g}^{-1}$)	Pore size (nm)	E_g (eV)
GCNN	150	18.18	0.638	13.03	2.77
CuAl-LDH	42	2.48	0.093	8.53	2.12
0.2CuAl-LDH/GCNN	222	19.80	0.738	12.38	2.70
1CuAl-LDH/GCNN	98	26.51	0.392	11.76	2.72
3CuAl-LDH/GCNN	105	13.92	0.380	10.83	2.74
7CuAl-LDH/GCNN	113	20.46	0.356	9.76	2.74

The N₂ isotherms and BJH pore size distribution curves of the samples are shown in **Figure 48**. The observed isotherm shapes and hysteresis behaviours can be assigned to type II and IUPAC-H3, respectively, indicating meso- and macroporous structures.³⁰⁴ This type of isotherm and hysteresis reflects the presence of non-rigid aggregation of plate-like particles,³⁰⁴ expected from the morphology of the composite components. These results can be further confirmed by the corresponding pore size distribution curves (**Figure 48**).

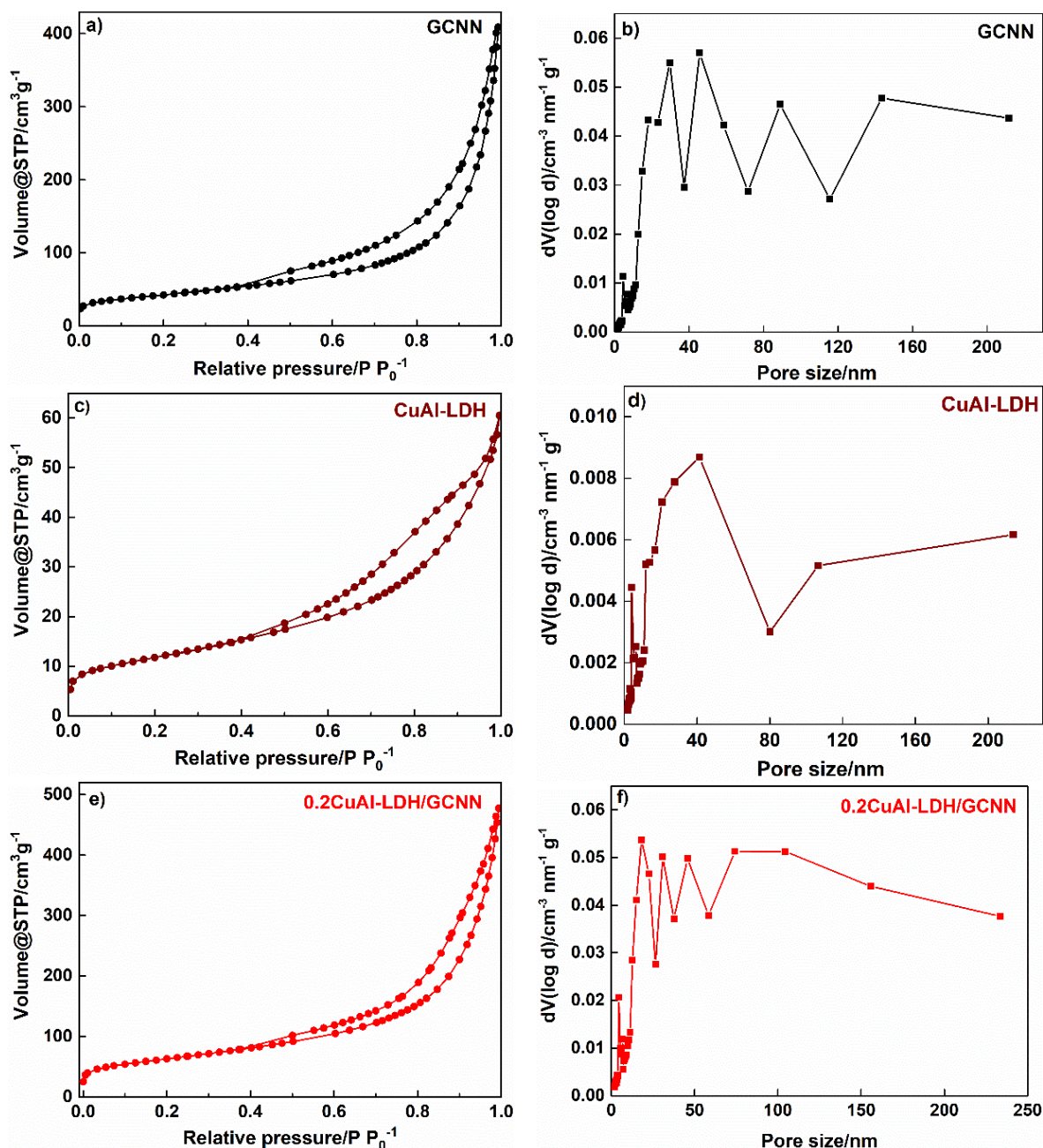


Figure 48. N₂ adsorption-desorption isotherms at –196 °C and BJH pore size distribution curves obtained from adsorption of a, b) GCNN; c, d) CuAl-LDH and e, f) 0.2CuAl-LDH/GCNN, respectively.

The crystallographic structure of the prepared materials was analysed by powder X-ray diffraction (XRD) (**Figure 49**). The as-prepared CuAl-LDH shows diffraction peaks at around 2θ values of 11.97° , 24.10° , 31.37° , 35.67° , 39.47° , 47.60° , 61.53° and 63.03° (associated with the diffraction planes (003), (006), (009), (012), (015), (018), (110) and (113), respectively), which are attributed to the LDH phase.^{377, 379-384} Minor amounts of impurities such as malachite, Cu(OH)₂ and Al₂O₃ – characteristic of the LDH synthesis – were also detected.^{377, 379-381} For the pristine GCNN, the prominent broad diffraction peaks were detected at 27.4° and 12.8° , corresponding to the (002) and (100) plans (as previously discussed in section 4.1.3).^{88, 333, 370} In the case of the composites, the diffraction patterns were similar to the pristine GCNN. However, for higher CuAl-LDH loadings, the diffraction peaks of the LDH appeared and became more intense for its higher loadings – in line with SEM/TEM results – which indicates the intact nature of the CuAl-LDH and GCNN in the resulting xCuAl-LDH/GCNN and confirms the formation of the nanohybrids.

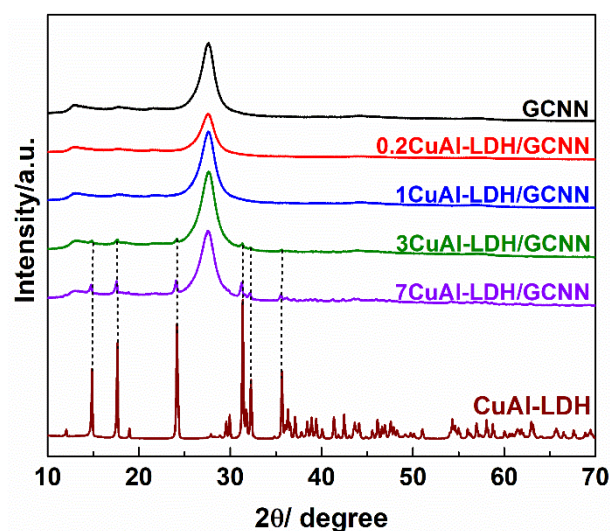


Figure 49. X-ray diffraction patterns of GCNN, CuAl-LDH and xCuAl-LDH/GCNN materials.

The information about the chemical structure of the prepared materials was obtained by ATR-FTIR measurement, as shown in **Figure 50**. The FTIR spectrum of pure GCNN shows the characteristic peaks of GCN, as previously discussed in section 5.1.3. The spectra of xCuAl-LDH/GCNN composites show similar characteristic bands of GCNN, due to the low weight wt.% of CuAl-LDH. On the other hand, the pristine CuAl-LDH shows absorption bands at around 3411 and 3305 cm^{-1} , which can be ascribed to the stretching mode of O–H vibration in the brucite-like layers and interlayer water.^{379-381, 385, 386} The two bands at 1507 and 1386 cm^{-1} are attributed to the antisymmetric vibrational mode of interlayer nitrate anions, and

the band around 1034 cm^{-1} is ascribed to the surface Cu–OH groups.³⁷⁹ The band at 870 cm^{-1} is assigned to the ν_2 mode of the nitrate ion, while the bands in the low-frequency fingerprint region below 800 cm^{-1} are attributed to the lattice vibrations of M–O, M–OH, O–M–O and M–O–M (where M is Cu, Al).^{379–381, 385, 386} Overall, the data indicate that the structure of the dominating GCNN was not affected by the composite formation, which goes in line with the electrostatic assembly model suggested before.

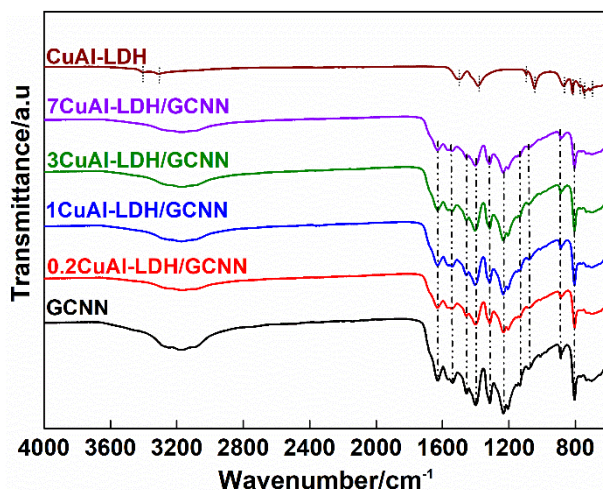


Figure 50. ATR-FTIR spectra of GCNN, CuAl-LDH and xCuAl-LDH/GCNN materials.

The surface chemical states of GCNN, CuAl-LDH, 0.2CuAl-LDH/GCNN and 7CuAl-LDH/GCNN were examined by X-ray photoelectron spectroscopy (XPS). The detailed Cu 2p spectrum of CuAl-LDH is shown in **Figure 51a**. The peaks located at 934.30 and 938.90 eV are attributed to Cu $2p_{3/2}$, accompanied by satellite bands at 941.80 and 944.42 eV, indicating Cu^{2+} state in the LDH layers.^{377, 387–389} As depicted in **Figure 51b**, the Al 2p spectrum possess a typical peak of Al $2p_{3/2}$ at 75.05 eV indicative of Al^{3+} cations.^{377, 390} The binding energies peaks of O 1s spectrum (532.35, 530.50 and 527.93 eV) are attributed to the adsorbed oxygen and lattice oxygen (**Figure 51c**).^{211, 391} These results confirm both Cu^{2+} and Al^{3+} cations in the prepared CuAl-LDH, as expected.

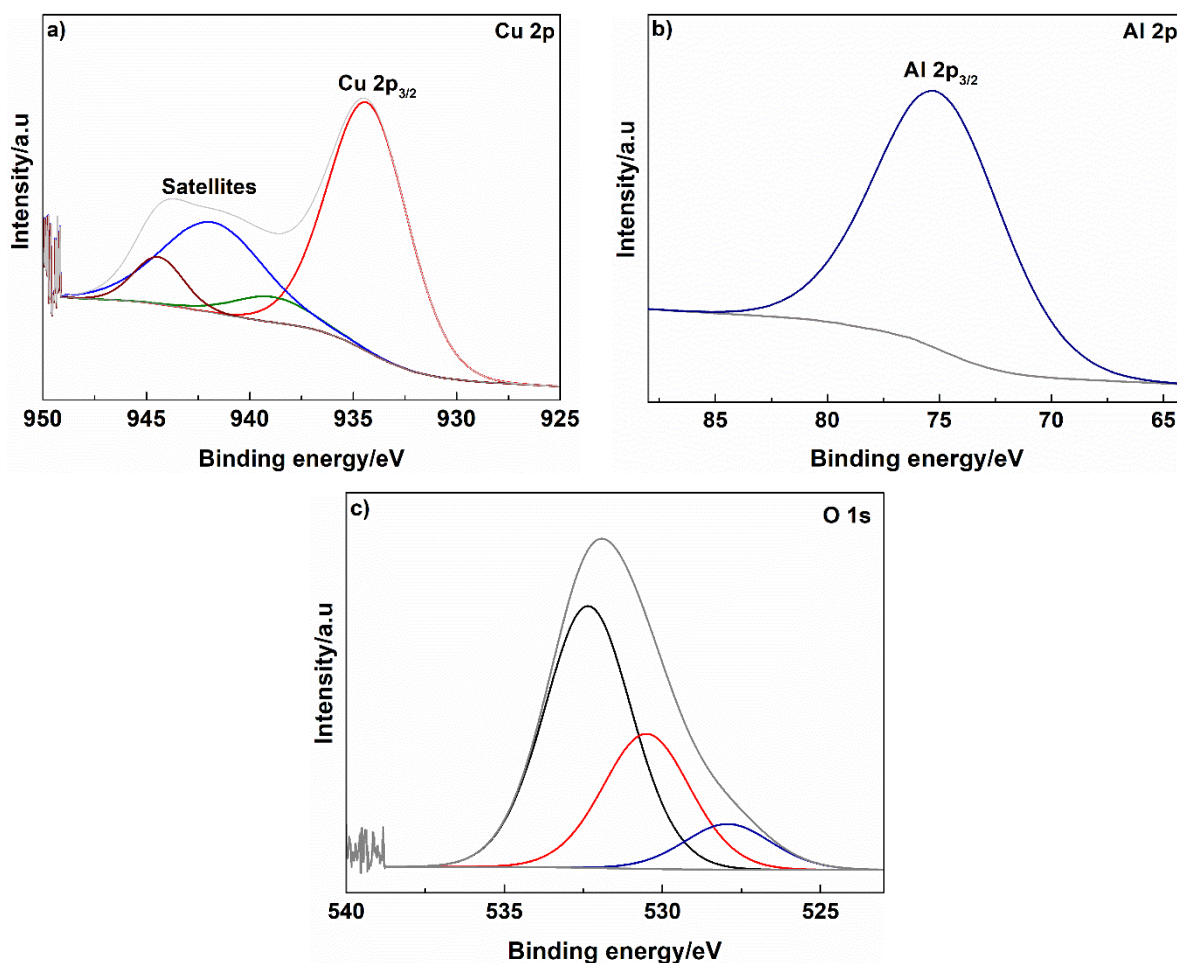


Figure 51. XPS spectra a) Cu 2p, b) Al 2p, and c) O 1s of CuAl-LDH.

No Cu or Al could be detected for the composites, probably due to the low amount of CuAl-LDH in the resulting materials. However, as an indirect indication for the composite formation, the atomic percentage of O increased from GCNN to 7CuAl-LDH/GCNN, which is likely related to the high O content of the loaded CuAl-LDH material (depicted from survey spectra; not shown). Survey spectra (not shown) of GCNN reveal C, N, and O, which corresponds to residual oxygen of adsorbed water.^{88, 115, 333, 392} The detailed spectra of C1s and N1s of GCNN, 0.2CuAl-LDH/GCNN and 7CuAl-LDH/GCNN are presented in **Figure 52a, b**. The C1s spectrum of GCNN shows three main peaks (C1, C2 and C3). The C1 peak at 284.39 eV belongs to the surface adventitious carbon (C–C bonds) or sp^2 -bonded carbon on the GCN surface.^{88, 115, 333, 392, 393} The C2 peaks located at 285.70 eV could be attributed to the aminated moieties (C–NH₂) and the sp^3 -coordinated carbon atoms characteristic of GCN defects.^{88, 115, 333, 392, 393} The C3 peak (287.66 eV) is assigned to the sp^2 -hybridised C atoms bonded to nitrogen (N=C–N) common for tri-s-triazine rings.^{88, 115, 333} The N1s spectrum of GCNN contains four peaks (N1, N2, N3 and N4). The predominant N1 peak located at

398.09 eV is ascribed to the sp^2 -hybridized aromatic nitrogen involved in the formation of triazine units (C–N=C). The peak at 399.41 eV (N2) is attributed to the tertiary N bonded to C atoms in the form of N–(C)₃. In addition, the peaks N3 and N4 located at 400.53 and 404.13 eV can be assigned to the amino groups (C–NH_x) and the N-oxides, respectively.^{88, 115, 333, 392-394}

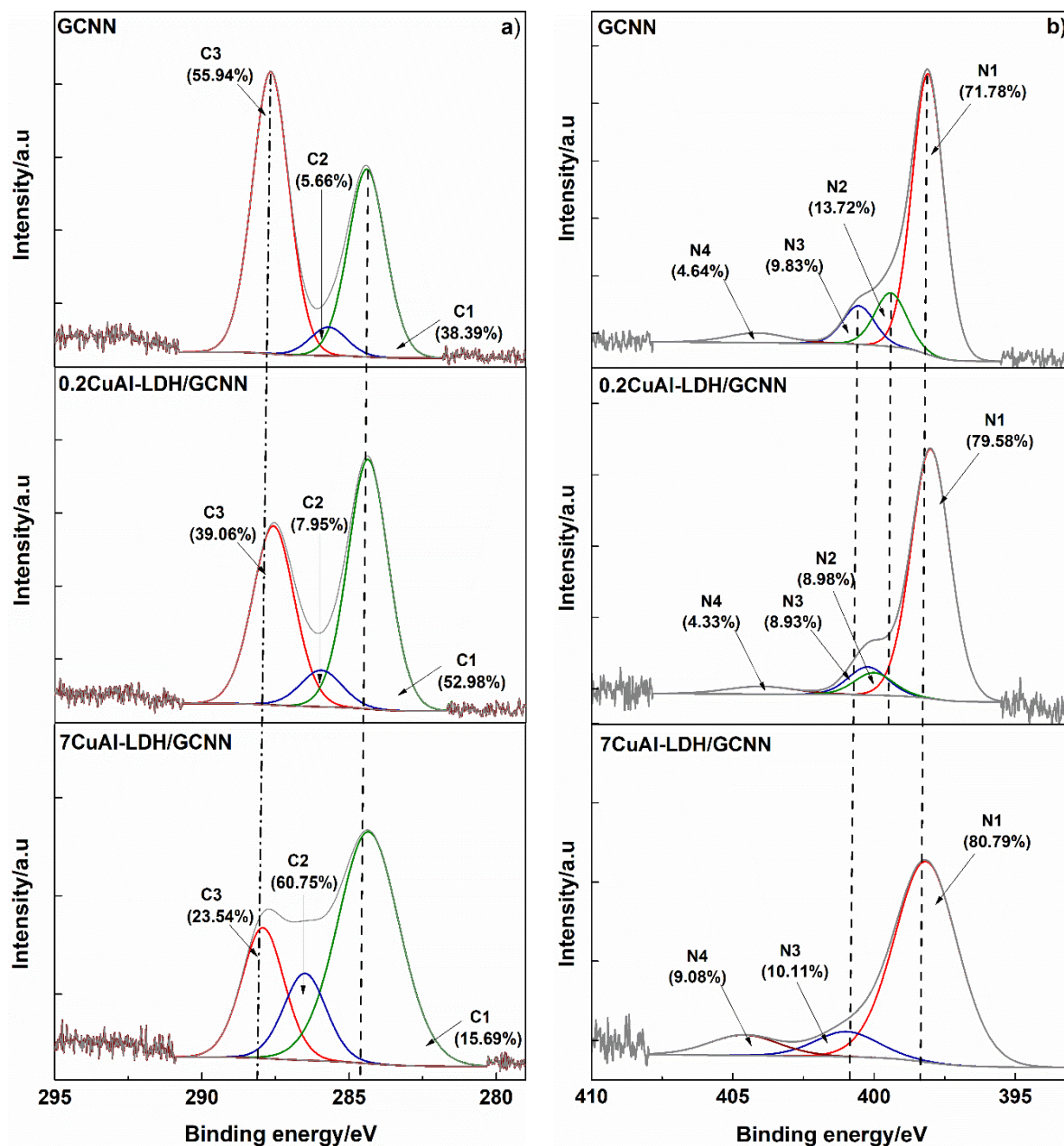


Figure 52. a) C1s and b) N1s XPS spectra of GCNN and xCuAl-LDH/GCNN materials (x = 0.2 and 7). The dashed lines indicate the shifted peaks.

