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DEVELOPMENT OF DYE-SENSITIZED SOLAR CELLS FOR SYNERGISTICALLY HOSTING SENSING DEVICES

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Development of Dye-Sensitized Solar Cells for Synergistically Hosting Sensing Devices

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Unlike the rest of my thesis, this section is going to be short and sweet. I apologize to whomever has to read this thesis... I don't know what I was thinking when I wrote more than 300 pages!

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Preface

The present work was developed at the Laboratory for Process Engineering, Environment, Biotechnology and Energy (LEPABE) facilities, in the Chemical Engineering Department of the Faculty of Engineering - University of Porto (FEUP), Polytechnic of Porto - School of Engineering (ISEP) and in the Chemical Engineering Department of Faculty of Sciences and Technology - University of Coimbra (FCTUC), between 2017 and 2022 under the FCT (Foundation for Science and Technology) grant SFRH/BD/129761/2017. The present work was supervised by Professor Adélio Mendes, Professor Goreti Sales and Doctor Dzmitry Ivanou.

This thesis presents six chapters: one introduction chapter; four scientific papers, where each paper represents one independent chapter; and a final chapter with the general conclusions and the outlook on future work.

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ABSTRACT

The world is constantly changing, and the energy demand is not decelerating. Small electronic devices interconnected by the Internet of Things (IoT) are expected to surpass seventy-five billion units by 2025, which is stimulating the search for cordless, long-lasting power sources as add-ons or alternatives for conventional batteries. A vast majority of these devices are designed for indoor use, thus promoting the indoor photovoltaic (iPV) market, which is expected to be ca. 7.70×10^8 € in 2023. Moreover, the global market size for biosensors, which are fundamental for point-of-care detection methods, was valued at 2.45×10^{10} € in 2021 and is expected to grow 8.0 % per year until 2030. Since many of these IoT devices and biosensors are battery-operated, a lot of batteries could end up in landfills if other alternative power sources are not considered. Thus, this thesis targeted the development of high-performing Dye-sensitized solar cells (DSSCs), which can provide enough power to fuel several small and low-power devices. DSSCs are one of the most promising iPV technologies due to their high-power conversion efficiency under weak indoor light and unique aesthetic adaptability to most interior designs. Likewise, they are suitable for powering both small electronic devices and biosensors, making them a desired alternative to conventional batteries.

To achieve the research goals of this thesis, DSSCs with various dye/electrolyte systems were developed and optimized in search of the best-performing device architecture under solar and artificial illumination. The suitability of each DSSC system was evaluated with the characteristic *J-V* curves, incident photon-to-current conversion efficiency (IPCE) and electrochemical impedance spectroscopy, whereas the counter-electrode materials were also assessed based on their apparent activation energy. Iodine solar cells were paired with N719 dye to achieve power conversion efficiencies (PCEs) of 9.84 % and 23.3 % under 1-Sun and 1000 lx, respectively. Cobalt solar cells were also optimized studying the interactions between electrolyte/catalytic material and a new PEDOT:PSS and graphene

composite counter-electrode. PCEs of 10.4 % and 29.7 % under 1-Sun and 1000 lx, respectively, were obtained when coupling a porphyrin dye (YD2-o-C8) with this counter-electrode catalyst. Further optimization of Cobalt solar cells under solar and artificial light resulted in an overall improvement of the performance under both light sources. The champion cobalt cell displayed a PCE of 11 % under 1-Sun; under artificial light (1000 lx), the PCE obtained was 32.0 % and 27.3 % when illuminated from the photoanode side or the counter-electrode side, respectively

Lastly, as proof-of-concept, an autonomous and self-signaling device was constructed coupling a DSSC with a biosensor and an electrochromic cell interfaced in the external circuit of the hybrid DSSC/biosensor. The biosensor was prepared using molecularly imprinted material as biorecognition element, meeting both low-cost and stability requirements. After suitable optimization approaches, the device demonstrated high sensitivity (0.47 Ω /decade of sarcosine concentration), good selectivity, a low detection limit (0.33 ng/mL), and a concentration range with clinical interest (1 ng/mL and 10 μ g/mL). Thus, the device ensured successful applicability to the detection of sarcosine in actual clinical samples.

SUMÁRIO

O mundo está em constante mudança e a procura de energia não irá abrandar. Os pequenos dispositivos electrónicos interligados pela Internet das Coisas (IoT) vão, certamente, ultrapassar os setenta e cinco bilhões de unidades até 2025, o que tem estimulado a procura por fontes de energia sem fio e de longa duração, que poderão ser utilizadas como complementos ou alternativas às baterias convencionais. A grande maioria desses dispositivos é idealizada para ser utilizada no interior, promovendo assim o mercado fotovoltaico de interiores (iPV), que deve chegar aos 7.70×10^8 € em 2023. Adicionalmente, o tamanho do mercado global de biossensores, que são fundamentais como métodos de deteção precoces, foi avaliado em 2.45×10^{10} € em 2021 e deve crescer 8.0% ao ano até 2030. Muitos desses dispositivos IoT e biossensores utilizam baterias não recarregáveis e, dada a tamanha procura destes dispositivos, muitas dessas baterias podem acabar em aterros sanitários se outras fontes alternativas de energia não forem consideradas. Por conseguinte, esta tese teve como objetivo o desenvolvimento de células solares sensibilizadas por corante (DSSCs) de alto desempenho, que podem fornecer energia suficiente para alimentar vários dispositivos pequenos e de baixa potência. As DSSCs são uma das tecnologias iPV mais promissoras devido à sua alta eficiência na conversão de energia proveniente da luz artificial de baixa intensidade e versatilidade que apresentam em relação à diversidade das decorações de interior. Da mesma forma, as DSSCs podem ser adaptadas para alimentar pequenos dispositivos electrónicos e biossensores, tornando-se numa ótima alternativa às baterias convencionais.

Para cumprir este plano de tese ambicioso, DSSCs utilizando vários sistemas corantes/electrólitos foram desenvolvidas e otimizadas na busca da estrutura que fornecessem o melhor desempenho sob iluminação solar e artificial. O desempenho de cada sistema de DSSCs foi avaliado com as curvas características *J-V*, eficiência de conversão fotão-corrente incidente (IPCE) e espectroscopia de impedância eletroquímica, enquanto os catalisadores utilizados como contra-eléktodos foram avaliados através da

energia de ativação aparente. As células solares de iodo foram testadas em conjunto com o corante N719 para atingir eficiências de conversão de energia (PCEs) de 9.84 % e 23.3 % sob 1-Sol e 1000 lx, respectivamente. Células solares de cobalto também foram otimizadas, estudando as interações entre eletrólito/catalisador e um novo contra-elétrodo compósito de PEDOT:PSS e grafeno. PCEs de 10.4 % e 29.7% sob 1-Sol e 1000 lx, respectivamente, foram obtidos ao utilizar uma porfirina (YD2-o-C8) com este catalisador como contra-elétrodo. A otimização adicional das células solares de cobalto sob luz solar e artificial resultou numa melhoria geral do desempenho em ambas as fontes de luz. A melhor DSSC de cobalto apresentou um PCE de 11 % sob 1-Sol; sob luz artificial (1000 lx), o PCE obtido foi de 32.0 % e 27.3 % quando iluminado do lado do fotoanodo ou do lado do contra-elétrodo, respectivamente.

Por fim, como prova de conceito, foi construído um dispositivo autónomo juntando uma DSSC com um biossensor e uma célula eletrocrômica interligada ao circuito externo do dispositivo híbrido DSSC/biossensor. O biossensor foi preparado usando material de impressão molecular como elemento de bioreconhecimento, método de baixo custo e que confere estabilidade ao dispositivo. Após várias etapas de otimização, o dispositivo demonstrou alta sensibilidade ($0.47 \text{ } \Omega/\text{década}$ de concentração de sarcosina), boa seletividade, baixo limite de detecção (0.33 ng/mL) e uma gama de concentrações com interesse clínico (1 ng/mL e $10 \text{ } \mu\text{g/mL}$). Assim, o dispositivo desenvolvido garante a detecção bem-sucedida de sarcosina em amostras reais.

LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations	Definition	Units
A	Area	cm^2
AIPV	Automotive-integrated photovoltaics	
BAPV	Building applied photovoltaics	
BIPV	Building-integrated photovoltaics	
c_0	Speed of light	$\text{m}\cdot\text{s}^{-1}$
CDA	Chenodeoxycholic acid	
CdTe	Cadmium telluride	
CFL	Compact fluorescent lamp	
CIGS	Copper indium gallium selenide	
CIS	Copper indium (di)selenide	
CPE	Constant phase element	
c-Si	Crystalline silicon	
DMSO	Dimethyl sulfoxide	
DSSC	Dye-sensitized solar cell	
e^-	Electrons	
E_a	Apparent activation energy	eV
E_{CB}	Conduction band energy	eV
E_F	Fermi Energy	eV
E_{redox}	Electrolyte redox potential	eV
ΔE_p	Peak-to-peak separation	
EDOT	3,4-ethylenedioxythiophene	
EIS	Electrochemical impedance spectra	

F	Faraday's constant ($F = 96\,500\text{ C}\cdot\text{mol}^{-1}$)	$\text{C}\cdot\text{mol}^{-1}$
FTO	Fluorine-doped tin oxide	
GNP	Graphene nanoplatelets	
h	Planck's constant ($h = 6.626\times 10^{-34}\text{ m}^2\cdot\text{kg}\cdot\text{s}^{-1}$)	$\text{m}^2\cdot\text{kg}\cdot\text{s}^{-1}$
HOMO	Highest occupied molecular orbital	eV
I	Current	mA
I_s	Incident light intensity	$\text{mA}\cdot\text{cm}^{-2}$
IPCE	Incident photon to current efficiency	%
I - V	Current -potential characteristics	
J_0	Exchange current density	$\text{A}\cdot\text{cm}^{-2}$
I_p	Peak current density	$\text{mA}\cdot\text{cm}^{-2}$
J - V	Current density-potential characteristics	
LED	Light-emitting diode	
LHE	Light-harvesting efficiency	%
LOD	Limit of detection	$\text{ng}\cdot\text{mL}^{-1}$
LUMO	Lowest unoccupied molecular orbital	eV
MIP	Molecularly imprinted polymer	
MPP	Maximum power point	
N719	di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II)	
NIP	Non-molecularly imprinted polymer	
NIR	Near-infrared	
Op - TiO_2	Scattering opaque titanium dioxide	
OSC	Organic solar cell	

PCE	Power conversion efficiency	
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate	
PP	PEDOT:PSS	
PP:GNP	PEDOT:PSS and graphene nanoplatelets composite	
P_{in}	Incident light power	$W \cdot m^{-2}$
Poly-Si	Polycrystalline silicon solar panels	
PSC	Perovskite solar cell	
Pt	Platinum	
Py	Pyrrole	
q	Elementary charge ($q = 1.602 \times 10^{-19} \text{ C}$)	C
R	Universal gas constant ($R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
R	Resistance	$\Omega \cdot \text{cm}^2$
S	Sensitizer	
SHE	Standard Hydrogen Electrode	eV
SEM	Scanning electron microscopy	
t	Time	s
T	Temperature	$^{\circ}\text{C}$
TCO	Transparent conductive oxide	
$Tr\text{-TiO}_2$	Transparent mesoporous titanium dioxide	
UV-Vis	Ultraviolet-visible spectrum	
V	Potential	V
W	Warburg diffusion	$\Omega \cdot \text{cm}^2$
wt	Weight	
YD2-o-C8	[5,15-bis(2,6-diethoxyphenyl)-10-(bis(4-hexyphenyl)amino)-20-(4-	

carboxyphenylethynyl)porphyrinato] zinc(II)		
Z	Impedance	Ω
Z'	Real part of impedance	Ω
Z''	Imaginary part of impedance	Ω