The same C1s and N1s peaks were detected in the case of the composites. However, the position of these peaks clearly presents a shift to lower binding energies and a variation in the atomic contents, which suggest charge redistribution and surface chemistry modifications on the GCN.^{115, 333, 394, 395} Over and above, the N2 peak was not detected in the case of the 7CuAl-LDH/GCNN composite. This behaviour can be owed to (i) the overcharging of CuAl-LDH on the surface of GCNN and its interference with equipment readings, (ii) the shading effect that 7 wt. % LDH can have on the GCNN matrix or (iii) to the augmentation of N4 (at.%) peak, indicating that with higher LDH content, more N-oxide units are present, which leads to the N2 signal loss. These observations indicate that a certain degree of electronic interaction was established between GCNN and CuAl-LDH components.

The degree of absorption and the migration of light-induced e⁻/h⁺ of the material are important factors that control photocatalytic reactions. The optical absorption properties of all materials were studied by UV-Vis DRS, as illustrated in **Figure 53a**. The absorption spectrum of CuAl-LDH shows two strong absorption bands in the spectral region of 220-500 nm and 550-800 nm. The large band in the region 220-500 nm could be attributed to the ligand-to-metal charge transfer (LMCT), specifically to the O₂²⁻ → Cu²⁺ LMCT transitions, whereas the band from 550 to 800 nm might be related to d-d transitions attributed to the Cu²⁺ ions in the octahedral coordination typical of this LDH.^{389, 396, 397}

The optical absorption spectrum of GCNN displays an intrinsic semiconductor-like behaviour in the blue region of the visible range, with a band edge peaking at 450 nm, as previously mentioned.^{88, 115, 333} After loading CuAl-LDH into GCNN, all the composites exhibited a considerable absorption over the entire visible light range. Minor redshifts in the absorption edges were also detected and attributed to the electrostatic interactions established between both materials. The increased absorption capacity in the visible range may result in more photogenerated charge carriers available for photocatalytic reactions, resulting in enhanced photocatalytic activity.

The value of the bandgap energies (E_g) of the hybrids were calculated using the Tauc plot method *via* the intercept of the tangents of the $(\alpha h\nu)^{1/n}$ plots vs photon energy^{96, 366} as shown in **Figure 53b**. The n value of 2 was applied corresponding to the indirect transition model. The estimated bandgap values of GCNN, CuAl-LDH and the exemplary 0.2CuAl-LDH/GCNN were 2.77, 2.12 and 2.70 eV, respectively. These results suggest a considerable bandgap narrowing, indicating strong interactions between the GCNN and CuAl-LDH. The bandgap values of all prepared hybrids are summarised in **Table 10**.

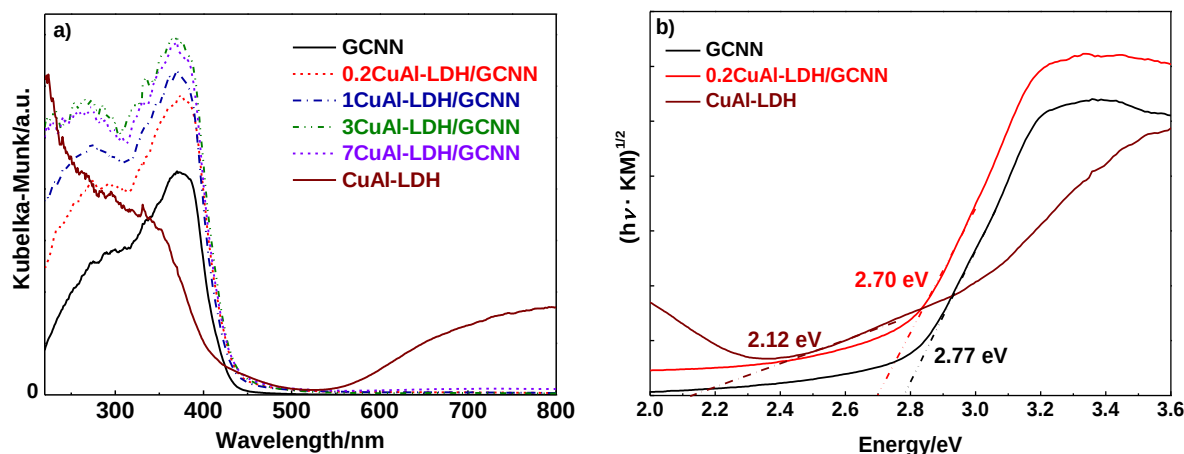


Figure 53. a) UV-Vis DRS GCNN, CuAl-LDH and xCuAl-LDH/GCNN materials; b) Tauc plot determination of GCNN, CuAl-LDH and 0.2CuAl-LDH/GCNN materials.

5.2.3.2 Photocatalytic water splitting

Next, the performance of all samples was investigated towards photocatalytic hydrogen evolution reaction (HER), while the most promising catalyst was also investigated for oxygen evolution reaction (OER). The reactions were carried out under visible-LED centred at 445 nm, in aqueous solutions of TEOA taking the role of the electron donor to facilitate HER and using AgNO₃ as an electron acceptor to evaluate OER. Blank tests show that no H₂ and O₂ were evolved in the absence of either light or catalyst, which validates our setup and confirms that the photocatalytic water splitting reactions are driven by light and the catalyst.

The H₂ evolution performance of the as-prepared materials (GCNN, CuAl-LDH, xCuAl-LDH/GCNN) is shown in **Figure 54a**. The results indicate that all the materials were active towards HER, even in the absence of any cocatalyst such as Pt. In these conditions, the H₂ evolution rate of as-prepared exfoliated GCNN and CuAl-LDH reached 1.65 and 1.14 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. Both values are much lower compared to the performance of the hybrids, which is in line with the rapid recombination of charge carriers in pristine GCNN and CuAl-LDH.^{197, 365} For the xCuAl-LDH/GCNN composites, the HER rate depends on the LDH loading in a volcano-type manner, with the highest H₂ amount of 54 $\mu\text{mol g}^{-1} \text{h}^{-1}$ obtained for the 0.2CuAl-LDH/GCNN, corresponding to a QY value of 0.0025%. This rate is up to 32- and 47-times higher than that of the individual GCNN and CuAl-LDH, respectively. The further increase of the wt.% CuAl-LDH results in a relative decrease in the H₂ evolution rate reaching as much as 9.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$ for the 7 wt.% LDH-loaded-GCN. As this rate is still significantly higher than that of the pristine GCNN, the overall decrease of HER efficiency for LDH loadings above 0.2 wt.% can in part be related to the shielding effect.^{144, 197, 398}

To find out the effect of different hole scavengers on the photocatalytic H₂ evolution rate for the 0.2CuAl-LDH/GCNN catalyst, three different sacrificial agents MeOH, TEOA, and EDTA were compared under identical reactions conditions (**Figure 54b**). The results indicate that TEOA provides the most efficient hole scavenging resulting in the highest H₂ generation rates. From the thermodynamic point of view, this can be related to the high TEOA redox potential (−3.4 eV), which facilitates a more effective hole extraction and thus separation of charge carriers.³⁹⁹ However, as the degradation of amino groups has been attributed to the photocorrosion of the conjugated g-C₃N₄ structure,^{400, 401} this difference in HER performance could also be attributed to the stabilizing effect of TEOA molecules that tend to anchor to the −NH₂ moieties, thus protecting them.³⁹⁹⁻⁴⁰¹

The dependence of H₂ generation on irradiation wavelength was assessed using a broadband Hg lamp equipped with a UV filter (emitted range is from 400 to 700 nm) and compared to the 445 nm LED (emitted range is from 410 to 490 nm). As presented in **Figure 54c**, the amount of H₂ produced by the 0.2CuAl-LDH/GCNN catalyst under the broadband visible light was 1.5-fold higher than the one generated under narrow-band illumination. As both activities are normalised to the activity of bare GCNN measured under identical illumination conditions, this result suggests that the 0.2CuAl-LDH/GCNN composite exhibits relatively stronger absorption at higher wavelengths (in line with DRS profiles in **Figure 53a**) and that this absorption results in additional excitons that contribute to the HER.

The best performing catalyst for HER (0.2CuAl-LDH/GCNN) and the neat catalysts (GCNN and CuAl-LDH) were also tested towards OER using the same light source (LED-445 nm) and the same catalyst concentration (0.5 g L^{−1}). As shown in **Figure 54d**, the three materials were active towards water oxidation. The OER rate of 0.2CuAl-LDH/GCNN heterostructure was 98.70 μmol g^{−1} h^{−1}, which is about 1.5-times higher than the pristine GCNN (66.57 μmol g^{−1} h^{−1}), likely attributed to its enhanced light absorption, and higher surface area. However, in the pure CuAl-LDH, the O₂ evolution rate was 117.55 μmol g^{−1} h^{−1}, slightly higher than the 0.2CuAl-LDH/GCNN composite. The higher activity of CuAl-LDH might be ascribed to its narrow bandgap (2.12 eV) and its band edge position, which favour OER, and the increased charge transfer owed to the presence of Cu²⁺ cations in the LDH lattice, forming Cu²⁺–O–Al³⁺ oxo-bridges,²²⁷ which might promote O₂ generation.

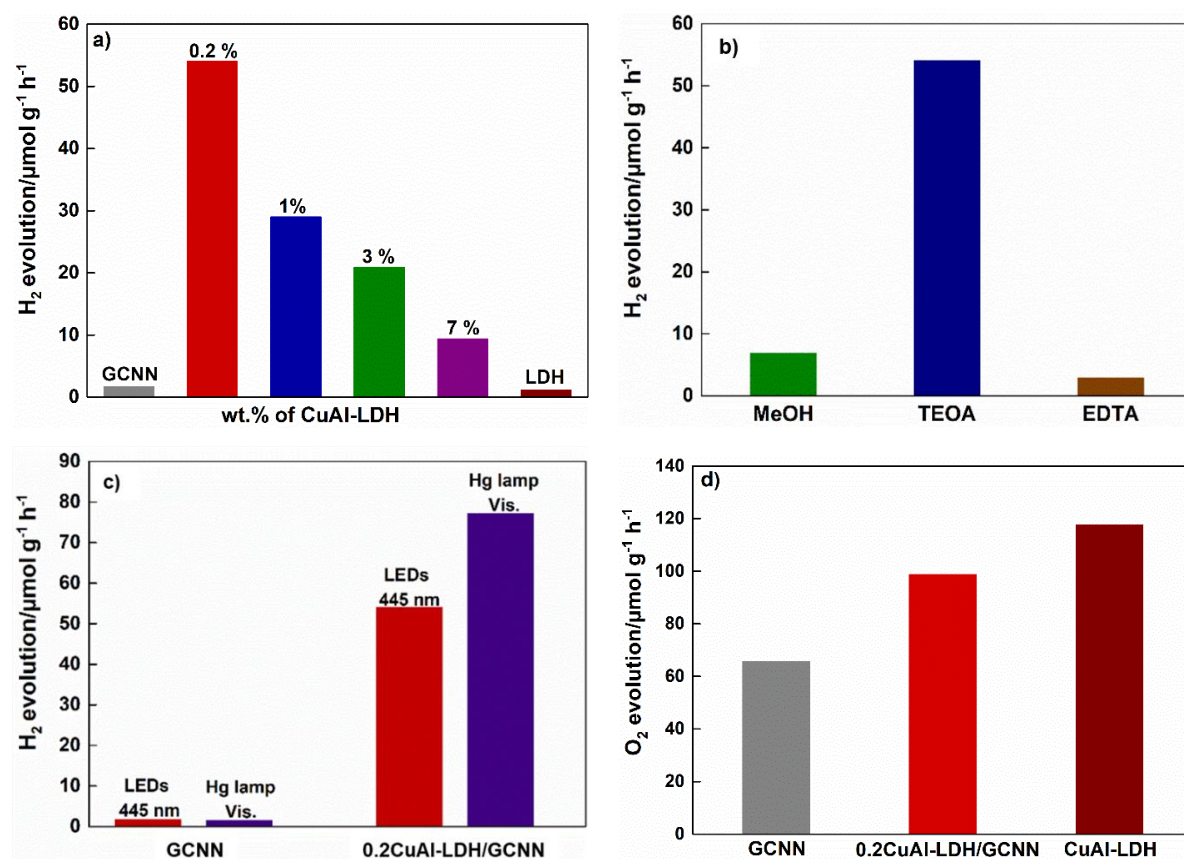


Figure 54. a) Photocatalytic H₂ generation rate for GCNN, CuAl-LDH and xCuAl-LDH/GCNN materials under visible-LED irradiation. b) Photocatalytic H₂ generation over 0.2CuAl-LDH/GCNN catalyst using different hole scavengers (MeOH, TEOA and EDTA (10% v/v)). c) Wavelength irradiation dependent H₂ evolution of GCNN and 0.2CuAl-LDH/GCNN catalysts in the presence of TEOA scavenger. d) OER evolution rate of GCNN, CuAl-LDH and 0.2CuAl-LDH/GCNN materials under visible-LED irradiation.

5.2.3.3. Charge carrier dynamics and photocatalytic mechanism

In order to unravel the dynamics of the charge carriers, their separation and recombination, steady-state and time-resolved photoluminescence (PL) measurements were carried out. The PL emission spectra of GCNN and xCuAl-LDH/GCNN nanohybrids were obtained upon excitation at 370 nm. As shown in

Figure 55a, the PL emission spectrum of GCNN exhibits a strong band centred at around 440 nm, which can be assigned to the band-to-band e^-/h^+ recombination of GCNN, as already explained in previous part 5.1.⁴⁰² For the composites, the PL intensity is quenched as compared to the pristine GCNN, suggesting that the charge recombination rate in the hybrids decreased. Moreover, a stronger PL quenching was observed in the xCuAl-LDH/GCNN composites for the higher loadings of CuAl-LDH, which means that it is highly effective at separating the

charges and suppressing their recombination. Besides this, a blueshift in the maximum wavelength of emission was observed for all the materials compared to GCNN, which indicates the active electronic communication between both materials. The enhanced visible light absorption, improved surface area and the suppression of photogenerated charge carriers are the main factors that define the superior photocatalytic activity of the composites.

To explain the non-linear HER dependency and elucidate the optimal LDH content in the materials, PL quenching factors were calculated (Eq. 16) from the maximum 440 nm emission drop normalised to the CuAl-LDH amount x in the corresponding x CuAl-LDH/GCNN samples.

$$\text{Relative quenching factor} = \frac{I_{\text{GCNN}} - I_{x\text{LDH}}}{I_{\text{GCNN}} \times \text{LDH wt.\%}} \quad (16)$$

Where I is the maximum PL intensity. When plotted against the CuAl-LDH loading (**Figure 55b**), a clear trend appears: the lowest CuAl-LDH content (0.2 wt. %) results in the strongest relative PL quenching; the more CuAl-LDH is present in the composite, the less pronounced is the relative effect of this heterojunction on the efficiency of charge separation. Considering that substantially high LDH loadings would additionally likely result in stronger shading effects, thus preventing efficient absorption by GCNN, an optimal amount of LDH in the composite lies below 1 wt. %, which explains the highest performance of the 0.2CuAl-LDH/GCNN composite.

The time-resolved emission measurements were further used to investigate the lifetimes of charge carriers in the most relevant samples. Deaerated aqueous solutions of GCNN and 0.2CuAl-LDH/GCNN were excited at 375 nm, and their emission decay curves were examined at the maximum emission wavelength of 451 nm. The obtained fluorescence lifetimes and their relative amplitudes are given in **Table 11**. According to the decay profiles shown in

Figure 55c, GCNN and 0.2CuAl-LDH/GCNN materials exhibit similar kinetics. The fitting of the decay curves yields four main components ($\tau_1, \tau_2, \tau_3, \tau_4$) as displayed in **Table 11**. It was found that for all components, the lifetimes of 0.2CuAl-LDH/GCNN were longer than those of GCNN, whereas the amplitude of component 4 increases, contrary to observed in components 1, 2 and 3. This might indicate the appearance of additional migration/trapping pathways for the photogenerated carriers in the composites.^{96, 198, 333} However, it is observed a strong PL quenching for the 0.2CuAl-LDH/GCNN in the steady-state experiments. The data suggest that a large portion of the charge carriers produced after the photoexcitation in GCNN (around 25%)

can be separated and extracted effectively at the heterojunction interface, which in turn leads to overall better utilisation of the photoexcited electrons.

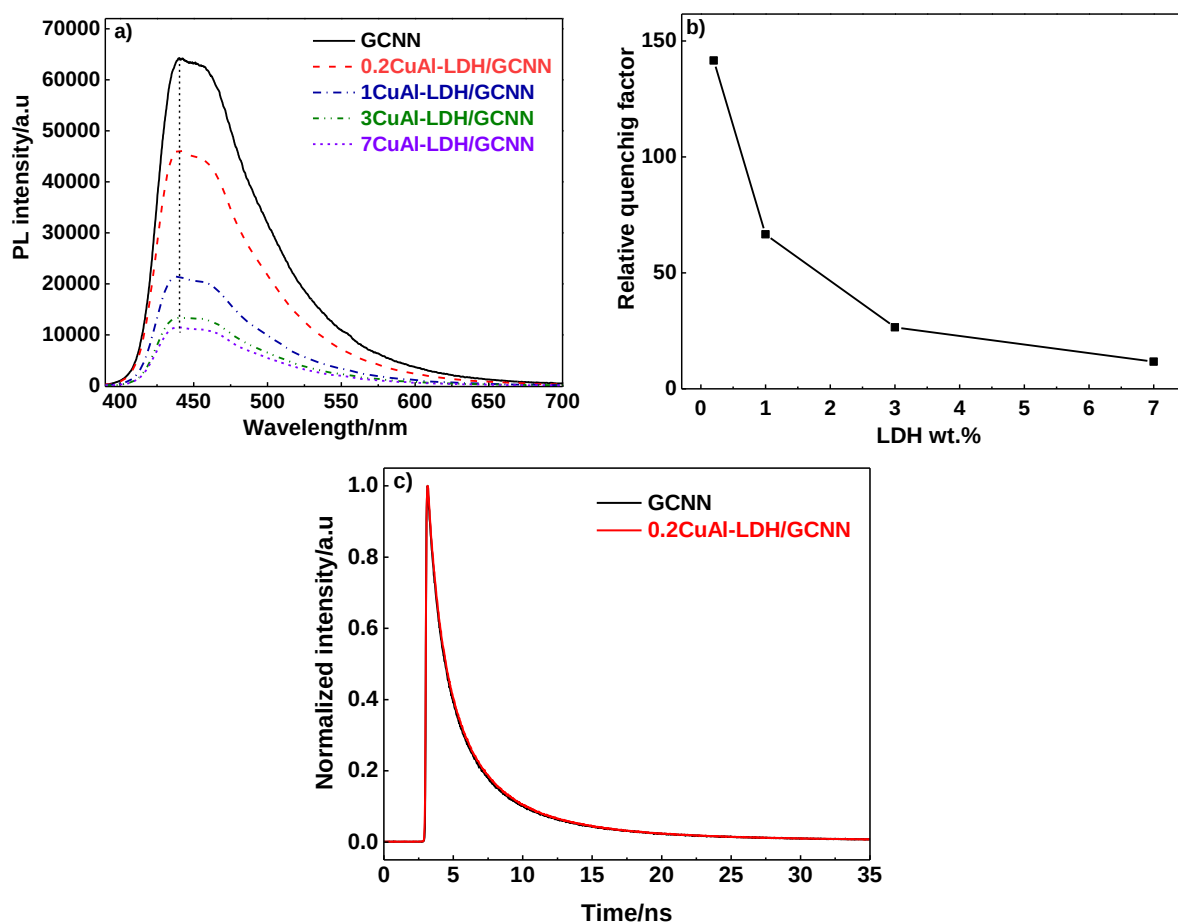


Figure 55. a) Solid steady-state PL spectra of GCNN and xCuAl-LDH/GCNN materials. b) Relative quenching factor vs wt.% of CuAl-LDH spectra of 0.2CuAl-LDH/GCNN materials. c) Fluorescence intensity decays of GCNN and 0.2CuAl-LDH/GCNN materials.

Table 11. Fluorescence lifetimes (τ_i , τ_{av}), normalised amplitudes (A_i) and chi-square (χ^2) of GCNN and 0.2CuAl-LDH/GCNN materials ($\lambda_{ex} = 375$ nm; $\lambda_{em} = 451$ nm).