Greek Symbols	Definition	Units
θ	Phase shift	
λ	Wavelength	m
η_{FF}	Fill factor	%
η_{PCE}	Power conversion efficiency	%
ν	frequency	Hz
Φ_{coll}	Electron collection efficiency	%
Φ_{inj}	Electron injection efficiency	%
ω	Angular frequency	rad·s ⁻¹

Subscripts	Definition
*	Excited-state
+	Oxidized-state
CB	Conduction band
CE	Counter-electrode
CT	Charge-transfer in the counter-electrode/electrolyte interface
EI	Electrolyte
i	Initial value
k	Photoanode/electrolyte interface
mpp	Maximum power point

p	peak
oc	Open-circuit
s	Series
sc	Short-circuit

CHAPTER 1

INTRODUCTION

“I have not failed. I've just found 10 000 ways that won't work”.

Thomas A. Edison

In submission

INTRODUCTION

Climate is changing and it is our responsibility to mitigate the consequences of global warming. A worldwide transition to renewable energy sources is needed to reduce the carbon-footprint. According to **Figure 1.1** [1], fossil fuels still represent over 60 % of the world electricity consumption in 2020, while hydro, nuclear, wind and solar share 35.2 % of the same market.

World Electricity Consumption in 2020

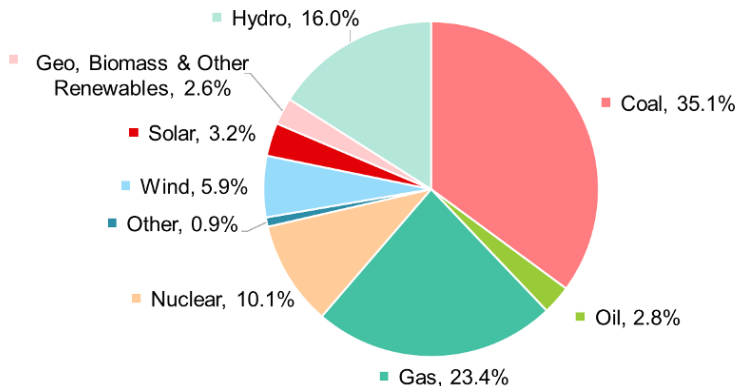


Figure 1.1. Energy sources for World electricity generation in 2020 (adapted from [1]).

Solar radiation is by far the most powerful renewable energy source, delivering 23 000 TW per year while the world primary energy consumption was ca. 17.6 TW in 2020 [2,3]. Thus, only 10 % of the sun's power is needed to fulfill the world's energy requirements. The Renewables 2021 Global Status Report states that, in 2020, it was installed 256 GW of renewables power

fields, where solar PV and wind power account for more than 90 % of it [4]. In 2020, due to the SARS-CoV-2 pandemic and global lockdowns, electricity demand dropped abruptly, and favorable conditions for renewable power resulted in an increase of its market share, reaching ca. 29 % of global electricity [4]. The rise in wind and solar electricity generation helped to decrease the share of fossil fuels, such as from coal, falling by a record of 4 % (ca. -39.5 GW) [5].

Currently, the solar PV market is still dominated by first- and second-generation solar cells. First-generation solar cells include single junction crystalline and polycrystalline silicon solar panels (c-Si and poly-Si) and represent ca. 85 % - 90 % of the market [6]. Second-generation cells introduced the heterojunction concept and use materials like cadmium telluride (CdTe), copper indium gallium selenide (CIGS), copper indium (di)selenide (CIS) and amorphous silicon (a-Si), that can be deposited as thin-films on glass or ceramic substrates [7]; these solar cells only represent ca. 10 % - 15 % of the PV market [6]. Very recently, third-generation solar cells have started to enter the PV market because they offer simpler fabrication process, lower manufacturing costs, and better low-light performance [7–11]; this category includes dye-sensitized solar cells (DSSCs), perovskite solar cells (PSCs), organic solar cells (OSC), and quantum dot solar cells.

Since 1991, with the seminal work by Grätzel and O'Regan [12], DSSCs have been rapidly evolving, reaching now efficiencies between 13 % and 15 % (AM1.5G) [13–18]. Yet, they are routinely surpassed by PSCs [19–23], which in 2021 displayed a certified power conversion efficiency (PCE) of 25.7 % (AM1.5G) [18]. However, PSCs are an emerging technology with still major scientific and technological issues such as the use of lead in the most efficient perovskite absorbers [24,25], and their high sensitivity to moisture and oxygen, leading to faster degradation of the perovskite absorber [26]. Among other third PV devices, DSSCs are the most mature technology, presenting interesting features as low toxicity, pleasant aesthetics, and, given the existent portfolio of different dyes, they are highly customizable [15,17,27,28]. Additionally, the

fabrication process of DSSCs is much simpler compared to other emerging PVs [29,30], and can be printed on both flexible, hard substrates or textiles [31–33]. Another advantage of DSSCs is the possibility of been illuminated from both sides, which helps achieve high photovoltage in diffuse light conditions [34,35]. In fact, outperforming other existing technologies, the high performance of DSSCs under dim or indoor lighting unveiled a paradigm shift in the field and introduced the potential of DSSCs to the indoor photovoltaic (IPV) market [17,34,36,37]. In these new testing conditions, DSSCs have already a record PCE of 34.5 % [17] and can truly rival other emerging PVs. Currently, PSCs hold the highest PCE record of 40.2 % [38] and OSCs display a record of 28.1 % [39] under artificial illumination (1000 lx) (**Figure 1.2a**).

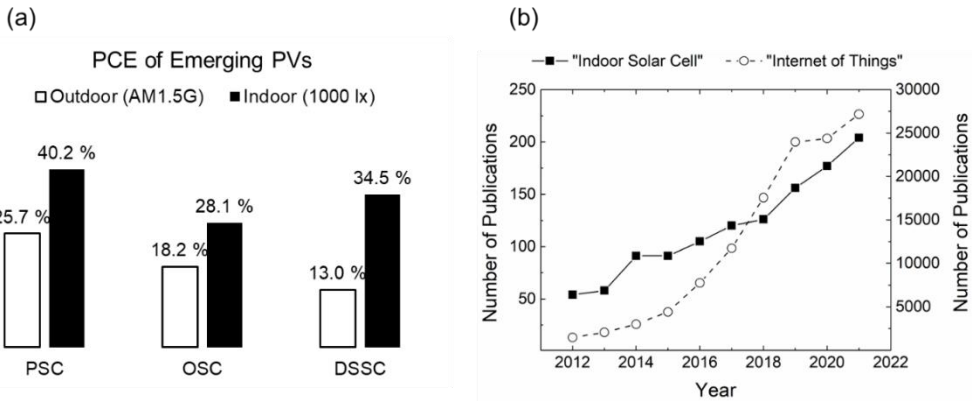


Figure 1.2. (a) Highest certified (Outdoor – AM1.5G, empty bars) [18] and highest reported (Indoor – 1000 lx, full bars) PCE of emerging PVs: perovskite solar cells (PSC) [38], organic solar cells (OSC) [39], and dye-sensitized solar cells (DSSC) [17]. (b) Number of publications released from 2012 to 2021 on the topic of “indoor solar cell” (full squares, on the left) and “Internet of Things” (open circles, on the right) – data source: Web of Science.

The Internet of Things (IoT) describes an ecosystem of smart objects equipped with sensors, all linked in network and working together to provide smart services to end users [40]. Since 2012, there has been an exponential growth in the number of publications regarding the topic “Internet of Things” (**Figure 1.2b**), and this has been translated into an increase in the IoT market, which is expected to reach 7.7×10^8 € in 2023 [41]. IoT related electronic

devices, already present in our daily lives, are expected to surpass the 75 billion units by 2025, and most of them are designed for indoor use [36]. Currently, these devices are powered by batteries that must be discarded when depleted. With the rampant increase of battery-powered devices, the number of batteries discarded is increasing exponentially, adding more environmental concern. Many IoT devices need little power to operate [42,43], making DSSCs very attractive for powering these devices (**Figure 1.2b**). The aesthetic appeal and the use of harmless chemicals, make DSSCs compatible for indoor applications. They can also be made much thinner and better suited to the indoor light spectrum than the conventional silicon PV cells; as DSSCs are the most suitable PV technology for indoor applications it is expected to become fully commercial quite soon [34,36,37,41,44–49]. According to **Figure 1.3** [50], the DSSC market is primarily distributed among portable charging, building-integrated photovoltaics (BIPV) / building applied photovoltaics (BAPV), embedded electronics, outdoor advertising, and automotive-integrated photovoltaics (AIPV); the portable charging sector accounts for 33.3 % of the total market share, followed by BIPV (24 %) and embedded electronics (15 %). This last sector is expected to grow in the coming years.

Global DSSCs market share, by application, 2019

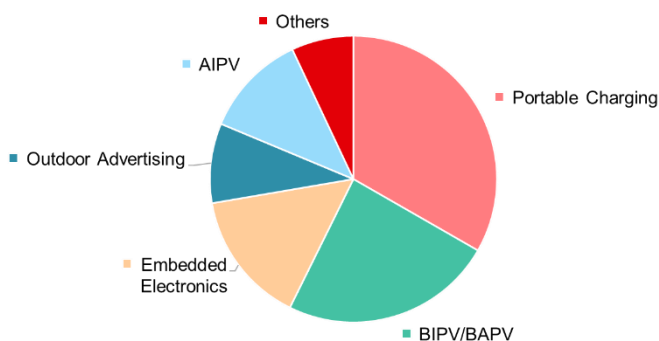


Figure 1.3. Global dye-sensitized solar cells market share, by application, in 2019 (adapted from [51]).

This chapter aims at reviewing the working principle of the most efficient devices, n-type DSSCs, and the role of the different redox mediators used

under both simulated sunlight and artificial illumination. There are different ways to classify DSSCs, either by the type of sensitizer – e.g., metal-based complexes vs. organic sensitizers, or by the type of counter-electrode, *i.e.*, platinum counter-electrodes vs. polymer counter-electrodes. In this chapter, DSSCs are classified according to the redox couple used. Since there were published over 21,665 articles related to DSSCs, this review will only cover studies reporting power converting efficiencies over 9 % for iodine, cobalt, and copper mediated devices. This review also highlights the systematic development of DSSCs, presenting current and future photovoltaic applications of this technology.

1.1. WORKING PRINCIPLE

A DSSC has three main elements: photoanode, counter-electrode and electrolyte. These third-generation solar cells mimic the natural process of photosynthesis, and the main difference from standard p-n junction devices is the separation between charge separation (light harvesting) and charge transport [51]. The operation of a DSSC starts by the photoexcitation of the dye molecules (**1**), where an electron moves from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [52]. Thus, the sensitizer is responsible for the light harvesting. In conventional DSSCs, the photoelectrode is n-type and then, after photoexcitation, the electrons from the valence band are injected into the conduction band of a semiconductor (**2**) and travel through the semiconductor mesoporous layer until the transparent conductive oxide (TCO) layer, which coats the glass substrate of the photoanode. Therefore, the semiconductor is responsible for the extraction and transport of the electrons. From the photoelectrode, electrons travel through the external circuit until the counter-electrode, where they reduce the redox mediator (**3**). The redox mediator diffuses until the mesoporous for regenerating the oxidized dye (**4**) [53,54] (see **Figure 1.4**). There are competing reactions in which electrons flow through different pathways, namely, decay from the excited state to the ground state at the dye molecules (**5**), injected electrons may recombine with oxidized dye molecules (**6**), and

injected electrons may recombine with the oxidized redox mediator at the mesoporous layer (**7**). [55]. Reactions **1** and **2** are considered irreversible because their forward kinetic constants are much higher than the corresponding reverse reactions (**5** and **6**, respectively). Thus, the reaction between the photoinjected electrons with the oxidized species of the redox shuttle (**7**) is the preferential recombination mechanism, and the main source of the dark current [56].