Materials	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_3 (ns)	A_3 (%)	τ_4 (ns)	A_4 (%)	$\tau_{av.}$ (ns)	χ^2
GCNN	32.34	1.16	7.54	14.15	2.67	45.84	0.837	38.84	7.935	1.063
0.2CuAl/GCNN	33.32	1.06	7.77	13.31	2.823	45.21	0.890	40.39	7.869	1.040

Electrochemical properties of the prepared materials (GCNN, CuAl-LDH, 0.2CuAl-LDH/GCNN) were evaluated in a typical three-electrode system in an aqueous

0.1 M Na₂SO₄ solution as the electrolyte. The experiments were carried out in dark conditions. The linear sweep voltammetry (LSV) curves were recorded vs NHE to calculate the conduction band edge potential position (**Figure 56**). Considering the bandgap values of the materials obtained *via* Tauc plots, and based on the $E_{VB} = E_{CB} + E_g$ equation,¹⁹⁷ the valence band maximum (E_{VB}) values can be derived. For the pure GCNN, the value of the CB edge is -0.85 V and, since the bandgap energy is 2.77 eV, the VB is estimated to be +1.92 V. In the case of CuAl-LDH, the onset potential for CB was observed to be -0.52 V. The VB is calculated to be +1.6 V. Concerning the 0.2CuAl-LDH/GCNN material, the conduction band edge potential (E_{CB}) was measured to be -0.69 V, and the valence band maximum is estimated to be +2.01 V (E_{VB}). The CB and VB positions of 0.2CuAl-LDH/GCNN are thus located at a more negative reduction and more positive oxidation potentials with respect to proton reduction and water oxidation levels, respectively, which confirms the thermodynamic possibility to drive both half-reactions of water splitting.

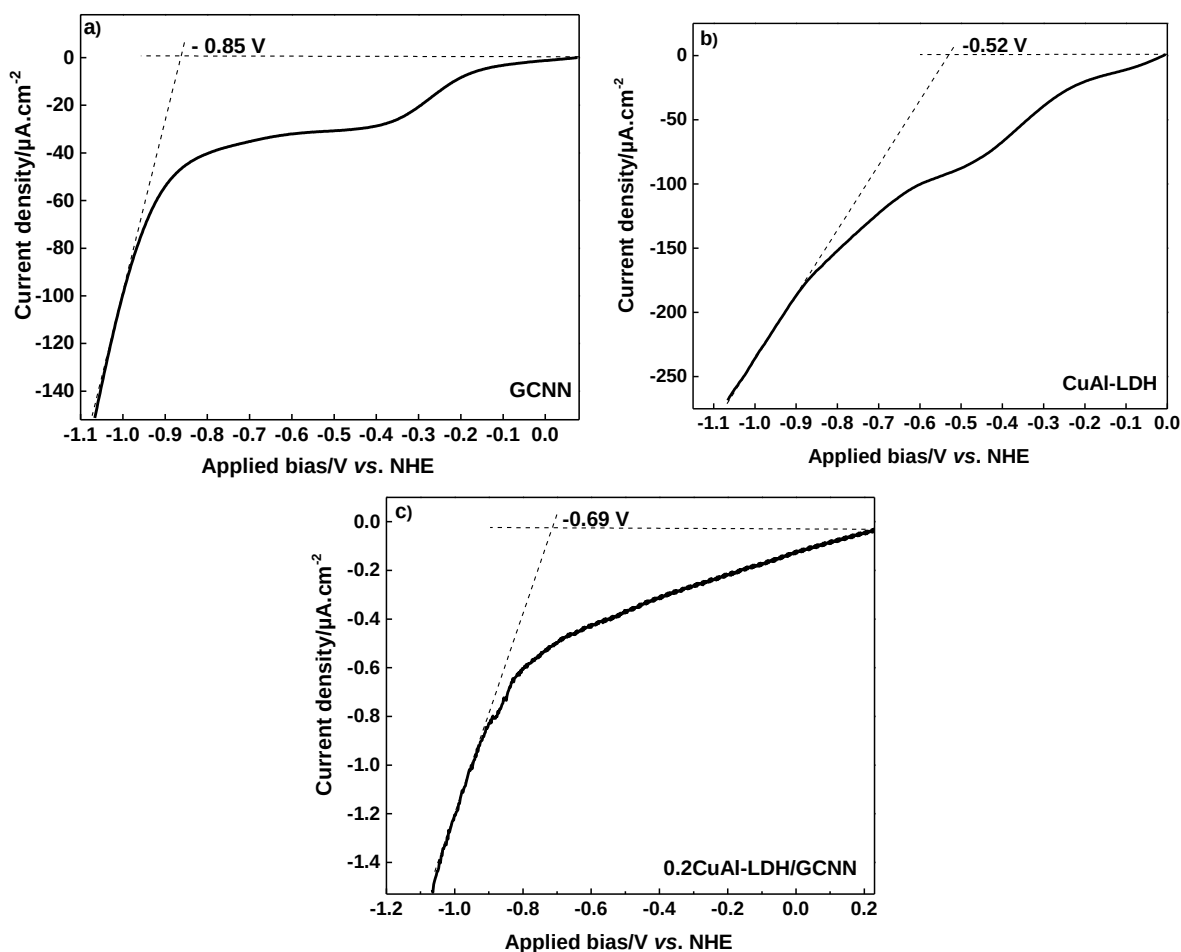


Figure 56. Current potential curves of a) GCNN, b) CuAl-LDH, and c) 0.2CuAl-LDH/GCNN materials in dark conditions.

Based on the band positions of GCNN and CuAl-LDH materials, the charge transfer mechanism for photocatalytic water splitting can be proposed (**Figure 57**). Under visible light irradiation, both GCNN and CuAl-LDH can be excited and generate e^-/h^+ pairs. Since the CB edge of GCNN (-0.85 V) is more negative than the CB edge of CuAl-LDH (-0.52 V), the photoexcited electrons of GCNN are directly transferred into the CB of LDH, which restricts their annihilation. Based on the higher HER rates of the composites, these electrons can migrate to the CuAl-LDH surface and be involved in the H₂ generation reaction. In other words, the CuAl-LDH serves as a sink for the photoexcited electrons, while its surface further facilitates the H⁺ reduction reaction. The VB edge potential of GCNN (+1.92 V) is more positive than the VB edge potential of CuAl-LDH (+1.60 V). When the photoexcited holes are generated in the VB of GCNN, they can directly migrate to the VB of CuAl-LDH – as it lies at a higher potential – and react with water molecules promoting the water-splitting reaction and generating O₂.

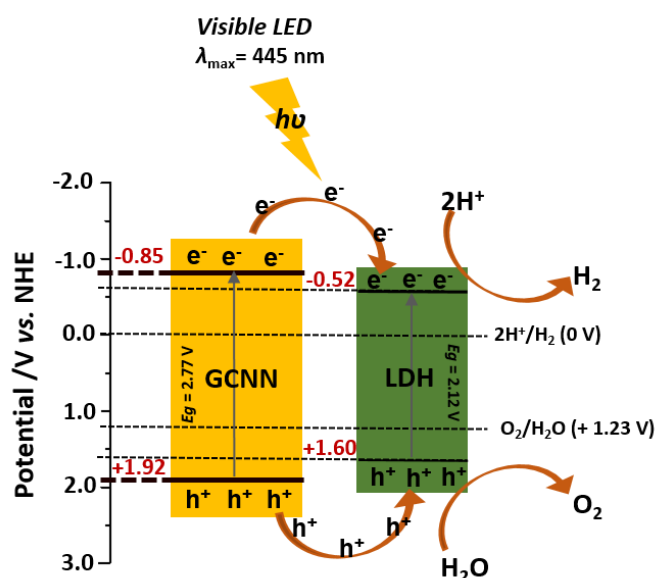


Figure 57. Proposed mechanism for water splitting over CuAl-LDH/GCNN under visible-light irradiation (type I heterojunction).

5.2.4. Conclusions

The development of a novel series of 2D/2D based photocatalysts achieved *via* electrostatic co-assembly of positively charged CuAl-LDH (0.2-7 wt.%) and negatively charged GCNN sheets was successful. Morphology, chemical structure, and optical and electronic properties of the nanohybrids were comprehensively studied by advanced physicochemical techniques, followed by their evaluation towards visible-light-driven photocatalytic water splitting half-reactions. Electron microscopy (TEM/SEM) confirmed the layered structure of both parent

materials and suggested the proximity of the components in the final nanocomposites. Spectroscopic data (IR/XPS) suggested a largely intact chemical structure of the major GCNN component but indicated a certain degree of electronic interaction between GCNN and CuAl-LDH. Following this, optical spectroscopy (UV-Vis) revealed enhanced visible light absorption and narrower bandgaps of the heterostructure (Tauc plots). Electrochemical studies (LSV) further confirmed the thermodynamic possibility of the composite to drive both half-reactions of water splitting. Optimal photocatalytic rates were achieved for the 0.2CuAl-LDH/GCNN composite that displayed the highest surface area (BET) and generated 32- and 1.5-times more H₂ and O₂ than pristine GCNN, respectively. In-depth studies of the formed nanohybrids using steady-state and time-resolved PL indicated a strong suppression of the e⁻/h⁺ recombination, which is considered to be the main contribution to the observed enhancements.

Chapter 6

Summary and future work

This chapter reviews the major findings of the described research. The aim and objectives of the study, outlined earlier, are reviewed, and their achievement addressed. Suggestions for future work are also included as intended guidelines for exploring new vectors in the field.

6.1 Summary

In the present Thesis, several modifications to graphitic carbon nitride ($\text{g-C}_3\text{N}_4$, GCN) semiconductor were performed to improve its photocatalytic performance towards H_2 and O_2 generation through water splitting. Selected 2D materials, mainly layered double hydroxides (LDH) and graphene-based materials, were prepared and coupled with GCN and tested under visible LED irradiation. The materials were prepared to take into account the sustainability and eco-friendliness of the synthesis process using earth-abundant precursors (*e.g.*, DCN), non-heavy metals and appropriate solvents (such as water and ethanol). In addition, the use of an LED system as a light source allowed to reduce the energetic input required to facilitate photocatalyst activation and, thus, a decrease in the ecological impact of the overall process. All synthesised materials were thoroughly characterised by different techniques to rationalise the photocatalytic activity with the structure and optical properties of the materials. The following are the major outcomes of this Thesis.

- i. One way to improve the photocatalytic performance of bulk $\text{g-C}_3\text{N}_4$ (GCN) was to assemble it directly with few-layer graphene (FLG), a metal-free carbon-based material, to obtain 2D/2D heterostructures. The GCN/FLG heterostructures displayed higher visible-light-driven photocatalytic H_2 generation dependent on the FLG morphology and loading. The FLG acted as a conductive material and electron sink capable of separating the electron/hole pairs and accelerating charge transfer at the interface, thus preventing recombination. EDTA was used as the sacrificial agent and Pt as cocatalyst. Both were found to be indispensable for H_2 generation. The recovery and reuse of catalyst is an essential factor in heterogeneous photocatalysis. Therefore, reutilisation runs of the best performing catalyst presented high stability after four successive cycles with no significant change in its activity.
- ii. The thermal exfoliation of bulk GCN resulted in a nanosheets-like material (GCNN) with relatively high surface area and thin-layered structure, leading to enhanced photocatalytic efficiency.
- iii. In a different approach, $\text{g-C}_3\text{N}_4$ nanosheets (GCNN) were assembled with LDH materials to obtain 2D/2D heterostructures that revealed outstanding performance as photocatalysts in water reduction to generate hydrogen. The layered nature of both components and the intimate contact between the interfaces during the synthesis made them excellent photocatalysts under visible light irradiation. Two types of LDH have been employed, one composed of three metals (NiCeAl-LDH) and the other with two metals

(CuAl-LDH). The effect of loading in the photoactivity was evaluated in both cases, as well as the influence of cocatalyst and sacrificial agents.

- iv. Regarding the NiCeAl-LDH/GCNN heterostructure, it was found that with low loading of LDH (1.5wt.%), the photocatalytic activity towards H_2 generation was improved 2 times compared to the pristine GCNN, in the presence of Pt as cocatalyst and EDTA as hole scavenger. In contrast, the photocatalytic activity of CuAl-LDH/GCNN towards H_2 generation was enhanced 32 times as compared to GCNN in absence of a cocatalyst. This might be due to the electronic structure, the metal types, the molar ratio of the LDH used, and the interaction of these LDH with the GCNN matrix. Moreover, the experimental conditions and the type of sacrificial agent were different, affecting the obtained results.
- v. Reutilisation runs were also assessed for NiCeAl-LDH/GCNN heterostructure, and once again, good stability was obtained.
- vi. Different hole scavengers were studied (MeOH, TEOA and EDTA) for CuAl-LDH/GCNN heterostructures under visible-LED irradiation. It was found that TEOA presents the best activity due to its redox potential and stability.
- vii. The CuAl-LDH/GCNN heterostructures were tested towards O_2 evolution and showed better performance, being 1.5 times higher than pristine GCNN. Furthermore, CuAl-LDH also presents interesting values of O_2 generation ($120 \mu\text{mol g}^{-1} \text{h}^{-1}$), being for the first time investigated for this reaction which highlights its use for more photocatalytic applications. This enhancement was attributed to the excellent charge carrier transfer and separation, enhanced light absorption, appropriate band edges position and high surface area.

All the results suggest that the prepared materials can be considered as an excellent option to tune the photoactivity of g- C_3N_4 for photocatalytic water splitting. Consolidating all the previous topics, it is possible to expect proficient prospects of these smartly engineered heterostructures for further photocatalytic applications.

6.2 Future work

- Considering the financial costs and from an environmental point of view, it would be interesting to replace the use of noble metals such as platinum (cocatalyst) with molybdenum disulphide (MoS_2).

- It is known that exfoliation is an excellent process to obtain materials with ultrathin and separated layers, generating materials with high surface area, extended light-harvesting

ability, and enhanced separation of charge carriers as compared to their bulk counterparts. Therefore, the exfoliation effect on the formation of 2D/2D heterostructures could be envisaged towards photocatalytic water splitting.

- Based on some preliminary results (not shown), the LDH materials have shown some promising activity towards H_2 and O_2 production. However, further investigation into preparation and modification methods could tune the properties of these materials in order to enhance their activity.

- Some theoretical kinetic modelling could be performed to understand the recombination rate during heterostructure creation.

- The type of materials developed within this Thesis could also be applied for other photocatalytic applications such as CO_2 reduction and water electrolysis.

- The need to move from laboratory-scale research to pilot plant and industrial-scale processes is another challenge for photocatalysis heterojunction system for H_2 generation technologies. Parameters such as reactor size, light source dispersion, catalyst loading, and recovery have to be further explored to reach the industrial H_2 production level.

References

1. Smalley, R. E., Future global energy prosperity: The terawatt challenge, *MRS Bull.*, 30 (2005) 412-417.
2. Jianping, L.; Minrong, L.; Jinnan, W.; Jianjian, L.; Hongwen, S.; Maoxing, H., Global environmental issues and human wellbeing, in: Report on global environmental competitiveness (2013), Springer Berlin Heidelberg, Berlin, Germany, 2014.
3. International Energy Outlook: 2021, U.S. Energy Information Administration. <http://www.eia.gov>. (accessed on 18th November 2021).
4. Olah, G. A., Beyond oil and gas: The methanol economy, *Angew. Chem. Int. Ed.*, 44 (2005) 2636-2639.
5. Muradov, N. Z.; Veziroğlu, T. N., “Green” path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies, *Int. J. Hydrog. Energy*, 33 (2008) 6804-6839.
6. Abbasi, T.; Abbasi, S. A., Decarbonization of fossil fuels as a strategy to control global warming, *Renew. Sustain. Energy Rev.*, 15 (2011) 1828-1834.
7. Hejazi, R., Nuclear energy: Sense or nonsense for environmental challenges, *Int. J. Sustain. Built Environ.*, 6 (2017) 693-700.
8. Robert Foster, M. G., Alma Cota, Solar energy: Renewable energy and the environment, CRC Press, New York, USA, 2009
9. Mohtasham, J., Review article-renewable energies, *Energy Procedia*, 74 (2015) 1289-1297.
10. Andrews, J.; Shabani, B., Where does hydrogen fit in a sustainable energy economy?, *Procedia Eng.*, 49 (2012) 15-25.
11. Rhodes, C. J., Solar energy: principles and possibilities, *Sci. Prog.*, 93 (2010) 37-112.
12. Ravikrishnan, V.; Giridhar, M., Renewable energy via photocatalysis, *Curr. Org. Chem.*, 17 (2013) 2538-2558.
13. Hosseini, S. E.; Wahid, M. A., Hydrogen production from renewable and sustainable energy resources: Promising green energy carrier for clean development, *Renew. Sustain. Energy Rev.*, 57 (2016) 850-866.
14. Bockris, J. O. m., *Energy: The solar-hydrogen alternative*, Halsted Press, New York, USA, 1975.
15. Møller, K. T.; Jensen, T. R.; Akiba, E.; Li, H.-w., Hydrogen - A sustainable energy carrier, *Prog. Nat. Sci.*, 27 (2017) 34-40.

16. Transforming Our World: The 2030 Agenda for Sustainable Development. UN General Assembly: 2015.
17. Safari, F.; Dincer, I., A review and comparative evaluation of thermochemical water splitting cycles for hydrogen production, *Energy Convers. Manage.*, 205 (2020) 112182.
18. Jing, D.; Guo, L.; Zhao, L.; Zhang, X.; Liu, H.; Li, M.; Shen, S.; Liu, G.; Hu, X.; Zhang, X.; Zhang, K.; Ma, L.; Guo, P., Efficient solar hydrogen production by photocatalytic water splitting: From fundamental study to pilot demonstration, *Int. J. Hydrog. Energy*, 35 (2010) 7087-7097.
19. Kudo, A., Photocatalysis and solar hydrogen production, *Pure Appl. Chem.*, 79 (2007) 1917-1927.
20. Maitra, U.; Lingampalli, S. R.; Rao, C. N. R., Artificial photosynthesis and the splitting of water to generate hydrogen, *Curr. Sci*, 106 (2014) 518-527.
21. Cox, N.; Pantazis, D. A.; Neese, F.; Lubitz, W., Artificial photosynthesis: Understanding water splitting in nature, *Interface Focus*, 5 (2015) 20150009.
22. Li, R.; Li, C., Chapter One - Photocatalytic water splitting on semiconductor-based photocatalysts, in: *Advances in Catalysis*, Academic Press, Inc., New York, USA, 2017.
23. Maeda, K., Photocatalytic water splitting using semiconductor particles: History and recent developments, *J. Photochem. Photobiol. C*, 12 (2011) 237-268.
24. Wang, Z.; Li, C.; Domen, K., Recent developments in heterogeneous photocatalysts for solar-driven overall water splitting, *Chem. Soc. Rev.*, 48 (2019) 2109–2125.
25. Tee, S. Y.; Win, K. Y.; Teo, W. S.; Koh, L.-D.; Liu, S.; Teng, C. P.; Han, M.-Y., Recent progress in energy-driven water splitting, *Adv. Sci.*, 4 (2017) 1600337.
26. Teoh, W. Y.; Scott, J. A.; Amal, R., Progress in heterogeneous photocatalysis: From classical radical chemistry to engineering nanomaterials and solar reactors, *J. Phys. Chem. Lett*, 3 (2012) 629-639.
27. Ran, J.; Zhang, J.; Yu, J.; Jaroniec, M.; Qiao, S. Z., Earth-abundant cocatalysts for semiconductor-based photocatalytic water splitting, *Chem. Soc. Rev.*, 43 (2014) 7787-7812.
28. Teichner, S. J., The origins of photocatalysis, *J. Porous Mater.*, 15 (2008) 311-314.
29. Eibner, A., Action of light on pigments I, *Chem. Ztg.*, 35 (1911) 753-755.
30. Barry, T. I.; Stone, F. S.; Tompkins, F. C., The reactions of oxygen at dark and irradiated zinc oxide surfaces, *Proc. Math. Phys. Eng. Sci.*, 255 (1960) 124-144.
31. Fujishima, A.; Honda, K., Electrochemical photolysis of water at a semiconductor electrode, *Nature*, 238 (1972) 37-38.

-
32. Kudo, A.; Miseki, Y., Heterogeneous photocatalyst materials for water splitting, *Chem. Soc. Rev.*, 38 (2009) 253–278.
 33. Wang, H.; Zhang, L.; Chen, Z.; Hu, J.; Li, S.; Wang, Z.; Liu, J.; Wang, X., Semiconductor heterojunction photocatalysts: Design, construction, and photocatalytic performances, *Chem. Soc. Rev.*, 43 (2014) 5234–5244.
 34. Chen, X.; Shen, S.; Guo, L.; Mao, S. S., Semiconductor-based photocatalytic hydrogen generation, *Chem. Rev.*, 110 (2010) 6503–6570.
 35. Li, X.; Yu, J.; Jaroniec, M., Hierarchical photocatalysts, *Chem. Soc. Rev.*, 45 (2016) 2603–2636.
 36. Ganguly, P.; Harb, M.; Cao, Z.; Cavallo, L.; Breen, A.; Dervin, S.; Dionysiou, D. D.; Pillai, S. C., 2D nanomaterials for photocatalytic hydrogen production, *ACS Energy Lett.*, 4 (2019) 1687–1709.
 37. Bhosale, R.; Tonda, S.; Kumar, S.; Ogale, S. B., 7 - Two-dimensional materials for photocatalytic water splitting and CO₂ reduction, in: *Nanostructured Photocatalysts*, Elsevier, Edinburgh, UK, 2020.
 38. Li, Y.; Li, Y.-L.; Sa, B.; Ahuja, R., Review of two-dimensional materials for photocatalytic water splitting from a theoretical perspective, *Catal. Sci. Technol.*, 7 (2017) 545–559.
 39. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A., Electric field effect in atomically thin carbon films, *Science*, 306 (2004) 666–669.
 40. Liu, G.; Zhen, C.; Kang, Y.; Wang, L.; Cheng, H.-M., Unique physicochemical properties of two-dimensional light absorbers facilitating photocatalysis, *Chem. Soc. Rev.*, 47 (2018) 6410–6444.
 41. Sumesh, C. K.; Peter, S. C., Two-dimensional semiconductor transition metal based chalcogenide based heterostructures for water splitting applications, *Dalton Trans.*, 48 (2019) 12772–12802.
 42. Qin, D.; Zhou, Y.; Wang, W.; Zhang, C.; Zeng, G.; Huang, D.; Wang, L.; Wang, H.; Yang, Y.; Lei, L.; Chen, S.; He, D., Recent advances in two-dimensional nanomaterials for photocatalytic reduction of CO₂: Insights into performance, theories and perspective, *J. Mater. Chem. A*, 8 (2020) 19156–19195.

43. Yang, S.; Gong, Y.; Zhang, J.; Zhan, L.; Ma, L.; Fang, Z.; Vajtai, R.; Wang, X.; Ajayan, P. M., Exfoliated graphitic carbon nitride nanosheets as efficient catalysts for hydrogen evolution under visible light, *Adv. Mater.*, 25 (2013) 2452-2456.
44. Silva, C. G.; Bouizi, Y.; Fornés, V.; García, H., Layered double hydroxides as highly efficient photocatalysts for visible light oxygen generation from water, *J. Am. Chem. Soc.*, 131 (2009) 13833-13839.
45. Low, J.; Yu, J.; Jaroniec, M.; Wageh, S.; Al-Ghamdi, A. A., Heterojunction photocatalysts, *Adv. Mater.*, 29 (2017) 1601694.
46. Su, J.; Li, G.-D.; Li, X.-H.; Chen, J.-S., 2D/2D Heterojunctions for catalysis, *Adv. Sci.*, 6 (2019) 1801702.
47. Liu, H.; Zhu, X.; Han, R.; Dai, Y.; Sun, Y.; Lin, Y.; Gao, D.; Wang, X.; Luo, C., Study on the internal electric field in the Cu₂O/g-C₃N₄ p-n heterojunction structure for enhancing visible light photocatalytic activity, *New J. Chem.*, 44 (2020) 1795-1805.
48. Giampietri, A.; Drera, G.; Sangaletti, L., Band alignment at heteroepitaxial perovskite oxide interfaces. Experiments, methods, and perspectives, *Adv. Mater. Interfaces*, 4 (2017) 1700144.
49. San Martín, S.; Rivero, M. J.; Ortiz, I., Unravelling the mechanisms that drive the performance of photocatalytic hydrogen production, *Catalysts*, 10 (2020) 901.
50. Guo, Y.; Li, H.; Ma, W.; Shi, W.; Zhu, Y.; Choi, W., Photocatalytic activity enhanced via surface hybridization, *Carbon Energy*, 2 (2020) 308-349.
51. Xu, Q.; Zhang, L.; Yu, J.; Wageh, S.; Al-Ghamdi, A. A.; Jaroniec, M., Direct Z-scheme photocatalysts: Principles, synthesis, and applications, *Mater. Today*, 21 (2018) 1042-1063.
52. Thomas, A.; Fischer, A.; Goettmann, F.; Antonietti, M.; Müller, J.-O.; Schlögl, R.; Carlsson, J. M., Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts, *J. Mater. Chem.*, 18 (2008) 4893-4908.
53. Miller, T. S.; Jorge, A. B.; Suter, T. M.; Sella, A.; Corà, F.; McMillan, P. F., Carbon nitrides: Synthesis and characterization of a new class of functional materials, *Phys. Chem. Chem. Phys.*, 19 (2017) 15613-15638.
54. Franklin, E. C., The ammono carbonic acids, *J. Am. Chem. Soc.*, 44 (1922) 486-509.
55. Pauling, L.; Sturdivant, J. H., The structure of cyameluric acid, hydromelonic acid and related substances, *Proc. Natl. Acad. Sci.*, 23 (1937) 615-620.

-
56. Redemann, C. E.; Lucas, H. J., Some derivatives of cyameluric acid and probable structures of melam, melem and melon, *J. Am. Chem. Soc.*, 62 (1940) 842-846.
57. Ong, W.-J.; Tan, L.-L.; Ng, Y. H.; Yong, S.-T.; Chai, S.-P., Graphitic carbon nitride (g-C₃N₄)-based photocatalysts for artificial photosynthesis and environmental remediation: Are we a step closer to achieving sustainability?, *Chem. Rev.*, 116 (2016) 7159-7329.
58. Kroke, E.; Schwarz, M., Novel group 14 nitrides, *Coord. Chem. Rev.*, 248 (2004) 493-532.
59. Teter, D. M.; Hemley, R. J., Low-compressibility carbon nitrides, *Science*, 271 (1996) 53-55.
60. Jr., R. H. W., Cubic form of boron nitride, *J. Chem. Phys.*, 26 (1957) 956-956.
61. Sheng, X.-L.; Yan, Q.-B.; Ye, F.; Zheng, Q.-R.; Su, G., T-carbon: A novel carbon allotrope, *Phys. Rev. Lett.*, 106 (2011) 155703.
62. Liu, A. Y.; Wentzcovitch, R. M., Stability of carbon nitride solids, *Phys. Rev. B*, 50 (1994) 10362-10365.
63. Alves, I.; Demazeau, G.; Tanguy, B.; Weill, F., On a new model of the graphitic form of C₃N₄, *Solid State Commun.*, 109 (1999) 697-701.
64. Fan, Q.; Chai, C.; Wei, Q.; Yang, Y., Two novel C₃N₄ phases: Structural, mechanical and electronic properties, *Materials (Basel)*, 9 (2016) 427.
65. Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M., A metal-free polymeric photocatalyst for hydrogen production from water under visible light, *Nat. Mater.*, 8 (2009) 76–80.
66. Jürgens, B.; Irran, E.; Senker, J.; Kroll, P.; Müller, H.; Schnick, W., Melem (2,5,8-Triamino-tri-s-triazine), an important intermediate during condensation of melamine rings to graphitic carbon nitride: Synthesis, structure determination by X-ray powder diffractometry, solid-state NMR, and theoretical studies, *J. Am. Chem. Soc.*, 125 (2003) 10288-10300.
67. Zhang, Y.; Liu, J.; Wu, G.; Chen, W., Porous graphitic carbon nitride synthesized via direct polymerization of urea for efficient sunlight-driven photocatalytic hydrogen production, *Nanoscale*, 4 (2012) 5300-5303.
68. Martin, D. J.; Qiu, K.; Shevlin, S. A.; Handoko, A. D.; Chen, X.; Guo, Z.; Tang, J., Highly efficient photocatalytic H₂ evolution from water using visible light and structure-controlled graphitic carbon nitride, *Angew. Chem. Int. Ed.*, 53 (2014) 9240-9245.
-

69. Mao, J.; Peng, T.; Zhang, X.; Li, K.; Ye, L.; Zan, L., Effect of graphitic carbon nitride microstructures on the activity and selectivity of photocatalytic CO₂ reduction under visible light, *Catal. Sci. Technol.*, 3 (2013) 1253-1260.
70. Yan, S. C.; Li, Z. S.; Zou, Z. G., Photodegradation performance of g-C₃N₄ fabricated by directly heating melamine, *Langmuir*, 25 (2009) 10397-10401.
71. Liu, J.; Zhang, T.; Wang, Z.; Dawson, G.; Chen, W., Simple pyrolysis of urea into graphitic carbon nitride with recyclable adsorption and photocatalytic activity, *J. Mater. Chem.*, 21 (2011) 14398-14401.
72. Mo, Z.; She, X.; Li, Y.; Liu, L.; Huang, L.; Chen, Z.; Zhang, Q.; Xu, H.; Li, H., Synthesis of g-C₃N₄ at different temperatures for superior visible/UV photocatalytic performance and photoelectrochemical sensing of MB solution, *RSC Adv.*, 5 (2015) 101552-101562.
73. Gu, Q.; Gao, Z.; Zhao, H.; Lou, Z.; Liao, Y.; Xue, C., Temperature-controlled morphology evolution of graphitic carbon nitride nanostructures and their photocatalytic activities under visible light, *RSC Adv.*, 5 (2015) 49317-49325.
74. Dong, F.; Wang, Z.; Sun, Y.; Ho, W.-K.; Zhang, H., Engineering the nanoarchitecture and texture of polymeric carbon nitride semiconductor for enhanced visible light photocatalytic activity, *J. Colloid Interface Sci.*, 401 (2013) 70-79.
75. Lau, V. W.-h.; Mesch, M. B.; Duppel, V.; Blum, V.; Senker, J.; Lotsch, B. V., Low-molecular-weight carbon nitrides for solar hydrogen evolution, *J. Am. Chem. Soc.*, 137 (2015) 1064-1072.
76. Niu, P.; Yin, L.-C.; Yang, Y.-Q.; Liu, G.; Cheng, H.-M., Increasing the visible light absorption of graphitic carbon nitride (Melon) photocatalysts by homogeneous self-modification with nitrogen vacancies, *Adv. Mater.*, 26 (2014) 8046-8052.
77. Dong, G.; Ho, W.; Wang, C., Selective photocatalytic N₂ fixation dependent on g-C₃N₄ induced by nitrogen vacancies, *J. Mater. Chem. A*, 3 (2015) 23435-23441.
78. Yuan, Y.; Zhang, L.; Xing, J.; Utama, M. I. B.; Lu, X.; Du, K.; Li, Y.; Hu, X.; Wang, S.; Genç, A.; Dunin-Borkowski, R.; Arbiol, J.; Xiong, Q., High-yield synthesis and optical properties of g-C₃N₄, *Nanoscale*, 7 (2015) 12343-12350.
79. Li, X.; Hartley, G.; Ward, A. J.; Young, P. A.; Masters, A. F.; Maschmeyer, T., Hydrogenated defects in graphitic carbon nitride nanosheets for improved photocatalytic hydrogen evolution, *J. Phys. Chem. C*, 119 (2015) 14938-14946.

-
80. Yan, H.; Chen, Y.; Xu, S., Synthesis of graphitic carbon nitride by directly heating sulfuric acid treated melamine for enhanced photocatalytic H₂ production from water under visible light, *Int. J. Hydrog. Energy*, 37 (2012) 125-133.
81. Gao, J.; Zhou, Y.; Li, Z.; Yan, S.; Wang, N.; Zou, Z., High-yield synthesis of millimetre-long, semiconducting carbon nitride nanotubes with intense photoluminescence emission and reproducible photoconductivity, *Nanoscale*, 4 (2012) 3687-3692.
82. He, F.; Chen, G.; Yu, Y.; Zhou, Y.; Zheng, Y.; Hao, S., The sulfur-bubble template-mediated synthesis of uniform porous g-C₃N₄ with superior photocatalytic performance, *Chem. Commun.*, 51 (2015) 425-427.
83. Dong, G.; Zhang, L., Porous structure dependent photoreactivity of graphitic carbon nitride under visible light, *J. Mater. Chem.*, 22 (2012) 1160-1166.
84. Zhang, X.-S.; Hu, J.-Y.; Jiang, H., Facile modification of a graphitic carbon nitride catalyst to improve its photoreactivity under visible light irradiation, *Chem. Eng. J.*, 256 (2014) 230-237.
85. Wang, Y.; Di, Y.; Antonietti, M.; Li, H.; Chen, X.; Wang, X., Excellent visible-light photocatalysis of fluorinated polymeric carbon nitride solids, *Chem. Mater.*, 22 (2010) 5119-5121.
86. Liu, G.; Niu, P.; Sun, C.; Smith, S. C.; Chen, Z.; Lu, G. Q.; Cheng, H.-M., Unique electronic structure induced high photoreactivity of sulfur-doped graphitic C₃N₄, *J. Am. Chem. Soc.*, 132 (2010) 11642-11648.
87. Dong, G.; Zhao, K.; Zhang, L., Carbon self-doping induced high electronic conductivity and photoreactivity of g-C₃N₄, *Chem. Commun.*, 48 (2012) 6178-6180.
88. Lima, M. J.; Silva, A. M. T.; Silva, C. G.; Faria, J. L., Graphitic carbon nitride modified by thermal, chemical and mechanical processes as metal-free photocatalyst for the selective synthesis of benzaldehyde from benzyl alcohol, *J. Catal.*, 353 (2017) 44-53.
89. Lin, Q.; Li, L.; Liang, S.; Liu, M.; Bi, J.; Wu, L., Efficient synthesis of monolayer carbon nitride 2D nanosheet with tunable concentration and enhanced visible-light photocatalytic activities, *Appl. Catal. B: Environ.*, 163 (2015) 135-142.
90. Xu, J.; Zhang, L.; Shi, R.; Zhu, Y., Chemical exfoliation of graphitic carbon nitride for efficient heterogeneous photocatalysis, *J. Mater. Chem. A*, 1 (2013) 14766-14772.
91. Sano, T.; Tsutsui, S.; Koike, K.; Hirakawa, T.; Teramoto, Y.; Negishi, N.; Takeuchi, K., Activation of graphitic carbon nitride (g-C₃N₄) by alkaline hydrothermal treatment for photocatalytic NO oxidation in gas phase, *J. Mater. Chem. A*, 1 (2013) 6489-6496.
-

92. Niu, P.; Liu, G.; Cheng, H.-M., Nitrogen vacancy-promoted photocatalytic activity of graphitic carbon nitride, *J. Phys. Chem. C*, 116 (2012) 11013-11018.
93. Dong, F.; Li, Y.; Wang, Z.; Ho, W.-K., Enhanced visible light photocatalytic activity and oxidation ability of porous graphene-like g-C₃N₄ nanosheets via thermal exfoliation, *Appl. Surf. Sci.*, 358 (2015) 393-403.
94. Qiu, P.; Chen, H.; Xu, C.; Zhou, N.; Jiang, F.; Wang, X.; Fu, Y., Fabrication of an exfoliated graphitic carbon nitride as a highly active visible light photocatalyst, *J. Mater. Chem. A*, 3 (2015) 24237-24244.
95. Ong, W.-J., 2D/2D Graphitic carbon nitride (g-C₃N₄) heterojunction nanocomposites for photocatalysis: Why does face-to-face interface matter?, *Front. Mater.*, 4 (2017) 11.
96. Nayak, S.; Mohapatra, L.; Parida, K., Visible light-driven novel g-C₃N₄/NiFe-LDH composite photocatalyst with enhanced photocatalytic activity towards water oxidation and reduction reaction, *J. Mater. Chem. A*, 3 (2015) 18622-18635.
97. Tonda, S.; Kumar, S.; Bhardwaj, M.; Yadav, P.; Ogale, S., g-C₃N₄/NiAl-LDH 2D/2D hybrid heterojunction for high-performance photocatalytic reduction of CO₂ into renewable fuels, *ACS Appl. Mater. Interfaces*, 10 (2018) 2667-2678.
98. Ge, L.; Zuo, F.; Liu, J.; Ma, Q.; Wang, C.; Sun, D.; Bartels, L.; Feng, P., Synthesis and efficient visible light photocatalytic hydrogen evolution of polymeric g-C₃N₄ coupled with CdS quantum dots, *J. Phys. Chem. C*, 116 (2012) 13708-13714.
99. Cao, S.-W.; Yuan, Y.-P.; Fang, J.; Shahjamali, M. M.; Boey, F. Y. C.; Barber, J.; Joachim Loo, S. C.; Xue, C., In-situ growth of CdS quantum dots on g-C₃N₄ nanosheets for highly efficient photocatalytic hydrogen generation under visible light irradiation, *Int. J. Hydrog. Energy*, 38 (2013) 1258-1266.
100. Chai, B.; Peng, T.; Mao, J.; Li, K.; Zan, L., Graphitic carbon nitride (g-C₃N₄)-Pt-TiO₂ nanocomposite as an efficient photocatalyst for hydrogen production under visible light irradiation, *Phys. Chem. Chem. Phys.*, 14 (2012) 16745-16752.
101. Zhou, X.; Jin, B.; Li, L.; Peng, F.; Wang, H.; Yu, H.; Fang, Y., A carbon nitride/TiO₂ nanotube array heterojunction visible-light photocatalyst: synthesis, characterization, and photoelectrochemical properties, *J. Mater. Chem.*, 22 (2012) 17900-17905.
102. Pan, C.; Xu, J.; Wang, Y.; Li, D.; Zhu, Y., Dramatic activity of C₃N₄/BiPO₄ photocatalyst with core/shell structure formed by self-assembly, *Adv. Funct. Mater.*, 22 (2012) 1518-1524.