To minimize the recombination at the TCO layer, a very thin layer of TiO_2 (known as blocking layer) is often deposited on the TCO layer to mitigate the recombination between the injected electrons and the reduced redox species [57–60]. The overall recombination rate of the injected electrons with the reduced redox mediator depends on several factors such as, photoelectrode mesoporous layer thickness, chemical composition of the sensitizer, redox mediator diffusion rate, and co-adsorbant properties of the reduced redox species [61].

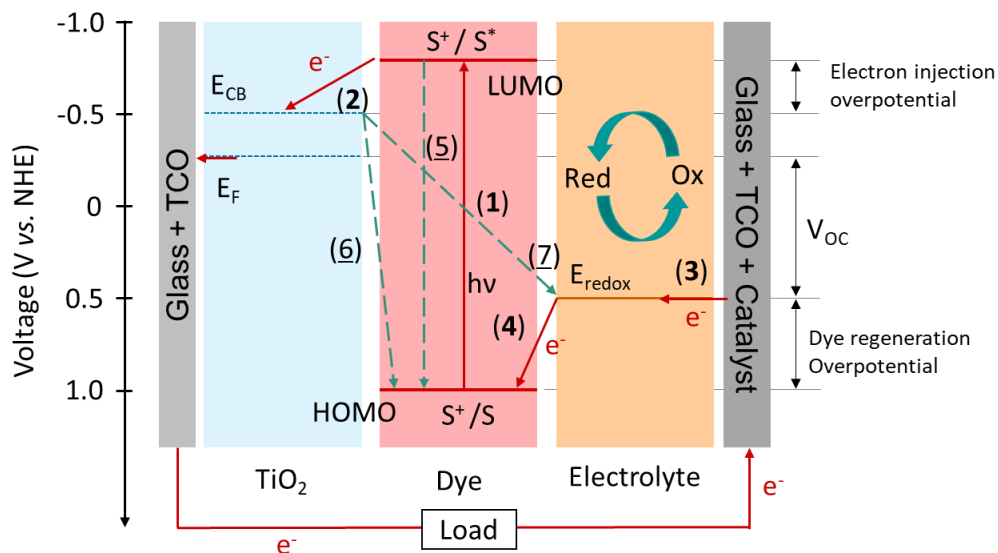


Figure 1.4. Schematic representation of DSSCs operating principle, kinetic reactions, and energy levels of materials used in DSSC. Forward reactions are represented by full arrows and recombination reactions are represented by dashed arrows. E_{CB} – conduction band energy; E_F – Fermi energy; S – sensitizer in the ground state; S^+ – sensitizer in the oxidized state; S^* – excited state of the sensitizer; e^- – electrons; E_{redox} – electrolyte redox potential; TCO – transparent conductive oxide; LUMO – lowest unoccupied molecular orbital; HOMO – highest occupied molecular orbital.

The energy performance of a solar cell is first characterized by the power conversion efficiency (PCE), which depends on the incident light intensity (I_s), photocurrent density at the maximum power point (J_{MPP}), and on the open-circuit photovoltage at the maximum power point (V_{MPP}). All these parameters can be obtained from the J - V characteristic curve (**Figure 1.5**). At 0 V, the device is at short-circuit where the highest current density is produced, J_{SC} ; at 0 mA, when there is no current flow, the circuit is open and the potential generated is the V_{OC} . The power plot is calculated multiplying the current density by the potential, defining the point where the device reaches its maximum power output (or maximum power point, MPP). The fill factor, η_{FF} , is

the ratio between the power delivered at the maximum power point and the power obtained from the product of J_{SC} by V_{OC} , as indicated in (Eq. 1.2) and the power conversion efficiency is obtained from the product between J_{SC} and V_{OC} , corrected by η_{FF} and normalized by the irradiance, as indicated in (Eq. 1.2):

$$\eta_{FF} = \frac{P_{MPP}}{J_{SC}V_{OC}} = \frac{J_{MPP}V_{MPP}}{J_{SC}V_{OC}} \quad (\text{Eq. 1.1})$$

$$\eta_{PCE} = \frac{J_{SC}V_{OC}}{I_s} \eta_{FF} \times 100 \quad (\text{Eq. 1.2})$$

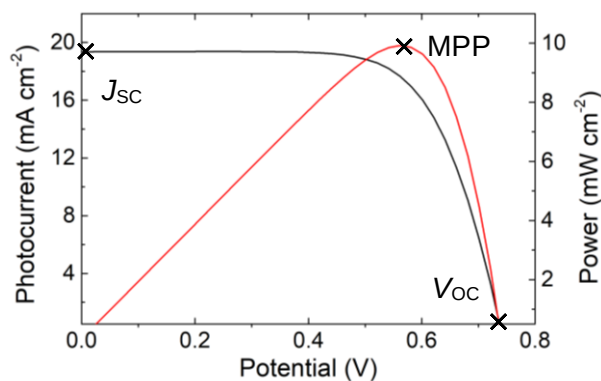


Figure 1.5. Typical J-V curve and power plot of a solar cell; J_{SC} – short circuit current density, MPP – maximum power point; V_{OC} – open circuit potential.