-
103. Ji, Y.; Cao, J.; Jiang, L.; Zhang, Y.; Yi, Z., G-C₃N₄/BiVO₄ composites with enhanced and stable visible light photocatalytic activity, *J. Alloys Compd.*, 590 (2014) 9-14.
 104. Wang, Y.; Shi, R.; Lin, J.; Zhu, Y., Enhancement of photocurrent and photocatalytic activity of ZnO hybridized with graphite-like C₃N₄, *Energy Environ. Sci.*, 4 (2011) 2922-2929.
 105. Wang, Y.; Wang, Z.; Muhammad, S.; He, J., Graphite-like C₃N₄ hybridized ZnWO₄ nanorods: Synthesis and its enhanced photocatalysis in visible light, *CrystEngComm*, 14 (2012) 5065-5070.
 106. Han, C.; Ge, L.; Chen, C.; Li, Y.; Xiao, X.; Zhang, Y.; Guo, L., Novel visible light induced Co₃O₄-g-C₃N₄ heterojunction photocatalysts for efficient degradation of methyl orange, *Appl. Catal. B: Environ.*, 147 (2014) 546-553.
 107. Yuan, Y.-J.; Yang, Y.; Li, Z.; Chen, D.; Wu, S.; Fang, G.; Bai, W.; Ding, M.; Yang, L.-X.; Cao, D.-P.; Yu, Z.-T.; Zou, Z.-G., Promoting charge separation in g-C₃N₄/graphene/MoS₂ photocatalysts by two-dimensional nanojunction for enhanced photocatalytic H₂ production, *ACS Appl. Energy Mater.*, 1 (2018) 1400–1407.
 108. Xiang, Q.; Yu, J.; Jaroniec, M., Preparation and enhanced visible-light photocatalytic H₂ production activity of graphene/C₃N₄ composites, *J. Phys. Chem. C*, 115 (2011) 7355–7363.
 109. Lee, S. P., Synthesis and characterization of carbon nitride films for micro humidity sensors, *Sensors*, 8 (2008) 1508-1518.
 110. Zhang, R.; Wang, Y.; Zhang, Z.; Cao, J., Highly sensitive acetone gas sensor based on g-C₃N₄ decorated MgFe₂O₄ porous microspheres composites, *Sensors*, 18 (2018) 2211.
 111. Chen, X.; Zhang, J.; Fu, X.; Antonietti, M.; Wang, X., Fe-g-C₃N₄-catalyzed oxidation of benzene to phenol using hydrogen peroxide and visible light, *J. Am. Chem. Soc.*, 131 (2009) 11658-11659.
 112. Shiravand, G.; Badiei, A.; Ziarani, G. M.; Jafarabadi, M.; Hamzehloo, M., Photocatalytic synthesis of phenol by direct hydroxylation of benzene by a modified nanoporous silica (LUS-1) under sunlight, *Chinese J. Catal.*, 33 (2012) 1347-1353.
 113. Verma, S.; Baig, R. B. N.; Nadagouda, M. N.; Varma, R. S., Selective oxidation of alcohols using photoactive VO@g-C₃N₄, *ACS Sustain. Chem. Eng.*, 4 (2016) 1094-1098.
 114. Torres-Pinto, A.; Sampaio, M. J.; Silva, C. G.; Faria, J. L.; Silva, A. M. T., Metal-free carbon nitride photocatalysis with in situ hydrogen peroxide generation for the degradation of aromatic compounds, *Appl. Catal. B: Environ.*, 252 (2019) 128-137.
 115. Fernandes, R. A.; Sampaio, M. J.; Da Silva, E. S.; Boumeriame, H.; Lopes, T.; Andrade, L.; Mendes, A.; Faria, J. L.; Silva, C. G., Sustainable production of value-added

- chemicals and fuels by using a citric acid-modified carbon nitride optical semiconductor, *Appl. Catal. A-Gen.*, 609 (2021) 117912.
116. Bai, X. D.; Zhong, D.; Zhang, G. Y.; Ma, X. C.; Liu, S.; Wang, E. G.; Chen, Y.; Shaw, D. T., Hydrogen storage in carbon nitride nanobells, *Appl. Phys. Lett.*, 79 (2001) 1552-1554.
117. Wu, M.; Wang, Q.; Sun, Q.; Jena, P., Functionalized graphitic carbon nitride for efficient energy storage, *J. Phys. Chem. C*, 117 (2013) 6055-6059.
118. Panigrahi, P.; Kumar, A.; Kartan, A.; Ahuja, R.; Hussain, T., Remarkable improvement in hydrogen storage capacities of two-dimensional carbon nitride (g-C₃N₄) nanosheets under selected transition metal doping, *Int. J. Hydrog. Energy*, 45 (2020) 3035-3045.
119. Tang, J.-Y.; Kong, X. Y.; Ng, B.-J.; Chew, Y.-H.; Mohamed, A. R.; Chai, S.-P., Midgap-state-mediated two-step photoexcitation in nitrogen defect-modified g-C₃N₄ atomic layers for superior photocatalytic CO₂ reduction, *Catal. Sci. Technol.*, 9 (2019) 2335-2343.
120. Ye, S.; Wang, R.; Wu, M.-Z.; Yuan, Y.-P., A review on g-C₃N₄ for photocatalytic water splitting and CO₂ reduction, *Appl. Surf. Sci.*, 358 (2015) 15-27.
121. Nasir, M. S.; Yang, G.; Ayub, I.; Wang, S.; Wang, L.; Wang, X.; Yan, W.; Peng, S.; Ramakarishna, S., Recent development in graphitic carbon nitride based photocatalysis for hydrogen generation, *Appl. Catal. B: Environ.*, 257 (2019) 117855.
122. Mishra, A.; Mehta, A.; Basu, S.; Shetti, N. P.; Reddy, K. R.; Aminabhavi, T. M., Graphitic carbon nitride (g-C₃N₄)-based metal-free photocatalysts for water splitting: A review, *Carbon*, 149 (2019) 693-721.
123. Maeda, K.; Wang, X.; Nishihara, Y.; Lu, D.; Antonietti, M.; Domen, K., Photocatalytic activities of graphitic carbon nitride powder for water reduction and oxidation under visible light, *J. Phys. Chem. C*, 113 (2009) 4940-4947.
124. Yu, J.; Wang, S.; Cheng, B.; Lin, Z.; Huang, F., Noble metal-free Ni(OH)₂-g-C₃N₄ composite photocatalyst with enhanced visible-light photocatalytic H₂-production activity, *Catal. Sci. Technol.*, 3 (2013) 1782-1789.
125. Li, X.-H.; Wang, X.; Antonietti, M., Mesoporous g-C₃N₄ nanorods as multifunctional supports of ultrafine metal nanoparticles: hydrogen generation from water and reduction of nitrophenol with tandem catalysis in one step, *Chem. Sci.*, 3 (2012) 2170-2174.

-
126. Di, Y.; Wang, X.; Thomas, A.; Antonietti, M., Making metal carbon nitride heterojunctions for improved photocatalytic hydrogen evolution with visible light, *ChemCatChem*, 2 (2010) 834-838.
127. Xu, Y.-S.; Zhang, W.-D., Ag/AgBr-grafted graphite-like carbon nitride with enhanced plasmonic photocatalytic activity under visible light, *ChemCatChem*, 5 (2013) 2343-2351.
128. Han, Q.; Wang, B.; Gao, J.; Cheng, Z.; Zhao, Y.; Zhang, Z.; Qu, L., Atomically thin mesoporous nanomesh of graphitic C₃N₄ for high-efficiency photocatalytic hydrogen evolution, *ACS Nano*, 10 (2016) 2745-2751.
129. Zeng, Z.; Li, K.; Yan, L.; Dai, Y.; Guo, H.; Huo, M.; Guo, Y., Fabrication of carbon nitride nanotubes by a simple water-induced morphological transformation process and their efficient visible-light photocatalytic activity, *RSC Adv.*, 4 (2014) 59513-59518.
130. Gu, Q.; Liao, Y.; Yin, L.; Long, J.; Wang, X.; Xue, C., Template-free synthesis of porous graphitic carbon nitride microspheres for enhanced photocatalytic hydrogen generation with high stability, *Appl. Catal. B: Environ.*, 165 (2015) 503-510.
131. Zhang, J.; Zhang, M.; Yang, C.; Wang, X., Nanospherical carbon nitride frameworks with sharp edges accelerating charge collection and separation at a soft photocatalytic interface, *Adv. Mater.*, 26 (2014) 4121-4126.
132. Sun, J.; Zhang, J.; Zhang, M.; Antonietti, M.; Fu, X.; Wang, X., Bioinspired hollow semiconductor nanospheres as photosynthetic nanoparticles, *Nat. Commun.*, 3 (2012) 1139.
133. Zheng, D.; Zhang, G.; Hou, Y.; Wang, X., Layering MoS₂ on soft hollow g-C₃N₄ nanostructures for photocatalytic hydrogen evolution, *Appl. Catal. A-Gen.*, 521 (2016) 2-8.
134. Han, Q.; Wang, B.; Zhao, Y.; Hu, C.; Qu, L., A graphitic-C₃N₄ “Seaweed” architecture for enhanced hydrogen evolution, *Angew. Chem. Int. Ed.*, 54 (2015) 11433-11437.
135. Shen, L.; Xing, Z.; Zou, J.; Li, Z.; Wu, X.; Zhang, Y.; Zhu, Q.; Yang, S.; Zhou, W., Black TiO₂ nanobelts/g-C₃N₄ nanosheets laminated heterojunctions with efficient visible-light-driven photocatalytic performance, *Sci. Rep.*, 7 (2017) 41978.
136. Wu, M.; Zhang, J.; Liu, C.; Gong, Y.; Wang, R.; He, B.; Wang, H., Rational design and fabrication of noble-metal-free Ni_xP cocatalyst embedded 3D N-TiO₂/g-C₃N₄ heterojunctions with enhanced photocatalytic hydrogen evolution, *ChemCatChem*, 10 (2018) 3069-3077.
137. Zhang, J.; Wang, Y.; Jin, J.; Zhang, J.; Lin, Z.; Huang, F.; Yu, J., Efficient visible-light photocatalytic hydrogen evolution and enhanced photostability of core/shell CdS/g-C₃N₄ nanowires, *ACS Appl. Mater. Interfaces*, 5 (2013) 10317-10324.
-

138. Liu, L.; Qi, Y.; Hu, J.; Liang, Y.; Cui, W., Efficient visible-light photocatalytic hydrogen evolution and enhanced photostability of core@shell Cu₂O@g-C₃N₄ octahedra, *Appl. Surf. Sci.*, 351 (2015) 1146-1154.
139. Sun, Q.; Wang, P.; Yu, H.; Wang, X., In situ hydrothermal synthesis and enhanced photocatalytic H₂-evolution performance of suspended rGO/g-C₃N₄ photocatalysts, *J. Mol. Catal. A: Chem.*, 424 (2016) 369-376.
140. Song, C.; Fan, M.; Shi, W.; Wang, W., High-performance for hydrogen evolution and pollutant degradation of reduced graphene oxide/two-phase g-C₃N₄ heterojunction photocatalysts, *Environ. Sci. Pollut. Res.*, 25 (2018) 14486-14498.
141. Ge, L.; Han, C.; Xiao, X.; Guo, L., Synthesis and characterization of composite visible light active photocatalysts MoS₂-g-C₃N₄ with enhanced hydrogen evolution activity, *Int. J. Hydrog. Energy*, 38 (2013) 6960-6969.
142. Hou, Y.; Laursen, A. B.; Zhang, J.; Zhang, G.; Zhu, Y.; Wang, X.; Dahl, S.; Chorkendorff, I., Layered nanojunctions for hydrogen-evolution catalysis, *Angew. Chem. Int. Ed.*, 52 (2013) 3621-3625.
143. Shi, X.; Fujitsuka, M.; Kim, S.; Majima, T., Faster electron injection and more active sites for efficient photocatalytic H₂ evolution in g-C₃N₄/MoS₂ hybrid, *Small*, 14 (2018) 1703277.
144. Shi, J.; Li, S.; Wang, F.; Gao, L.; Li, Y.; Zhang, X.; Lu, J., 2D/2D g-C₃N₄/MgFe MMO nanosheet heterojunctions with enhanced visible-light photocatalytic H₂ production, *J. Alloys Compd.*, 769 (2018) 611-619.
145. Prasad, C.; Tang, H.; Liu, Q. Q.; Zulfiqar, S.; Shah, S.; Bahadur, I., An overview of semiconductors/layered double hydroxides composites: Properties, synthesis, photocatalytic and photoelectrochemical applications, *J. Mol. Liq.*, 289 (2019) 111114.
146. Zhao, Y.; Zhang, S.; Shi, R.; Waterhouse, G. I. N.; Tang, J.; Zhang, T., Two-dimensional photocatalyst design: A critical review of recent experimental and computational advances, *Mater. Today*, 34 (2020) 78-91.
147. Zhao, Y.; Waterhouse, G. I. N.; Chen, G.; Xiong, X.; Wu, L.-Z.; Tung, C.-H.; Zhang, T., Two-dimensional-related catalytic materials for solar-driven conversion of CO_x into valuable chemical feedstocks, *Chem. Soc. Rev.*, 48 (2019) 1972-2010.
148. Sun, X.; Huang, H.; Zhao, Q.; Ma, T.; Wang, L., Thin-layered photocatalysts, *Adv. Funct. Mater.*, 30 (2020) 1910005.

-
149. Sun, X.; Shi, L.; Huang, H.; Song, X.; Ma, T., Surface engineered 2D materials for photocatalysis, *Chem. Commun.*, 56 (2020) 11000-11013.
150. Boumeriame, H.; Da Silva, E. S.; Cherevan, A. S.; Chafik, T.; Faria, J. L.; Eder, D., Layered double hydroxide (LDH)-based materials: A mini-review on strategies to improve the performance for photocatalytic water splitting, *J. Energy Chem.*, 64 (2022) 406–431.
151. Manasse, E., *Idrotalcite e piroaurite*, Stabilimento Tipografia Successori Fratelli Nistri, Pisa, Italy, 1915.
152. Evans, D. G.; Slade, R. C. T., Structural aspects of layered double hydroxides, in: *Layered double hydroxides*, Springer Berlin Heidelberg, Berlin, Germany, 2006.
153. Khan, A. I.; O'Hare, D., Intercalation chemistry of layered double hydroxides: Recent developments and applications, *J. Mater. Chem.*, 12 (2002) 3191-3198.
154. Williams, G. R.; O'Hare, D., Towards understanding, control and application of layered double hydroxide chemistry, *J. Mater. Chem.*, 16 (2006) 3065-3074.
155. Wang, Y.; Yan, D.; El Hankari, S.; Zou, Y.; Wang, S., Recent progress on layered double hydroxides and their derivatives for electrocatalytic water splitting, *Adv. Sci.*, 5 (2018) 1800064.
156. Wang, Q.; O'Hare, D., Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets, *Chem. Rev.*, 112 (2012) 4124-4155.
157. Chen, Y.; Jing, C.; Zhang, X.; Jiang, D.; Liu, X.; Dong, B.; Feng, L.; Li, S.; Zhang, Y., Acid-salt treated CoAl layered double hydroxide nanosheets with enhanced adsorption capacity of methyl orange dye, *J. Colloid Interface Sci.*, 548 (2019) 100-109.
158. Tang, S.; Yao, Y.; Chen, T.; Kong, D.; Shen, W.; Lee, H. K., Recent advances in the application of layered double hydroxides in analytical chemistry: A review, *Anal. Chim. Acta*, 1103 (2020) 32-48.
159. Chen, J.; Sheng, Q.; Wang, Y.; Zheng, J., Dispersed nickel nanoparticles on flower-like layered nickel-cobalt double hydroxides for non-enzymic amperometric sensing of glucose, *Electroanalysis*, 28 (2016) 979-984.
160. Yao, L.; Wei, D.; Yan, D.; Hu, C., ZnCr layered double hydroxide (LDH) nanosheets assisted formation of hierarchical flower-like CdZnS@LDH microstructures with improved visible-light-driven H₂ production, *Chem. Asian J.*, 10 (2015) 630-636.
161. Tang, S.; Chia, G. H.; Lee, H. K., Magnetic core-shell iron(II,III) oxide@layered double oxide microspheres for removal of 2,5-dihydroxybenzoic acid from aqueous solutions, *J. Colloid Interface Sci.*, 437 (2015) 316-323.
-

162. Li, Y.; Zhou, F.; Gao, L.; Duan, G., Co₃O₄ nanosheet-built hollow spheres containing ultrafine neck-connected grains templated by PS@Co-LDH and their ppb-level gas-sensing performance, *Sens. Actuator B-Chem.*, 261 (2018) 553-565.
163. Yu, J.; Wang, Q.; O'Hare, D.; Sun, L., Preparation of two dimensional layered double hydroxide nanosheets and their applications, *Chem. Soc. Rev.*, 46 (2017) 5950-5974.
164. Mohapatra, L.; Parida, K., A review on the recent progress, challenges and perspective of layered double hydroxides as promising photocatalysts, *J. Mater. Chem. A*, 4 (2016) 10744-10766.
165. Yan, K.; Wu, G.; Jin, W., Recent advances in the synthesis of layered double-hydroxide-based materials and their applications in hydrogen and oxygen evolution, *Energy Technol.*, 4 (2016) 354-368.
166. Li, X.; Du, D.; Zhang, Y.; Xing, W.; Xue, Q.; Yan, Z., Layered double hydroxides toward high-performance supercapacitors, *J. Mater. Chem. A*, 5 (2017) 15460-15485.
167. Zhang, M.; Luo, Z.; Zhou, M.; Zhang, G.; Alamry, K. A.; Taib, L. A.; Asiri, A. M.; Wang, X., Ni-Co layered double hydroxides cocatalyst for sustainable oxygen photosynthesis, *Appl. Catal. B: Environ.*, 210 (2017) 454-461.
168. Ma, J.; Ding, J.; Yu, L.; Li, L.; Kong, Y.; Komarneni, S., Synthesis of Fe₂O₃-NiO-Cr₂O₃ composites from NiFe-layered double hydroxide for degrading methylene blue under visible light, *Appl. Clay Sci.*, 107 (2015) 85-89.
169. Li, R.; Wang, Y.; Li, W.; Zhou, S.; Tian, P.; Gao, H.; Liu, X.; Zang, J., Ternary NiFeZr layered double hydroxides: A highly efficient catalyst for oxygen evolution reaction, *Chem. Commun.*, 55 (2019) 13370-13373.
170. Tao, X.; Han, Y.; Sun, C.; Huang, L.; Xu, D., Plasma modification of NiAlCe-LDH as improved photocatalyst for organic dye wastewater degradation, *Appl. Clay Sci.*, 172 (2019) 75-79.
171. Zhang, G.; Hu, L.; Zhao, R.; Su, R.; Wang, Q.; Wang, P., Microwave-assisted synthesis of ZnNiAl-layered double hydroxides with calcination treatment for enhanced PNP photo-degradation under visible-light irradiation, *J. Photochem. Photobiol. A*, 356 (2018) 633-641.
172. Chowdhury, P. R.; Bhattacharyya, K. G., Ni/Co/Ti layered double hydroxide for highly efficient photocatalytic degradation of rhodamine B and acid red G: A comparative study, *Photochem. Photobiol. Sci.*, 16 (2017) 835-839.

-
173. Chaillot, D.; Bennici, S.; Brendlé, J., Layered double hydroxides and LDH-derived materials in chosen environmental applications: A review, *Environ. Sci. Pollut. Res.*, 28 (2020) 24375-24405.
174. Mishra, G.; Dash, B.; Pandey, S., Layered double hydroxides: A brief review from fundamentals to application as evolving biomaterials, *Appl. Clay Sci.*, 153 (2018) 172-186.
175. He, J.; Wei, M.; Li, B.; Kang, Y.; Evans, D. G.; Duan, X., Preparation of layered double hydroxides, in: *Layered double hydroxides*, Springer Berlin Heidelberg, Berlin, Germany, 2006.
176. Theiss, F. L.; Ayoko, G. A.; Frost, R. L., Synthesis of layered double hydroxides containing Mg^{2+} , Zn^{2+} , Ca^{2+} and Al^{3+} layer cations by co-precipitation methods—A review, *Appl. Surf. Sci.*, 383 (2016) 200-213.
177. Abelló, S.; Mitchell, S.; Santiago, M.; Stoica, G.; Pérez-Ramírez, J., Perturbing the properties of layered double hydroxides by continuous coprecipitation with short residence time, *J. Mater. Chem.*, 20 (2010) 5878-5887.
178. Miyata, S., Anion-exchange properties of hydrotalcite-like compounds, *Clays Clay Miner.*, 31 (1983) 305-311.
179. Zhang, D.; Ji, T.; Yu, J.; Jiang, X.; Jiao, F., Solvothermal synthesis of $Cs_{0.33}WO_3/LDHs$ composite as a novel visible-light-driven photocatalyst, *Photochem. Photobiol.*, 94 (2018) 219-227.
180. Labajos, F. M.; Rives, V.; Ulibarri, M. A., Effect of hydrothermal and thermal treatments on the physicochemical properties of Mg-Al hydrotalcite-like materials, *J. Mater. Sci.*, 27 (1992) 1546-1552.
181. Adachi-Pagano, M.; Forano, C.; Besse, J.-P., Synthesis of Al-rich hydrotalcite-like compounds by using the urea hydrolysis reaction—control of size and morphology, *J. Mater. Chem.*, 13 (2003) 1988-1993.
182. Aramendí; x; a, M.; x; a, A.; Borau, V.; Jiménez, C.; Marinas, J. M.; Ruiz, J. R.; Urbano, F. J., Comparative study of $Mg/M^{(III)}$ ($M=Al, Ga, In$) layered double hydroxides obtained by coprecipitation and the sol–gel method, *J. Solid State Chem.*, 168 (2002) 156-161.
183. Xu, S.-M.; Yan, H.; Wei, M., Band structure engineering of transition-metal-based layered double hydroxides toward photocatalytic oxygen evolution from water: A theoretical–experimental combination study, *J. Phys. Chem. C*, 121 (2017) 2683-2695.
-

184. Mostafa, M. S.; Lan, C.; Betiha, M. A.; Zhang, R.; Gao, Y.; Ge, G., Enhanced infrared-induced water oxidation by one-pot synthesized CoTi-Nanorods as highly infrared responsive photocatalyst, *J. Power Sources*, 464 (2020) 228176.
185. Chen, J.; Wang, C.; Zhang, Y.; Guo, Z.; Luo, Y.; Mao, C.-J., Engineering ultrafine NiS cocatalysts as active sites to boost photocatalytic hydrogen production of MgAl layered double hydroxide, *Appl. Surf. Sci.*, 506 (2020) 144999.
186. Xu, M.; Wei, M., Layered double hydroxide-based catalysts: Recent advances in preparation, structure, and applications, *Adv. Funct. Mater.*, 28 (2018) 1802943.
187. Suárez-Quezada, M.; Romero-Ortiz, G.; Samaniego-Benítez, J. E.; Suárez, V.; Mantilla, A., H₂ production by the water splitting reaction using photocatalysts derived from calcined ZnAl LDH, *Fuel*, 240 (2019) 262-269.
188. Nayak, S.; Pradhan, A. C.; Parida, K. M., Topotactic transformation of solvated MgCr-LDH nanosheets to highly efficient porous MgO/MgCr₂O₄ nanocomposite for photocatalytic H₂ evolution, *Inorg. Chem.*, 57 (2018) 8646-8661.
189. Shi, J.; Islam, I. U.; Chen, W.; Wang, F.; Xu, Z.; Xu, S.; Li, Y.; Lu, J., Two-dimensional ultrathin Zn_xCd_{1-x}S nanosheet with exposed polar facet by using layered double hydroxide template for photocatalytic hydrogen generation, *Int. J. Hydrog. Energy*, 43 (2018) 19481-19491.
190. Shi, J.; Li, S.; Wang, F.; Gao, L.; Li, Y.; Zhang, X.; Lu, J., In situ topotactic formation of 2D/2D direct Z-scheme Cu₂S/Zn_{0.67}Cd_{0.33}S in-plane intergrowth nanosheet heterojunctions for enhanced photocatalytic hydrogen production, *Dalton Trans.*, 48 (2019) 3327-3337.
191. Liu, G.; Yu, J. C.; Lu, G. Q.; Cheng, H.-M., Crystal facet engineering of semiconductor photocatalysts: Motivations, advances and unique properties, *Chem. Commun.*, 47 (2011) 6763-6783.
192. Xu, Y.; Wang, Z.; Tan, L.; Yan, H.; Zhao, Y.; Duan, H.; Song, Y.-F., Interface engineering of high-energy faceted Co₃O₄/ZnO heterostructured catalysts derived from layered double hydroxide nanosheets, *Ind. Eng. Chem. Res.*, 57 (2018) 5259-5267.
193. Wang, X.; Zhou, S.; Wu, L., Fabrication of Fe³⁺ doped Mg/Al layered double hydroxides and their application in UV light-shielding coatings, *J. Mater. Chem. C*, 2 (2014) 5752-5758.
194. Fu, Y.; Ning, F.; Xu, S.; An, H.; Shao, M.; Wei, M., Terbium doped ZnCr-layered double hydroxides with largely enhanced visible light photocatalytic performance, *J. Mater. Chem. A*, 4 (2016) 3907-3913.

-
195. Khodam, F.; Amani-Ghadim, H. R.; Aber, S.; Amani-Ghadim, A. R.; Ahadzadeh, I., Neodymium doped mixed metal oxide derived from CoAl-layered double hydroxide: Considerable enhancement in visible light photocatalytic activity, *J. Ind. Eng. Chem.*, 68 (2018) 311-324.
196. Parida, K.; Satpathy, M.; Mohapatra, L., Incorporation of Fe^{3+} into Mg/Al layered double hydroxide framework: Effects on textural properties and photocatalytic activity for H_2 generation, *J. Mater. Chem.*, 22 (2012) 7350-7357.
197. Megala, S.; Sathish, M.; Harish, S.; Navaneethan, M.; Sohila, S.; Liang, B.; Ramesh, R., Enhancement of photocatalytic H_2 evolution from water splitting by construction of two dimensional g- C_3N_4 /NiAl layered double hydroxides, *Appl. Surf. Sci.*, 509 (2020) 144656.
198. Patnaik, S.; Sahoo, D. P.; Mohapatra, L.; Martha, S.; Parida, K., ZnCr_2O_4 @ ZnO /g- C_3N_4 : A triple-junction nanostructured material for effective hydrogen and oxygen evolution under visible light, *Energy Technol.*, 5 (2017) 1687-1701.
199. Mancipe, S.; Tzompantzi, F.; Gómez, R., Synthesis of CdS/MgAl layered double hydroxides for hydrogen production from methanol-water decomposition, *Appl. Clay Sci.*, 136 (2017) 67-74.
200. Nayak, S.; Swain, G.; Parida, K., Enhanced photocatalytic activities of RhB degradation and H_2 evolution from in situ formation of the electrostatic heterostructure MoS_2 /NiFe-LDH nanocomposite through the Z-Scheme mechanism via p-n heterojunctions, *ACS Appl. Mater. Interfaces*, 11 (2019) 20923-20942.
201. Alberio, J.; Mateo, D.; García, H., Graphene-based materials as efficient photocatalysts for water splitting, *Molecules*, 24 (2019) 906.
202. Prasad, C.; Liu, Q.; Tang, H.; Yuvaraja, G.; Long, J.; Rammohan, A.; Zyryanov, G. V., An overview of graphene oxide supported semiconductors based photocatalysts: Properties, synthesis and photocatalytic applications, *J. Mol. Liq.*, 297 (2020) 111826.
203. Kumaresan, A.; Yang, S.; Zhao, K.; Ahmad, N.; Zhou, J.; Zheng, Z.; Zhang, Y.; Gao, Y.; Zhou, H.; Tang, Z., Facile development of CoAl-LDHs/RGO nanocomposites as photocatalysts for efficient hydrogen generation from water splitting under visible-light irradiation, *Inorg. Chem. Front.*, 6 (2019) 1753-1760.
204. Li, G.; Wang, Y.; Mao, L., Recent progress in highly efficient Ag-based visible-light photocatalysts, *RSC Adv.*, 4 (2014) 53649-53661.
-

205. Han, J.; Zou, H. Y.; Liu, Z. X.; Yang, T.; Gao, M. X.; Huang, C. Z., Efficient visible-light photocatalytic heterojunctions formed by coupling plasmonic Cu_{2-x}Se and graphitic carbon nitride, *New J. Chem.*, 39 (2015) 6186-6192.
206. Shi, H.; Zhang, C.; Zhou, C., g- C_3N_4 hybridized with AgVO_3 nanowires: preparation and its enhanced visible-light-induced photocatalytic activity, *RSC Adv.*, 5 (2015) 50146-50154.
207. Li, Z.; Zhang, Q.; Liu, X.; Wu, L.; Hu, H.; Zhao, Y., One-step mechanochemical synthesis of plasmonic Ag/Zn-Al LDH with excellent photocatalytic activity, *J. Mater. Sci.*, 53 (2018) 12795-12806.
208. Sahoo, D. P.; Patnaik, S.; Rath, D.; Parida, K. M., Synergistic effects of plasmon induced $\text{Ag@Ag}_3\text{VO}_4/\text{ZnCr-LDH}$ ternary heterostructures towards visible light responsive O_2 evolution and phenol oxidation reactions, *Inorg. Chem. Front.*, 5 (2018) 879-896.
209. Zhu, Y.; Zhu, R.; Zhu, G.; Wang, M.; Chen, Y.; Zhu, J.; Xi, Y.; He, H., Plasmonic Ag coated Zn/Ti-LDH with excellent photocatalytic activity, *Appl. Surf. Sci.*, 433 (2018) 458-467.
210. Luo, B.; Song, R.; Jing, D., ZnCr LDH nanosheets modified graphitic carbon nitride for enhanced photocatalytic hydrogen production, *Int. J. Hydrog. Energy*, 42 (2017) 23427–23436.
211. Zhang, J.; Zhu, Q.; Wang, L.; Nasir, M.; Cho, S.-H.; Zhang, J., g- $\text{C}_3\text{N}_4/\text{CoAl-LDH}$ 2D/2D hybrid heterojunction for boosting photocatalytic hydrogen evolution, *Int. J. Hydrog. Energy*, 45 (2020) 21331-21340.
212. Adeli, B.; Taghipour, F., Facile synthesis of highly efficient nano-structured gallium zinc oxynitride solid solution photocatalyst for visible-light overall water splitting, *Appl. Catal. A-Gen.*, 521 (2016) 250-258.
213. Adeli, B.; Taghipour, F., Atomic-scale synthesis of nanoporous gallium–zinc oxynitride-reduced graphene oxide photocatalyst with tailored carrier transport mechanism, *RSC Adv.*, 10 (2020) 14906-14914.
214. Li, X.; Zhang, Q.; Wang, H.; Li, Y., Synthesis of mesoporous $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ using layered double hydroxides as precursors for enhanced visible-light driven H_2 production, *Chin. J. Chem.*, 35 (2017) 196-202.
215. Lee, J. M.; Yang, J.-H.; Kwon, N. H.; Jo, Y. K.; Choy, J.-H.; Hwang, S.-J., Intercalative hybridization of layered double hydroxide nanocrystals with mesoporous g- C_3N_4

- for enhancing visible light-induced H₂ production efficiency, *Dalton Trans.*, 47 (2018) 2949-2955.
216. Zhou, H.; Song, Y.; Liu, Y.; Li, H.; Li, W.; Chang, Z., Fabrication of CdS/NiFe LDH heterostructure for improved photocatalytic hydrogen evolution from aqueous methanol solution, *Int. J. Hydrog. Energy*, 43 (2018) 14328-14336.
217. Lee, H.; Reddy, D. A.; Kim, Y.; Chun, S. Y.; Ma, R.; Kumar, D. P.; Song, J. K.; Kim, T. K., Drastic improvement of 1D-CdS solar-driven photocatalytic hydrogen evolution rate by integrating with NiFe layered double hydroxide nanosheets synthesized by liquid-phase pulsed-laser ablation, *ACS Sustain. Chem. Eng.*, 6 (2018) 16734-16743.
218. Li, S.; Wang, L.; Li, Y.; Zhang, L.; Wang, A.; Xiao, N.; Gao, Y.; Li, N.; Song, W.; Ge, L.; Liu, J., Novel photocatalyst incorporating Ni-Co layered double hydroxides with P-doped CdS for enhancing photocatalytic activity towards hydrogen evolution, *Appl. Catal. B: Environ.*, 254 (2019) 145-155.
219. Wang, Y.; Wang, G.; Zhang, L.; Jin, Z.; Zhao, T., Hydroxides Ni(OH)₂&Ce(OH)₃ as a novel hole storage layer for enhanced photocatalytic hydrogen evolution, *Dalton Trans.*, 48 (2019) 17660-17672.
220. Sohail, M.; Kim, H.; Kim, T. W., Enhanced photocatalytic performance of a Ti-based metal-organic framework for hydrogen production: Hybridization with ZnCr-LDH nanosheets, *Sci. Rep.*, 9 (2019) 7584.
221. Reddy, D. A.; Kim, H. K.; Kim, Y.; Lee, S.; Choi, J.; Islam, M. J.; Kumar, D. P.; Kim, T. K., Multicomponent transition metal phosphides derived from layered double hydroxide double-shelled nanocages as an efficient non-precious co-catalyst for hydrogen production, *J. Mater. Chem. A*, 4 (2016) 13890-13898.
222. Wang, C.; Ma, B.; Xu, S.; Li, D.; He, S.; Zhao, Y.; Han, J.; Wei, M.; Evans, D. G.; Duan, X., Visible-light-driven overall water splitting with a largely-enhanced efficiency over a Cu₂O@ZnCr-layered double hydroxide photocatalyst, *Nano Energy*, 32 (2017) 463-469.
223. Wang, C.; Ma, B.; Cao, X.; He, S.; Han, J.; Wei, M.; Evans, D. G.; Duan, X., Bridge-type interface optimization on a dual-semiconductor heterostructure toward high performance overall water splitting, *J. Mater. Chem. A*, 6 (2018) 7871-7876.
224. Sahoo, D. P.; Nayak, S.; Reddy, K. H.; Martha, S.; Parida, K., Fabrication of a Co(OH)₂/ZnCr LDH “p-n” heterojunction photocatalyst with enhanced separation of charge carriers for efficient visible-light-driven H₂ and O₂ evolution, *Inorg. Chem.*, 57 (2018) 3840-3854.

225. Acharya, S.; Parida, K., A visible light-driven Zn/Cr–LaFeO₃ nanocomposite with enhanced photocatalytic activity towards H₂ production and RhB degradation, *ChemistrySelect*, 2 (2017) 10239-10248.
226. Nayak, S.; Parida, K. M., Nanostructured CeO₂/MgAl-LDH composite for visible light induced water reduction reaction, *Int. J. Hydrog. Energy*, 41 (2016) 21166-21180.
227. Carja, G.; Gilea, D.; Cool, P.; Seftel, E. M., In Situ synthesis of Bi₂O₃ nanoparticles on ZincMe (Me=Al or Cr) layered double hydroxide frameworks for photocatalytic oxygen evolution from water under solar-light activation, *ChemCatChem*, 10 (2018) 1598-1606.
228. Jafari Foruzin, L.; Rezvani, Z.; Nejati, K.; Hou, Z.; Dai, H.; Asadpour-Zeynali, K., High quantum efficiency of photocatalytic water oxidation over the TiO₂/MMO nanocomposite under visible-light irradiation, *J. Mol. Liq.*, 288 (2019) 111035.
229. Gil, J. J.; Aguilar-Martínez, O.; Piña-Pérez, Y.; Pérez-Hernández, R.; Santolalla-Vargas, C. E.; Gómez, R.; Tzompantzi, F., Efficient ZnS–ZnO/ZnAl-LDH composite for H₂ production by photocatalysis, *Renew. Energ.*, 145 (2020) 124-132.
230. Amani-Ghadim, A. R.; Khodam, F.; Seyed Dorraji, M. S., ZnS quantum dot intercalated layered double hydroxide semiconductors for solar water splitting and organic pollutant degradation, *J. Mater. Chem. A*, 7 (2019) 11408-11422.
231. Kandi, D.; Sahoo, D. P.; Martha, S.; Parida, K., Rational design of a coupled confronting Z-scheme system toward photocatalytic refractory pollutant degradation and water splitting reaction, *Adv. Mater. Interfaces*, 6 (2019) 1900370.
232. Nayak, S.; Parida, K. M., Deciphering Z-scheme charge transfer dynamics in heterostructure NiFe-LDH/N-rGO/g-C₃N₄ nanocomposite for photocatalytic pollutant removal and water splitting reactions, *Sci. Rep.*, 9 (2019) 2458.
233. Boppella, R.; Choi, C. H.; Moon, J.; Ha Kim, D., Spatial charge separation on strongly coupled 2D-hybrid of rGO/La₂Ti₂O₇/NiFe-LDH heterostructures for highly efficient noble metal free photocatalytic hydrogen generation, *Appl. Catal. B: Environ.*, 239 (2018) 178-186.
234. Sahoo, D. P.; Patnaik, S.; Parida, K., Construction of a Z-Scheme dictated WO₃-x/Ag/ZnCr-LDH synergistically visible light-induced photocatalyst towards tetracycline degradation and H₂ evolution, *ACS Omega*, 4 (2019) 14721-14741.
235. Das, S.; Patnaik, S.; Parida, K. M., Fabrication of a Au-loaded CaFe₂O₄/CoAl LDH p–n junction based architecture with stoichiometric H₂ & O₂ generation and Cr(vi) reduction under visible light, *Inorg. Chem. Front.*, 6 (2019) 94-109.

-
236. Wang, J.; Xu, Q.; Wei, X.; Zhang, N.; Wang, Z.; Qu, P., Fabricating $\text{Ni}_x\text{Co}_{1-x}\text{O}@\text{C}$ cocatalysts sensitized by CdS through electrostatic interaction for efficient photocatalytic H_2 evolution, *Int. J. Hydrog. Energy*, 45 (2020) 28437-28446.
237. Sengupta, R.; Bhattacharya, M.; Bandyopadhyay, S.; Bhowmick, A. K., A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites, *Prog. Polym. Sci.*, 36 (2011) 638-670.
238. Singh, V.; Joung, D.; Zhai, L.; Das, S.; Khondaker, S. I.; Seal, S., Graphene based materials: Past, present and future, *Prog. Mater. Sci.*, 56 (2011) 1178-1271.
239. Bai, L.; Zhang, Y.; Tong, W.; Sun, L.; Huang, H.; An, Q.; Tian, N.; Chu, P. K., Graphene for energy storage and conversion: Synthesis and interdisciplinary applications, *Electrochemical Energy Reviews*, 3 (2020) 395-430.
240. Lee, X. J.; Hiew, B. Y. Z.; Lai, K. C.; Lee, L. Y.; Gan, S.; Thangalazhy-Gopakumar, S.; Rigby, S., Review on graphene and its derivatives: Synthesis methods and potential industrial implementation, *J. Taiwan Inst. Chem. Eng.*, 98 (2019) 163-180.
241. Torres-Pinto, A.; Silva, C. G.; Faria, J. L.; Silva, A. M. T., Advances on graphyne-family members for superior photocatalytic behavior, *Adv. Sci.*, 8 (2021) 2003900.
242. Tang, H.; Hessel, C. M.; Wang, J.; Yang, N.; Yu, R.; Zhao, H.; Wang, D., Two-dimensional carbon leading to new photoconversion processes, *Chem. Soc. Rev.*, 43 (2014) 4281-4299.
243. Mahmoudi, T.; Wang, Y.; Hahn, Y.-B., Graphene and its derivatives for solar cells application, *Nano Energy*, 47 (2018) 51-65.
244. Yeh, T.-F.; Syu, J.-M.; Cheng, C.; Chang, T.-H.; Teng, H., Graphite oxide as a photocatalyst for hydrogen production from water, *Adv. Funct. Mater.*, 20 (2010) 2255-2262.
245. Khan, M. E.; Khan, M. M.; Cho, M. H., Recent progress of metal-graphene nanostructures in photocatalysis, *Nanoscale*, 10 (2018) 9427-9440.
246. Machado, B. F.; Serp, P., Graphene-based materials for catalysis, *Catal. Sci. Technol.*, 2 (2012) 54-75.
247. Niu, P.; Zhang, L.; Liu, G.; Cheng, H.-M., Graphene-like carbon nitride nanosheets for improved photocatalytic activities, *Adv. Funct. Mater.*, 22 (2012) 4763-4770.
248. Edwards, R. S.; Coleman, K. S., Graphene synthesis: Relationship to applications, *Nanoscale*, 5 (2013) 38-51.
249. Huang, Y.; Pan, Y.-H.; Yang, R.; Bao, L.-H.; Meng, L.; Luo, H.-L.; Cai, Y.-Q.; Liu, G.-D.; Zhao, W.-J.; Zhou, Z.; Wu, L.-M.; Zhu, Z.-L.; Huang, M.; Liu, L.-W.; Liu, L.;
-

- Cheng, P.; Wu, K.-H.; Tian, S.-B.; Gu, C.-Z.; Shi, Y.-G.; Guo, Y.-F.; Cheng, Z. G.; Hu, J.-P.; Zhao, L.; Yang, G.-H.; Sutter, E.; Sutter, P.; Wang, Y.-L.; Ji, W.; Zhou, X.-J.; Gao, H.-J., Universal mechanical exfoliation of large-area 2D crystals, *Nat. Commun.*, 11 (2020) 2453.
250. Ikram, R.; Jan, B. M.; Ahmad, W., Advances in synthesis of graphene derivatives using industrial wastes precursors; prospects and challenges, *J. Mater. Res. Technol.*, 9 (2020) 15924-15951.
251. Lin, T.; Tang, Y.; Wang, Y.; Bi, H.; Liu, Z.; Huang, F.; Xie, X.; Jiang, M., Scotch-tape-like exfoliation of graphite assisted with elemental sulfur and graphene–sulfur composites for high-performance lithium-sulfur batteries, *Energy Environ. Sci.*, 6 (2013) 1283-1290.
252. Song, D.; Mahajan, A.; Secor, E. B.; Hersam, M. C.; Francis, L. F.; Frisbie, C. D., High-resolution transfer printing of graphene lines for fully printed, flexible electronics, *ACS Nano*, 11 (2017) 7431-7439.
253. Assouik, J.; Hajji, L.; Boukir, A.; Herold, C.; Lagrange, P., Synthesis, structure and electrical behavior of the heavy alkali metal-arsenic alloys based graphite intercalation compounds, *Synth. Met.*, 218 (2016) 34-42.
254. Bai, H.; Li, C.; Shi, G., Functional composite materials based on chemically converted graphene, *Adv. Mater.*, 23 (2011) 1089-1115.
255. Shin, H.-J.; Kim, K. K.; Benayad, A.; Yoon, S.-M.; Park, H. K.; Jung, I.-S.; Jin, M. H.; Jeong, H.-K.; Kim, J. M.; Choi, J.-Y.; Lee, Y. H., Efficient reduction of graphite oxide by sodium borohydride and Its effect on electrical conductance, *Adv. Funct. Mater.*, 19 (2009) 1987-1992.
256. Liu, M.; Zhang, X.; Wu, W.; Liu, T.; Liu, Y.; Guo, B.; Zhang, R., One-step chemical exfoliation of graphite to ~100% few-layer graphene with high quality and large size at ambient temperature, *Chem. Eng. J.*, 355 (2019) 181-185.
257. Cui, X.; Zhang, C.; Hao, R.; Hou, Y., Liquid-phase exfoliation, functionalization and applications of graphene, *Nanoscale*, 3 (2011) 2118-2126.
258. Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; Gun'Ko, Y. K.; Boland, J. J.; Niraj, P.; Duesberg, G.; Krishnamurthy, S.; Goodhue, R.; Hutchison, J.; Scardaci, V.; Ferrari, A. C.; Coleman, J. N., High-yield production of graphene by liquid-phase exfoliation of graphite, *Nat. Nanotechnol.*, 3 (2008) 563-568.
259. Ciesielski, A.; Samorì, P., Graphene via sonication assisted liquid-phase exfoliation, *Chem. Soc. Rev.*, 43 (2014) 381-398.