Since the PCE efficiency is related to the product of $J_{SC} \times V_{OC}$, optimizing the PCE is a trade-off between increasing the current density, which often implies decreasing the delivering potential [62–67]. The maximum value of V_{OC} generated under illumination corresponds to the difference between the Fermi energy (E_F) of the semiconductor and the electrolyte redox potential (E_{redox}), **Figure 1.4**. To ensure maximum V_{OC} , it is crucial to mitigate the dark current. Dark current, or recombination, is mostly related to the capture of injected electrons by the oxidized species of the redox mediator. Lower electron recombination rates lead to longer electron lifetimes, lower dark current, and improved η_{FF} [68]. The J_{SC} is intrinsically associated with the ability of the sensitizer to absorb the photons with energy above the sensitizer band gap

and injecting them in the conduction band of the photoanode. To characterize a sensitizer, a typical strategy is then to measure the incident photon to current conversion efficiency (IPCE), as function of the incident photon wavelength, which is defined as the ratio of the number of electrons flowing through the external circuit ($N_{\text{electrons}}$) and the number of incident photons with a given wavelength λ (N_{photons}), as indicated in **(Eq. 1.3)**:

$$\text{IPCE}(\lambda) = \frac{N_{\text{electrons}}}{N_{\text{photons}}} = \frac{\frac{q N_{\text{electrons}}}{t}}{\frac{q N_{\text{photons}}}{t}}, \text{ if } I_{\text{SC}} = \frac{q N_{\text{electrons}}}{t},$$

$$\text{then IPCE}(\lambda) = \frac{I_{\text{SC}}}{\frac{q N_{\text{photons}}}{t}} \quad \textbf{(Eq. 1.3)}$$

where q is the elementary charge, t is the time and I_{SC} is the photocurrent at short-circuit. The power of incident light (P_{in}) is related to N_{photons} , and it is given by **(Eq. 1.4)**:

$$P_{\text{in}} = \frac{N_{\text{photons}}}{t} h \nu = \frac{N_{\text{photons}}}{t} h \frac{c_0}{\lambda} \Leftrightarrow N_{\text{photons}} = \frac{t \lambda P_{\text{in}}}{c_0 h} \quad \textbf{(Eq. 1.4)}$$

where h is the Planck constant, ν is the frequency, c_0 is the speed of light and λ is the wavelength. Introducing **(Eq. 1.4)** in

(Eq. 1.3), the IPCE equation can be written as [7]:

$$\text{IPCE}(\lambda) = \frac{I_{\text{SC}}}{\frac{t \lambda P_{\text{in}}}{c_0 h}} = \frac{I_{\text{SC}} h c_0}{q \lambda P_{\text{in}}} = \frac{I_{\text{SC}}(\lambda)}{P_{\text{in}}(\lambda)} \frac{1240}{\lambda} \times 100 \% \quad \textbf{(Eq. 1.5)}$$

As equation **(Eq. 1.5)** shows, the IPCE measures the spectral response under short-circuit conditions. There are two methods to obtain the IPCE: AC mode and DC mode. The most common is the DC mode in which the photocurrent is measured under a monochromatic light source with a fixed photon flux [69]. The IPCE can be used to estimate the total photocurrent from the integral of the product between the incident photon flux density (I_{photon}) and the IPCE for a range of wavelengths, as indicated in **(Eq. 1.6)** [69]:

$$I_{\text{SC}} = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} I_{\text{photon}}(\lambda) \cdot \text{IPCE}(\lambda) d\lambda \quad \textbf{(Eq. 1.6)}$$

The IPCE of a device depends mainly on three factors: i) light-harvesting efficiency of the dye (LHE), ii) efficiency of electron injection (Φ_{INJ}) and, iii) collection efficiency of the injected electrons at the TCO (Φ_{COLL}):

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda) \Phi_{\text{INJ}}(\lambda) \Phi_{\text{COLL}}(\lambda) \quad (\text{Eq. 1.7})$$

LHE depends on the adsorption surface area of the mesoporous layer and on the molar extinction coefficient of the sensitizer. The first is optimized to display the largest specific surface area without compromising the redox mediator diffusion while the second depends primarily on the chemical nature of the sensitizer. Anyway, to increase the LHE a light-scattering layer, composed of larger TiO_2 particles and applied over the mesoporous layer, is used to reflect back part of the crossing radiation without imposing a significant transport resistance on the redox mediator [70–73]. The electron injection efficiency, Φ_{COLL} , depends on the residence time of the reduced redox species at the mesoporous and light-scattering layers and on the current density [70]. The collection efficiency of the injected electrons, Φ_{INJ} , depends on the ratio of photons harvested by the sensitizer that are successfully injected into the conduction band of the semiconductor; this process competes with the quenching of the excited sensitizer. The charge injection in a good performing solar cell should be at least 100 times faster than the decay rate constant of the dye [63,74].

Besides the steady-state J - V curves and IPCE spectra, dynamic techniques such as electrochemical impedance spectroscopy (EIS) allow the identification of charge transfer kinetics, which occur on different time scales as shown in **Figure 1.6** [75].

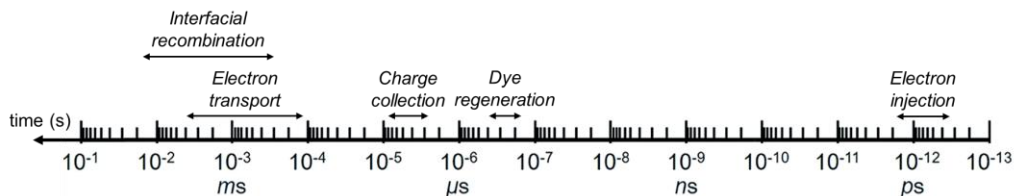


Figure 1.6. Dynamic competition of electrochemical processes during operation of a DSSC (adapted from [75]).