-
260. Hernandez, Y.; Lotya, M.; Rickard, D.; Bergin, S. D.; Coleman, J. N., Measurement of multicomponent solubility parameters for graphene facilitates solvent discovery, *Langmuir*, 26 (2010) 3208-3213.
261. Baig, Z.; Mamat, O.; Mustapha, M.; Mumtaz, A.; Munir, K. S.; Sarfraz, M., Investigation of tip sonication effects on structural quality of graphene nanoplatelets (GNPs) for superior solvent dispersion, *Ultrason. Sonochem.*, 45 (2018) 133-149.
262. Achee, T. C.; Sun, W.; Hope, J. T.; Quitzau, S. G.; Sweeney, C. B.; Shah, S. A.; Habib, T.; Green, M. J., High-yield scalable graphene nanosheet production from compressed graphite using electrochemical exfoliation, *Sci. Rep.*, 8 (2018) 14525.
263. Wu, W.; Liu, M.; Gu, Y.; Guo, B.; Ma, H.; Wang, P.; Wang, X.; Zhang, R., Fast chemical exfoliation of graphite to few-layer graphene with high quality and large size via a two-step microwave-assisted process, *Chem. Eng. J.*, 381 (2020) 122592.
264. Parvez, K.; Wu, Z.-S.; Li, R.; Liu, X.; Graf, R.; Feng, X.; Müllen, K., Exfoliation of graphite into graphene in aqueous solutions of inorganic salts, *J. Am. Chem. Soc.*, 136 (2014) 6083-6091.
265. Liu, X.; Zhan, D.; Chao, D.; Cao, B.; Yin, J.; Zhao, J.; Li, Y.; Lin, J.; Shen, Z., Microwave-assisted production of giant graphene sheets for high performance energy storage applications, *J. Mater. Chem. A*, 2 (2014) 12166-12170.
266. Kumar, S.; McEvoy, N.; Kim, H.-Y.; Lee, K.; Peltekis, N.; Rezvani, E.; Nolan, H.; Weidlich, A.; Daly, R.; Duesberg, G. S., CVD growth and processing of graphene for electronic applications, *physica status solidi (b)*, 248 (2011) 2604-2608.
267. Allen, M. J.; Tung, V. C.; Kaner, R. B., Honeycomb carbon: A review of graphene, *Chem. Rev.*, 110 (2010) 132-145.
268. Campos-Delgado, J.; Botello-Méndez, A. R.; Algara-Siller, G.; Hackens, B.; Pardo, T.; Kaiser, U.; Dresselhaus, M. S.; Charlier, J.-C.; Raskin, J.-P., CVD synthesis of mono- and few-layer graphene using alcohols at low hydrogen concentration and atmospheric pressure, *Chem. Phys. Lett.*, 584 (2013) 142-146.
269. Mishra, N.; Boeckl, J.; Motta, N.; Iacopi, F., Graphene growth on silicon carbide: A review (*Phys. Status Solidi A* 9/2016), *physica status solidi (a)*, 213 (2016) 2269-2269.
270. Yeh, T.-F.; Chan, F.-F.; Hsieh, C.-T.; Teng, H., Graphite oxide with different oxygenated levels for hydrogen and oxygen production from water under illumination: The band positions of graphite oxide, *J. Phys. Chem. C*, 115 (2011) 22587-22597.
-

271. Latorre-Sánchez, M.; Primo, A.; García, H., P-doped graphene obtained by pyrolysis of modified alginate as a photocatalyst for hydrogen generation from water–methanol mixtures, *Angew. Chem. Int. Ed.*, 52 (2013) 11813-11816.
272. Putri, L. K.; Ng, B.-J.; Ong, W.-J.; Lee, H. W.; Chang, W. S.; Chai, S.-P., Heteroatom nitrogen- and boron-doping as a facile strategy to improve photocatalytic activity of standalone reduced graphene oxide in hydrogen evolution, *ACS Appl. Mater. Interfaces*, 9 (2017) 4558-4569.
273. Yeh, T.-F.; Teng, C.-Y.; Chen, S.-J.; Teng, H., Nitrogen-doped graphene oxide quantum dots as photocatalysts for overall water-splitting under visible light illumination, *Adv. Mater.*, 26 (2014) 3297-3303.
274. Hummers, W. S.; Offeman, R. E., Preparation of graphitic oxide, *J. Am. Chem. Soc.*, 80 (1958) 1339-1339.
275. Oliva, J.; Gomez-solis, C.; Diaz-Torres, L. A.; Martinez-Luevanos, A.; Martinez, A. I.; Coutino-Gonzalez, E., Photocatalytic hydrogen evolution by flexible graphene composites decorated with Ni(OH)₂ nanoparticles, *J. Phys. Chem. C*, 122 (2018) 1477-1485.
276. Chen, L.-C.; Teng, C.-Y.; Lin, C.-Y.; Chang, H.-Y.; Chen, S.-J.; Teng, H., Architecting nitrogen functionalities on graphene oxide photocatalysts for boosting hydrogen production in water decomposition process, *Adv. Energy Mater.*, 6 (2016) 1600719.
277. Latorre-Sánchez, M.; Esteve-Adell, I.; Primo, A.; García, H., Innovative preparation of MoS₂–graphene heterostructures based on alginate containing (NH₄)₂MoS₄ and their photocatalytic activity for H₂ generation, *Carbon*, 81 (2015) 587-596.
278. Xiang, Q.; Yu, J.; Jaroniec, M., Synergetic effect of MoS₂ and graphene as cocatalysts for enhanced photocatalytic H₂ production activity of TiO₂ nanoparticles, *J. Am. Chem. Soc.*, 134 (2012) 6575-6578.
279. Xue, W.; Hu, X.; Liu, E.; Fan, J., Novel reduced graphene oxide-supported Cd_{0.5}Zn_{0.5}S/g-C₃N₄ Z-scheme heterojunction photocatalyst for enhanced hydrogen evolution, *Appl. Surf. Sci.*, 447 (2018) 783-794.
280. Rahman, M. Z.; Zhang, J.; Tang, Y.; Davey, K.; Qiao, S.-Z., Graphene oxide coupled carbon nitride homo-heterojunction photocatalyst for enhanced hydrogen production, *Mater. Chem. Front.*, 1 (2017) 562–571.
281. Zhao, J.; Liu, Y.; Wang, Y.; Li, H.; Wang, J.; Li, Z., Boron doped graphitic carbon nitride dots dispersed on graphitic carbon nitride/graphene hybrid nanosheets as high

- performance photocatalysts for hydrogen evolution reaction, *Appl. Surf. Sci.*, 470 (2019) 923-932.
282. Zhang, X.; Sun, Y.; Cui, X.; Jiang, Z., A green and facile synthesis of TiO₂/graphene nanocomposites and their photocatalytic activity for hydrogen evolution, *Int. J. Hydrog. Energy*, 37 (2012) 811-815.
283. Fan, W.; Lai, Q.; Zhang, Q.; Wang, Y., Nanocomposites of TiO₂ and reduced graphene oxide as efficient photocatalysts for hydrogen evolution, *J. Phys. Chem. C*, 115 (2011) 10694-10701.
284. Song, L.; Guo, C.; Li, T.; Zhang, S., C60/graphene/g-C₃N₄ composite photocatalyst and mutually- reinforcing synergy to improve hydrogen production in splitting water under visible light radiation, *Ceram. Int.*, 43 (2017) 7901-7907.
285. Yan, M.; Hua, Y.; Zhu, F.; Sun, L.; Gu, W.; Shi, W., Constructing nitrogen doped graphene quantum dots-ZnNb₂O₆/g-C₃N₄ catalysts for hydrogen production under visible light, *Appl. Catal. B: Environ.*, 206 (2017) 531-537.
286. Nie, Y.-C.; Yu, F.; Wang, L.-C.; Xing, Q.-J.; Liu, X.; Pei, Y.; Zou, J.-P.; Dai, W.-L.; Li, Y.; Suib, S. L., Photocatalytic degradation of organic pollutants coupled with simultaneous photocatalytic H₂ evolution over graphene quantum dots/Mn-N-TiO₂/g-C₃N₄ composite catalysts: Performance and mechanism, *Appl. Catal. B: Environ.*, 227 (2018) 312-321.
287. Huang, Z.; Chen, H.; Zhao, L.; He, X.; Du, Y.; Fang, W.; Li, W.; Tian, P., Constructing g-C₃N₄ quantum dots modified g-C₃N₄/GO nanosheet aerogel for UV-Vis-NIR driven highly efficient photocatalytic H₂ production, *Int. J. Hydrog. Energy*, 44 (2019) 31041-31052.
288. Li, J.; Tang, Y.; Jin, R.; Meng, Q.; Chen, Y.; Long, X.; Wang, L.; Guo, H.; Zhang, S., Ultrasonic-microwave assisted synthesis of GO/g-C₃N₄ composites for efficient photocatalytic H₂ evolution, *Solid State Sci.*, 97 (2019) 105990.
289. Liu, X.; Xu, S.; Chi, H.; Xu, T.; Guo, Y.; Yuan, Y.; Yang, B., Ultrafine 1D graphene interlayer in g-C₃N₄/graphene/recycled carbon fiber heterostructure for enhanced photocatalytic hydrogen generation, *Chem. Eng. J.*, 359 (2019) 1352-1359.
290. Yang, X.; Tian, Z.; Chen, Y.; Huang, H.; Hu, J., One-pot calcination preparation of graphene/g-C₃N₄-Co photocatalysts with enhanced visible light photocatalytic activity, *Int. J. Hydrog. Energy*, 45 (2020) 12889-12902.

291. Egerton, R. F., Physical principles of electron microscopy: An introduction to TEM, SEM, and AEM, Springer, New York, USA, 2006.
292. Goodhew, P. J.; Humphreys, J.; Beanland, R., Electron microscopy and analysis, CRC Press, New York, USA, 2000.
293. Hall, C. E., Introduction to electron microscopy, McGrawHill Publishing Co., New York, USA, 1953.
294. Nellist, P. D., Scanning transmission electron microscopy, in: Science of Microscopy, Springer New York, USA, 2007.
295. Akhtar, K.; Khan, S. A.; Khan, S. B.; Asiri, A. M., Scanning electron microscopy: Principle and applications in nanomaterials characterization, in: Handbook of materials characterization, Springer International Publishing AG, Zurich, Switzerland, 2018.
296. Reimer, L., Transmission electron microscopy : Physics of image formation and microanalysis, Springer-Verlag Berlin Heidelberg, Berlin, Germany, 1984.
297. West, A. R., Solid state chemistry and its applications, John Wiley & Sons, Chichester, UK, 2014.
298. Heide, P. v. d., X-ray photoelectron spectroscopy: An introduction to principles and practices, John Wiley & Sons, Hoboken, New Jersey, USA, 2011.
299. Guinier, A., X-ray diffraction in crystals, imperfect crystals, and amorphous bodies, Courier Corporation, New York, USA, 1994.
300. Welker, R. W., Chapter 4 - Size analysis and identification of particles, in: Developments in surface contamination and cleaning - detection, characterization, and analysis of contaminants, William Andrew Publishing, Los Angeles, USA, 2012.
301. Yut, I.; Zofka, A., Attenuated total reflection (ATR) Fourier transform infrared (FT-IR) spectroscopy of oxidized polymer-modified bitumens, Appl. Spectrosc., 65 (2011) 765-770.
302. Stuart, B. H., Infrared spectroscopy: Fundamentals and applications, John Wiley & Sons, Chichester, UK, 2004.
303. Langmuir, I., The constitution and fundamental properties of solids and liquids. Part I. Solids, J. Am. Chem. Soc., 38 (1916) 2221-2295.
304. Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W., Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure Appl. Chem., 87 (2015) 1051–1069.

-
305. Brunauer, S.; Emmett, P. H.; Teller, E., Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.*, 60 (1938) 309-319.
306. Mirabella, F. M., *Modern techniques in applied molecular spectroscopy*, John Wiley & Sons, New York, USA, 1998.
307. Kortüm, G., *Reflectance spectroscopy principles, methods, applications*, Springer-Verlag Berlin Heidelberg, Berlin, Germany, 1969.
308. Bert M. Weckhuysen, P. V. D. V., Gabriela Catana, *Spectroscopy of transition metal Ions on surfaces*, Leuven University Press, Belgium, Brussels, 2000.
309. Simmons, E. L., Relation of the diffuse reflectance remission function to the fundamental optical parameters, *Optica Acta: International Journal of Optics*, 19 (1972) 845-851.
310. Tauc, J., Optical properties and electronic structure of amorphous Ge and Si, *Mater. Res. Bull.*, 3 (1968) 37-46.
311. Gfroerer, T. H., Photoluminescence in analysis of surfaces and interfaces, in: *Encyclopedia of analytical chemistry*, John Wiley & Sons, Tarzana, CA, USA, 2006.
312. Anpo, M.; Che, M., Applications of photoluminescence techniques to the characterization of solid surfaces in relation to adsorption, catalysis, and photocatalysis, in: *Advances in catalysis*, Academic Press, San Diego, California, USA, 1999.
313. Gelderman, K.; Lee, L.; Donne, S. W., Flat-band potential of a semiconductor: using the Mott–Schottky equation, *J. Chem. Educ.*, 84 (2007) 685.
314. Hankin, A.; Bedoya-Lora, F. E.; Alexander, J. C.; Regoutz, A.; Kelsall, G. H., Flat band potential determination: avoiding the pitfalls, *J. Mater. Chem. A*, 7 (2019) 26162-26176.
315. Albery, W. J.; O'Shea, G. J.; Smith, A. L., Interpretation and use of Mott–Schottky plots at the semiconductor/electrolyte interface, *J. Chem. Soc., Faraday Trans.*, 92 (1996) 4083-4085.
316. Lopes, T.; Andrade, L.; Le Formal, F.; Gratzel, M.; Sivula, K.; Mendes, A., Hematite photoelectrodes for water splitting: evaluation of the role of film thickness by impedance spectroscopy, *Phys. Chem. Chem. Phys.*, 16 (2014) 16515–16523.
317. Capelo, S.; Homem, P. M.; Cavaleiro, J.; Fonseca, I. T. E., Linear sweep voltammetry: A cheap and powerful technique for the identification of the silver tarnish layer constituents, *J. Solid State Electrochem.*, 17 (2013) 223-234.
318. Bontempelli, G.; Dossi, N.; Toniolo, R., Linear sweep and cyclic, in: *Reference module in chemistry, molecular sciences and chemical engineering*, Elsevier, Udine, Italy, 2016.
-

319. Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L., A practical beginner's guide to cyclic voltammetry, *J. Chem. Educ.*, 95 (2018) 197-206.
320. Yan, D.; Bazant, M. Z.; Biesheuvel, P. M.; Pugh, M. C.; Dawson, F. P., Theory of linear sweep voltammetry with diffuse charge: Unsupported electrolytes, thin films, and leaky membranes, *Physical Review E*, 95 (2017) 033303.
321. Sharma, S.; Shukla, P.; Misra, A.; Mishra, P. R., Chapter 8 - Interfacial and colloidal properties of emulsified systems: Pharmaceutical and biological perspective, in: *Colloid and interface science in pharmaceutical research and development*, Elsevier, Amsterdam, Netherlands, 2014.
322. Shnoudeh, A. J.; Hamad, I.; Abdo, R. W.; Qadumii, L.; Jaber, A. Y.; Surchi, H. S.; Alkelany, S. Z., Chapter 15 - Synthesis, characterization, and applications of metal nanoparticles, in: *Biomaterials and bionanotechnology*, Academic Press, London, UK, 2019.
323. Lu, G. W.; Gao, P., Chapter 3 - Emulsions and microemulsions for topical and transdermal drug delivery, in: *Handbook of non-invasive drug delivery systems*, William Andrew Publishing, Boston, USA, 2010.
324. Bacsá, R. R.; Cameán, I.; Ramos, A.; García, A. B.; Tishkova, V.; Bacsá, W. S.; Gallagher, J. R.; Miller, J. T.; Navas, H.; Jourdain, V.; Girleanu, M.; Ersen, O.; Serp, P., Few layer graphene synthesis on transition metal ferrite catalysts, *Carbon*, 89 (2015) 350–360.
325. Machado, B. F.; Bacsá, R. R.; Rivera-Cárcamo, C.; Serp, P., Preparation of few-layer graphene/Carbon nanotube hybrids using oxide spinel catalysts, *C*, 5 (2019) 28–38.
326. Hossain, S.; Chu, W.-S.; Lee, C. S.; Ahn, S.-H.; Chun, D.-M., Photocatalytic performance of few-layer graphene/ WO_3 thin films prepared by a nano-particle deposition system, *Mater. Chem. Phys.*, 226 (2019) 141–150.
327. Purkait, T.; Singh, G.; Singh, M.; Kumar, D.; Dey, R. S., Large area few-layer graphene with scalable preparation from waste biomass for high-performance supercapacitor, *Sci. Rep.*, 7 (2017) 15239.
328. Thomas, R. T.; Abdul Rasheed, P.; Sandhyarani, N., Synthesis of nanotitania decorated few-layer graphene for enhanced visible light driven photocatalysis, *J. Colloid Interface Sci.*, 428 (2014) 214–221.
329. Lee, J.-S.; Ahn, H.-J.; Yoon, J.-C.; Jang, J.-H., Three-dimensional nano-foam of few-layer graphene grown by CVD for DSSC, *Phys. Chem. Chem. Phys.*, 14 (2012) 7938–7943.