To measure the impedance spectra, a small sinusoidal potential perturbation is normally applied, and the current response recorded as a function of the applied frequency [76]. The frequency-potential perturbation is typically performed under open-circuit conditions with a modulation signal of magnitude V_0 :

$$V(t) = V_{OC} + V_0 \cos(\omega t) \quad (\text{Eq. 1.8})$$

The corresponding response has a period equal to the period of the potential perturbation, but it is phase shifted by φ :

$$I(t) = I_{OC} + I_0 \cos(\omega t - \varphi) \quad (\text{Eq. 1.9})$$

where V_0 and I_0 are, respectively, the amplitudes of potential and current signals, ω is the radial frequency and I_{OC} (open-circuit current) is zero [7]. The impedance, Z , is the ratio between potential and current:

$$Z = \frac{V_0 \cos(\omega t)}{I_0 \cos(\omega t - \varphi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \varphi)} \quad (\text{Eq. 1.10})$$

Applying complex notation to this equation we obtain [77]:

$$Z = Z_0 \frac{e^{j\omega t}}{e^{j(\omega t - \varphi)}} = Z_0 e^{j\varphi} = Z_0 (\cos \varphi + j \sin \varphi) \quad (\text{Eq. 1.11})$$

$$Z' = Z_0 \cos \varphi \quad (\text{Eq. 1.12})$$

$$Z'' = Z_0 \sin \varphi \quad (\text{Eq. 1.13})$$

where j is the imaginary number and Z' is the real component of the impedance and Z'' the imaginary component (**Eq. 1.13**).

Figure 1.7a shows a typical Nyquist plot of a DSSC, which sweeps a defined frequency range to examine the different electrochemical processes that occur in the solar cell at different times (**Figure 1.6**). Analyzing **Figure 1.7a** from high to low frequencies (from left to right in the figure), semicircle #1 is assigned to the redox reaction at the counter-electrode; semicircle #2 is related to electron transfer in the TiO_2 /electrolyte interface; and semicircle #3 is ascribed to the Nernst diffusion of the redox couple [78–80].

EIS is a powerful diagnostic tool that can be used to quantify the electron transport, charge accumulation, and recombination as well as electrolyte diffusion by fitting the impedance spectra obtained to an equivalent circuit model [81]. **Figure 1.7a** shows the most used equivalent circuit to study the electronic and ionic transport in DSSCs. The first element of the EIS is a resistor, representing the series resistance of the device (R_s). Next, assembled in parallel, are another resistor with a capacitor; in this case, the resistor represents the kinetics of the electrochemical reaction and the capacitor embodies the charge separation in the counter-electrode/electrolyte interface [55]. The resistor is defined as the charge-transfer resistance between counter-electrode and electrolyte (R_{CT}) and, as the capacitor is rarely ideal, the double layer capacitor is represented by a constant phase element (CPE_{CT}). Next, the equivalent circuit shows a third resistor and a second capacitor connected in parallel, representing the charge-recombination resistance in the photoanode/electrolyte interface (R_k and CPE_k). Lastly, the equivalent circuit shows a third RC element, which represents the electrolyte charge transport (R_{EI} and CPE_{EI}). Lastly, the equivalent circuit shows a third RC element, which represents the electrolyte charge transport [82], as illustrated in **Figure 1.7b**.

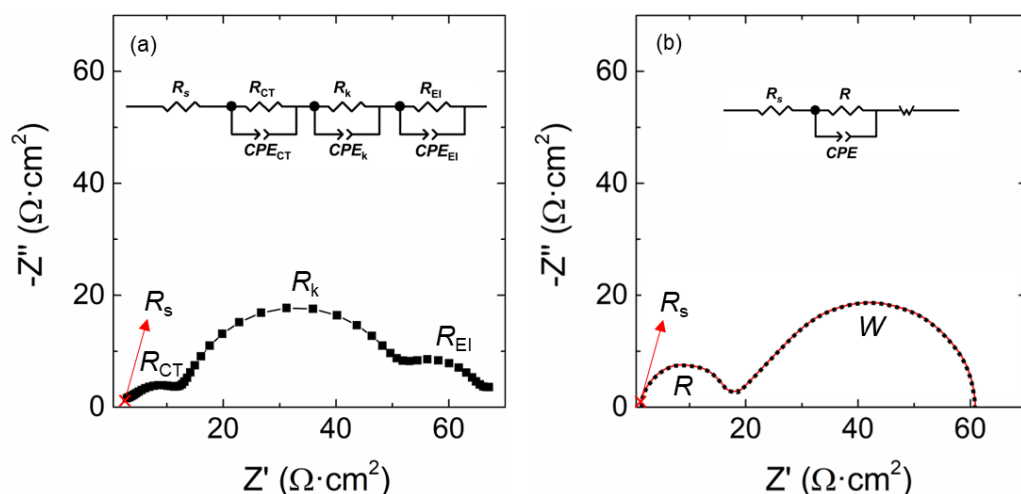


Figure 1.7. (a) Typical Nyquist plot of a DSSC and equivalent circuit used to fit the electrochemical impedance spectra; R_s – series resistance; R_{CT} – charge-transfer resistance; R_k – charge-recombination resistance; R_{EI} –diffusion

resistance in the electrolyte; CPE_{CT} – charge-transfer constant phase element; CPE_k – charge-recombination constant phase element; CPE_{EI} – diffusion constant phase element. **(b)** Nyquist plot and equivalent circuit representing a Nernst-Planck diffusion, W – Warburg diffusion.

1.2. DYE-SENSITIZED SOLAR CELLS

This chapter aims at presenting an overview of the most typical and efficient DSSCs that can be used to synergistically power electronic devices, highlighting the advantages and disadvantages of each DSSC configuration.