-
330. Gomes Silva, C.; Luz, I.; Llabrés i Xamena, F. X.; Corma, A.; García, H., Water stable Zr–benzenedicarboxylate metal–organic frameworks as photocatalysts for hydrogen generation, *Chem. Eur. J.*, 16 (2010) 11133–11138.
331. Da Silva, E. S.; Moura, N. M. M.; Neves, M. G. P. M. S.; Coutinho, A.; Prieto, M.; Silva, C. G.; Faria, J. L., Novel hybrids of graphitic carbon nitride sensitized with free-base meso-tetrakis(carboxyphenyl) porphyrins for efficient visible light photocatalytic hydrogen production, *Appl. Catal. B: Environ.*, 221 (2018) 56–69.
332. Wang, Y.; Bayazit, M. K.; Moniz, S. J. A.; Ruan, Q.; Lau, C. C.; Martsinovich, N.; Tang, J., Linker-controlled polymeric photocatalyst for highly efficient hydrogen evolution from water, *Energy Environ. Sci.*, 10 (2017) 1643–1651.
333. Da Silva, E. S.; Moura, N. M. M.; Coutinho, A.; Dražić, G.; Teixeira, B. M. S.; Sobolev, N. A.; Silva, C. G.; Neves, M. G. P. M. S.; Prieto, M.; Faria, J. L., β -cyclodextrin as a precursor to holey C-doped g-C₃N₄ nanosheets for photocatalytic hydrogen generation, *ChemSusChem*, 11 (2018) 2681–2694.
334. Sun, L.; Du, T.; Hu, C.; Chen, J.; Lu, J.; Lu, Z.; Han, H., Antibacterial activity of graphene oxide/g-C₃N₄ composite through photocatalytic disinfection under visible light, *ACS Sustain. Chem. Eng.*, 5 (2017) 8693–8701.
335. Makuła, P.; Pacia, M.; Macyk, W., How to correctly determine the band gap energy of modified semiconductor photocatalysts based on UV–Vis spectra, *J. Phys. Chem. Lett.*, 9 (2018) 6814–6817.
336. Wu, M.; Gong, Y.; Nie, T.; Zhang, J.; Wang, R.; Wang, H.; He, B., Template-free synthesis of nanocage-like g-C₃N₄ with high surface area and nitrogen defects for enhanced photocatalytic H₂ activity, *J. Mater. Chem. A*, 7 (2019) 5324–5332.
337. Shi, L.; Yang, L.; Zhou, W.; Liu, Y.; Yin, L.; Hai, X.; Song, H.; Ye, J., Photoassisted construction of holey defective g-C₃N₄ photocatalysts for efficient visible-light-driven H₂O₂ production, *Small*, 14 (2018) 1703142.
338. Liao, G.; Gong, Y.; Zhang, L.; Gao, H.; Yang, G.-J.; Fang, B., Semiconductor polymeric graphitic carbon nitride photocatalysts: The “holy grail” for the photocatalytic hydrogen evolution reaction under visible light, *Energy Environ. Sci.*, 12 (2019) 2080–2147.
339. Dong, G.; Zhang, Y.; Pan, Q.; Qiu, J., A fantastic graphitic carbon nitride (g-C₃N₄) material: Electronic structure, photocatalytic and photoelectronic properties, *J. Photochem. Photobiol. C*, 20 (2014) 33–50.
-

340. Najafi, L.; Bellani, S.; Oropesa-Nuñez, R.; Martín-García, B.; Prato, M.; Bonaccorso, F., Single-/few-layer graphene as long-lasting electrocatalyst for hydrogen evolution reaction, *ACS Appl. Energy Mater.*, 2 (2019) 5373–5379.
341. Jeong, T.; Piao, H.; Park, S.; Yang, J.-H.; Choi, G.; Wu, Q.; Kang, H.; Woo, H. J.; Jung, S. J.; Kim, H.; Shin, B. G.; Kim, Y.; Hwang, E. H.; Choy, J.-H.; Song, Y. J., Atomic and electronic structures of graphene-decorated graphitic carbon nitride (g-C₃N₄) as a metal-free photocatalyst under visible-light, *Appl. Catal. B: Environ.*, 256 (2019) 117850.
342. Sun, Z.; Masa, J.; Weide, P.; Fairclough, S. M.; Robertson, A. W.; Ebbinghaus, P.; Warner, J. H.; Tsang, S. C. E.; Muhler, M.; Schuhmann, W., High-quality functionalized few-layer graphene: Facile fabrication and doping with nitrogen as a metal-free catalyst for the oxygen reduction reaction, *J. Mater. Chem. A*, 3 (2015) 15444–15450.
343. Tonda, S.; Kumar, S.; Gawli, Y.; Bhardwaj, M.; Ogale, S., g-C₃N₄ (2D)/CdS (1D)/rGO (2D) dual-interface nano-composite for excellent and stable visible light photocatalytic hydrogen generation, *Int. J. Hydrog. Energy*, 42 (2017) 5971–5984.
344. Holzwarth, U.; Gibson, N., The Scherrer equation versus the 'Debye-Scherrer equation', *Nat. Nanotechnol.*, 6 (2011) 534–534.
345. Fina, F.; Callear, S. K.; Carins, G. M.; Irvine, J. T. S., Structural investigation of graphitic carbon nitride via XRD and neutron diffraction, *Chem. Mater.*, 27 (2015) 2612–2618.
346. Xing, W.; Li, C.; Chen, G.; Han, Z.; Zhou, Y.; Hu, Y.; Meng, Q., Incorporating a novel metal-free interlayer into g-C₃N₄ framework for efficiency enhanced photocatalytic H₂ evolution activity, *Appl. Catal. B: Environ.*, 203 (2017) 65–71.
347. Huang, H.; Xiao, K.; Tian, N.; Dong, F.; Zhang, T.; Du, X.; Zhang, Y., Template-free precursor-surface-etching route to porous, thin g-C₃N₄ nanosheets for enhancing photocatalytic reduction and oxidation activity, *J. Mater. Chem. A*, 5 (2017) 17452–17463.
348. Eckmann, A.; Felten, A.; Mishchenko, A.; Britnell, L.; Krupke, R.; Novoselov, K. S.; Casiraghi, C., Probing the nature of defects in graphene by Raman spectroscopy, *Nano Lett.*, 12 (2012) 3925–3930.
349. Rao, K. S.; Senthilnathan, J.; Liu, Y.-F.; Yoshimura, M., Role of peroxide ions in formation of graphene nanosheets by electrochemical exfoliation of graphite, *Sci. Rep.*, 4 (2014) 4237.
350. Casiraghi, C.; Hartschuh, A.; Qian, H.; Piscanec, S.; Georgi, C.; Fasoli, A.; Novoselov, K. S.; Basko, D. M.; Ferrari, A. C., Raman spectroscopy of graphene edges, *Nano Lett.*, 9 (2009) 1433–1441.

-
351. Basko, D. M., Theory of resonant multiphonon Raman scattering in graphene, *Phys. Rev. B*, 78 (2008) 125418.
352. Venezuela, P.; Lazzeri, M.; Mauri, F., Theory of double-resonant Raman spectra in graphene: Intensity and line shape of defect-induced and two-phonon bands, *Phys. Rev. B*, 84 (2011) 035433.
353. Cançado, L. G.; Jorio, A.; Ferreira, E. H. M.; Stavale, F.; Achete, C. A.; Capaz, R. B.; Moutinho, M. V. O.; Lombardo, A.; Kulmala, T. S.; Ferrari, A. C., Quantifying defects in graphene via Raman spectroscopy at different excitation energies, *Nano Lett.*, 11 (2011) 3190–3196.
354. Yu, X.; Li, Y.; Hu, X.; Zhang, D.; Tao, Y.; Liu, Z.; He, Y.; Haque, M. A.; Liu, Z.; Wu, T.; Wang, Q. J., Narrow bandgap oxide nanoparticles coupled with graphene for high performance mid-infrared photodetection, *Nat. Commun.*, 9 (2018) 4299.
355. Rao, C. N. R.; Voggu, R., Charge-transfer with graphene and nanotubes, *Mater. Today*, 13 (2010) 34–40.
356. Chen, J.; Xu, X.; Li, T.; Pandiselvi, K.; Wang, J., Toward high performance 2D/2D hybrid photocatalyst by electrostatic assembly of rationally modified carbon nitride on reduced graphene oxide, *Sci. Rep.*, 6 (2016) 37318.
357. Zhang, Y.; Mori, T.; Niu, L.; Ye, J., Non-covalent doping of graphitic carbon nitride polymer with graphene: Controlled electronic structure and enhanced optoelectronic conversion, *Energy Environ. Sci.*, 4 (2011) 4517–4521.
358. Ma, X.; Wei, Y.; Wei, Z.; He, H.; Huang, C.; Zhu, Y., Probing π - π stacking modulation of g-C₃N₄/graphene heterojunctions and corresponding role of graphene on photocatalytic activity, *J. Colloid Interface Sci.*, 508 (2017) 274–281.
359. Leenaerts, O.; Partoens, B.; Peeters, F. M.; Volodin, A.; Van Haesendonck, C., The work function of few-layer graphene, *J. Phys. Condens. Matter*, 29 (2017) 035003.
360. Bafekry, A.; Neek-Amal, M., Tuning the electronic properties of graphene–graphitic carbon nitride heterostructures and heterojunctions by using an electric field, *Phys. Rev. B*, 101 (2020) 085417.
361. Fu, Y.; Zhu, J.; Hu, C.; Wu, X.; Wang, X., Covalently coupled hybrid of graphitic carbon nitride with reduced graphene oxide as a superior performance lithium-ion battery anode, *Nanoscale*, 6 (2014) 12555–12564.
-

362. Yan, J.-Q.; Peng, W.; Zhang, S.-S.; Lei, D.-P.; Huang, J.-H., Ternary Ni₂P/reduced graphene oxide/g-C₃N₄ nanotubes for visible light-driven photocatalytic H₂ production, *Int. J. Hydrog. Energy*, 45 (2020) 16094–16104.
363. Fan, C.; Miao, J.; Xu, G.; Liu, J.; Lv, J.; Wu, Y., Graphitic carbon nitride nanosheets obtained by liquid stripping as efficient photocatalysts under visible light, *RSC Adv.*, 7 (2017) 37185-37193.
364. Zhang, J.; Zhang, M.; Sun, R. Q.; Wang, X., A facile band alignment of polymeric carbon nitride semiconductors to construct isotype heterojunctions, *Angew. Chem. Int. Ed. Engl.*, 51 (2012) 10145-9.
365. Song, B.; Zeng, Z.; Zeng, G.; Gong, J.; Xiao, R.; Ye, S.; Chen, M.; Lai, C.; Xu, P.; Tang, X., Powerful combination of g-C₃N₄ and LDHs for enhanced photocatalytic performance: A review of strategy, synthesis, and applications, *Adv. Colloid Interface Sci.*, 272 (2019) 101999.
366. Salehi, G.; Abazari, R.; Mahjoub, A. R., Visible-light-induced graphitic-C₃N₄@nickel–aluminum layered double hydroxide nanocomposites with enhanced photocatalytic activity for removal of dyes in water, *Inorg. Chem.*, 57 (2018) 8681-8691.
367. Pawar, R. C.; Kang, S.; Han, H.; Choi, H.; Lee, C. S., In situ reduction and exfoliation of g-C₃N₄ nanosheets with copious active sites via a thermal approach for effective water splitting, *Catal. Sci. Technol.*, 9 (2019) 1004-1012.
368. Thurston, J. H.; Hunter, N. M.; Cornell, K. A., Preparation and characterization of photoactive antimicrobial graphitic carbon nitride (g-C₃N₄) films, *RSC Adv.*, 6 (2016) 42240-42248.
369. Zhu, J.; Xiao, P.; Li, H.; Carabineiro, S. A. C., Graphitic carbon nitride: Synthesis, properties, and applications in catalysis, *ACS Appl. Mater. Interfaces*, 6 (2014) 16449-16465.
370. Fu, J.; Yu, J.; Jiang, C.; Cheng, B., g-C₃N₄-based heterostructured photocatalysts, *Adv. Energy Mater.*, 8 (2018) 1701503.
371. Li, L.; Hui, K. S.; Hui, K. N.; Cho, Y.-R., Ultrathin petal-like NiAl layered double oxide/sulfide composites as an advanced electrode for high-performance asymmetric supercapacitors, *J. Mater. Chem. A*, 5 (2017) 19687-19696.
372. Bian, J.; Huang, C.; Zhang, R.-Q., Graphitic carbon nitride film: An emerging star for catalytic and optoelectronic applications, *ChemSusChem*, 9 (2016) 2723-2735.

-
373. Zhang, X.; Xie, X.; Wang, H.; Zhang, J.; Pan, B.; Xie, Y., Enhanced photoresponsive ultrathin graphitic-phase C_3N_4 nanosheets for bioimaging, *J. Am. Chem. Soc.*, 135 (2013) 18-21.
374. Jiang, J.; Ou-yang, L.; Zhu, L.; Zheng, A.; Zou, J.; Yi, X.; Tang, H., Dependence of electronic structure of g- C_3N_4 on the layer number of its nanosheets: A study by Raman spectroscopy coupled with first-principles calculations, *Carbon*, 80 (2014) 213-221.
375. Cao, S.; Zhou, N.; Gao, F.; Chen, H.; Jiang, F., All-solid-state Z-scheme 3,4-dihydroxybenzaldehyde-functionalized Ga_2O_3 /graphitic carbon nitride photocatalyst with aromatic rings as electron mediators for visible-light photocatalytic nitrogen fixation, *Appl. Catal. B: Environ.*, 218 (2017) 600-610.
376. Zhao, F.; Zhan, G.; Zhou, S.-F., Intercalation of laminar Cu–Al LDHs with molecular TCPP(M) (M = Zn, Co, Ni, and Fe) towards high-performance CO_2 hydrogenation catalysts, *Nanoscale*, 12 (2020) 13145-13156.
377. Wu, L.; Wan, G.; Shi, S.; He, Z.; Xu, X.; Tang, Y.; Hao, C.; Wang, G., Atomic layer deposition-assisted growth of CuAl LDH on carbon fiber as a peroxidase mimic for colorimetric determination of H_2O_2 and glucose, *New J. Chem.*, 43 (2019) 5826-5832.
378. Peng, X.; Luo, W.; Wang, M.; Hu, F.; Qiu, F.; Dai, H., Insights into the adsorption mechanism of carbon cellulose fiber loaded globular flowers bimetallic layered double hydroxide for efficiency pollutant removal, *J. Mol. Liq.*, 290 (2019) 111201.
379. Zhang, C.; Liang, X.; Lu, Y.; Li, H.; Xu, X., Performance of CuAl-LDH/Gr nanocomposite-based electrochemical sensor with regard to trace glyphosate detection in water, *Sensors*, 20 (2020) 4146.
380. Song, Q.; Liu, W.; Bohn, C. D.; Harper, R. N.; Sivaniah, E.; Scott, S. A.; Dennis, J. S., A high performance oxygen storage material for chemical looping processes with CO_2 capture, *Energy Environ. Sci.*, 6 (2013) 288-298.
381. Hu, Q.; Yang, L.; Fan, G.; Li, F., Greatly enhanced stability of supported copper nanocatalyst with a thin nitrogen-doped carbon overlayer for transfer dehydrogenation, *ChemNanoMat*, 2 (2016) 888-896.
382. Chen, X.; Mi, F.; Zhang, H.; Zhang, H., Facile synthesis of a novel magnetic core-shell hierarchical composite submicrospheres $Fe_3O_4@CuNiAl-LDH$ under ambient conditions, *Mater. Lett.*, 69 (2012) 48-51.
-

383. Li, J.; Zhang, S.; Chen, Y.; Liu, T.; Liu, C.; Zhang, X.; Yi, M.; Chu, Z.; Han, X., A novel three-dimensional hierarchical CuAl layered double hydroxide with excellent catalytic activity for degradation of methyl orange, *RSC Adv.*, 7 (2017) 29051-29057.
384. Adhikari, S. P.; Awasthi, G. P.; Kim, K.-S.; Park, C. H.; Kim, C. S., Synthesis of three-dimensional mesoporous Cu–Al layered double hydroxide/g-C₃N₄ nanocomposites on Ni-foam for enhanced supercapacitors with excellent long-term cycling stability, *Dalton Trans.*, 47 (2018) 4455-4466.
385. Peng, X.; Wang, M.; Hu, F.; Qiu, F.; Zhang, T.; Dai, H.; Cao, Z., Multipath fabrication of hierarchical CuAl layered double hydroxide/carbon fiber composites for the degradation of ammonia nitrogen, *J. Environ. Manage.*, 220 (2018) 173-182.
386. González-Olvera, R.; Urquiza-Castro, C. I.; Negrón-Silva, G. E.; Ángeles-Beltrán, D.; Lomas-Romero, L.; Gutiérrez-Carrillo, A.; Lara, V. H.; Santillan, R.; Morales-Serna, J. A., Cu–Al mixed oxide catalysts for azide–alkyne 1,3-cycloaddition in ethanol–water, *RSC Adv.*, 6 (2016) 63660-63666.
387. Nie, G.; Zhang, L.; Lu, X.; Bian, X.; Sun, W.; Wang, C., A one-pot and in situ synthesis of CuS-graphene nanosheet composites with enhanced peroxidase-like catalytic activity, *Dalton Trans.*, 42 (2013) 14006-14013.
388. Dou, L.; Zhang, H., Facile assembly of nanosheet array-like CuMgAl-layered double hydroxide/rGO nanohybrids for highly efficient reduction of 4-nitrophenol, *J. Mater. Chem. A*, 4 (2016) 18990-19002.
389. Mureșeanu, M.; Pușcașu, M.; Șomărescu, S.; Cârjă, G., CuII(Sal-Ala)/CuAlLDH hybrid as novel efficient catalyst for artificial superoxide dismutase (SOD) and cyclohexene oxidation by H₂O₂, *Catal. Lett.*, 145 (2015) 1529-1540.
390. Almoisheer, N.; Alseroury, F. A.; Kumar, R.; Aslam, M.; Barakat, M. A., Adsorption and anion exchange insight of indigo carmine onto CuAl-LDH/SWCNTs nanocomposite: kinetic, thermodynamic and isotherm analysis, *RSC Adv.*, 9 (2019) 560-568.
391. Liu, J.; Li, J.; Bing, X.; Ng, D. H. L.; Cui, X.; Ji, F.; Kionga, D. D., ZnCr-LDH/N-doped graphitic carbon-incorporated g-C₃N₄ 2D/2D nanosheet heterojunction with enhanced charge transfer for photocatalysis, *Mater. Res. Bull.*, 102 (2018) 379-390.
392. Chang, F.; Li, C.; Luo, J.; Xie, Y.; Deng, B.; Hu, X., Enhanced visible-light-driven photocatalytic performance of porous graphitic carbon nitride, *Appl. Surf. Sci.*, 358 (2015) 270-277.

-
393. Thaweesak, S.; Wang, S.; Lyu, M.; Xiao, M.; Peerakiatkhajohn, P.; Wang, L., Boron-doped graphitic carbon nitride nanosheets for enhanced visible light photocatalytic water splitting, *Dalton Trans.*, 46 (2017) 10714-10720.
394. Pedrosa, M.; Sampaio, M. J.; Horvat, T.; Nunes, O. C.; Dražić, G.; Rodrigues, A. E.; Figueiredo, J. L.; Silva, C. G.; Silva, A. M. T.; Faria, J. L., Visible-light-induced self-cleaning functional fabrics using graphene oxide/carbon nitride materials, *Appl. Surf. Sci.*, 497 (2019) 143757.
395. Ding, J.; Xu, W.; Wan, H.; Yuan, D.; Chen, C.; Wang, L.; Guan, G.; Dai, W.-L., Nitrogen vacancy engineered graphitic C₃N₄-based polymers for photocatalytic oxidation of aromatic alcohols to aldehydes, *Appl. Catal. B: Environ.*, 221 (2018) 626-634.
396. Velu, S.; Suzuki, K.; Hashimoto, S.; Satoh, N.; Ohashi, F.; Tomura, S., The effect of cobalt on the structural properties and reducibility of CuCoZnAl layered double hydroxides and their thermally derived mixed oxides, *J. Mater. Chem.*, 11 (2001) 2049-2060.
397. Velu, S.; Suzuki, K.; Okazaki, M.; Kapoor, M. P.; Osaki, T.; Ohashi, F., Oxidative steam reforming of methanol over CuZnAl(Zr)-oxide catalysts for the selective production of hydrogen for fuel cells: Catalyst characterization and performance evaluation, *J. Catal.*, 194 (2000) 373-384.
398. Zhu, S.; Wang, D., Photocatalysis: Basic principles, diverse forms of implementations and emerging scientific opportunities, *Adv. Energy Mater.*, 7 (2017) 1700841.
399. Zhou, X.; Li, Y.; Xing, Y.; Li, J.; Jiang, X., Effects of the preparation method of Pt/g-C₃N₄ photocatalysts on their efficiency for visible-light hydrogen production, *Dalton Trans.*, 48 (2019) 15068-15073.
400. Wang, M.; Shen, S.; Li, L.; Tang, Z.; Yang, J., Effects of sacrificial reagents on photocatalytic hydrogen evolution over different photocatalysts, *J. Mater. Sci.*, 52 (2017) 5155-5164.
401. Kumaravel, V.; Imam, M. D.; Badreldin, A.; Chava, R. K.; Do, J. Y.; Kang, M.; Abdel-Wahab, A., Photocatalytic hydrogen production: Role of sacrificial reagents on the activity of oxide, carbon, and sulfide catalysts, *Catalysts*, 9 (2019) 276.
402. Aslam, I.; Hassan Farooq, M.; Ghani, U.; Rizwan, M.; Nabi, G.; Shahzad, W.; Boddula, R., Synthesis of novel g-C₃N₄ microrods: A metal-free visible-light-driven photocatalyst, *Mater. Sci. Energy Technol.*, 2 (2019) 401-407.
-