There are some guidelines that must be met when assembling high performing DSSCs, with each component of the device incorporating fundamental requirements. The most common semiconductor used for electron transport in DSSCs is TiO_2 – anatase. Titania has a wide band gap (ca. 3.2 V), a good conduction band alignment with the LUMO level of most dyes, and only absorbs light in the UV range. Moreover, it provides decent electronic conductivity, low back-electron recombination with electrolyte, and has high chemical stability and low toxicity [29,83]. The porosity and morphology of the semiconductor determines the amount of dye adsorbed on its surface and, consequently, how well it captures the incident light. So, the photoelectrode of a DSSC must have a large specific area, and this can be accomplished by applying a mesoporous layer. This layer, which is a semi-transparent film composed of highly dispersed anatase nanoparticles (with an average size ranging 20-30 nm), ensures very high surface area for dye adsorption – for a 10 μm mesoporous layer the specific surface area is ca. 120 m^2/m^2 . The mesoporous layer is often combined with a light-scattering layer, composed of larger nanoparticles (ca. 400 nm) of TiO_2 – anatase, which increase the optical path of light and enhance absorption in thinner films [71,83]. A TiO_2 blocking layer, also known as electron extraction layer, is also common practice to prevent direct contact between the TCO substrate and the redox couple, thus minimizing the recombination at the photoanode [57–60,84]. Lastly, a chemical bath deposition of $TiCl_4$, which after the sintering process originates TiO_2 , is

often applied to lower the recombination rate constant between conduction band electrons (e_{CB}^-) and the redox shuttle, improving the quantum efficiency of electron injection between the sensitizer and the titania layer and, consequently, increases the photocurrent. Moreover, it increases electron lifetime, which leads to higher electron diffusion length [59,70,85]. This post-treatment also improves the crystallinity of the TiO_2 layer, and the larger surface area leads to better dye adsorption [86].

The performance of DSSCs is restricted by the Shockley-Queisser limit (33 %) [87], which implies that the sensitizer should absorb all sunlight photons with energy above 1.3-1.4 eV (corresponding to a wavelength range of 940-890 nm) [88]. Ideally, the LUMO level of the sensitizer should match the edge of the conduction band of the TiO_2 to guarantee fast electron injection and minimize the electron injection overpotential – **Figure 1.4**. The HOMO level of the dye must be sufficiently low to accept electrons from the redox mediator to allow efficient regeneration of the dye [89]. Anchoring groups, such as $-COOH$, $-SO_3H$, $-H_2PO_3$, are essential for strong bonds between the TiO_2 and the sensitizer. They also enhance the electron injection into the semiconductor conduction band [63]. Aggregation of dye molecules on the semiconductor surface must be avoided, either by using co-adsorbents (cholic acid [90] or chenodeoxycholic acid [91]) or anchoring groups (carboxylic acid [73], alkoxy-silyl [92] or phosphoric acid [93]), to avoid competition between electron injection as well as recombination between e_{CB}^- and the redox shuttle. The chosen sensitizer must have long stability by enduring at least 10^8 redox turnovers, which corresponds to approximately 20 years of operation; it should also have low toxicity and high solubility [73,94].

The choice of redox mediator has a tremendous effect on the performance of the solar cell, and significant research has been conducted towards developing new and stable redox couples. While cobalt and copper electrolytes lead the record for the highest performing DSSCs, iodine solar cells remain ubiquitous as **Figure 1.8** demonstrates.

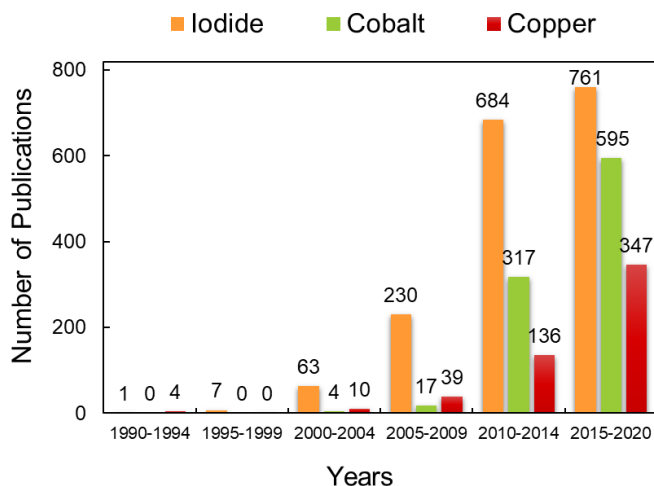


Figure 1.8. Number of publications released per year from a simple literature search using keywords “dye sensitized solar cells” and (**orange**) “iodide”, “I³⁻”; (**green**) “cobalt”, “Co(III)”; (**red**) “copper”, “Cu(II)”. Search from data source Web of Science.

1.2.1. IODINE SOLAR CELLS

Iodine electrolytes are still the most researched redox couple used in DSSCs, and one of their major advantages is ascribed to its slow recombination with $\text{TiO}_2 \text{ e}_{\text{CB}}^-$. This reduces the main recombination pathway in DSSCs, and therefore the cathodic dark current, while establishing a practically quantitative collection of photogenerated charge carriers [95,96]. The small size of the iodine redox couple helps to achieve rapid diffusion through the mesopores of the titania layer and increases the photocurrent for a given electrolyte concentration [97]. Introducing a dense TiO_2 blocking layer between the FTO and the semiconductor can effectively prevent short-circuits when the electrolyte encounters the conductive glass after permeating through the mesopores of the titania layer. Usually, iodine electrolytes are used with ruthenium sensitizers, and the mismatch between the redox potential of the I^-/I_3^- and the HOMO level increases the overpotential of the dye regeneration, decreasing the open-circuit potential of the solar cells [28,95,98]. The dye regeneration step is also complicated due to the two-electron reduction

reaction of I^- to I_3^- [99]. The I^-/I_3^- redox mediator absorbs a significant part of the visible light spectrum [100] and is corrosive towards most metals. This greatly limits the choice of counter-electrode materials and prevents the use of metal current collectors, namely silver, when scaling up the DSSCs [99,101].

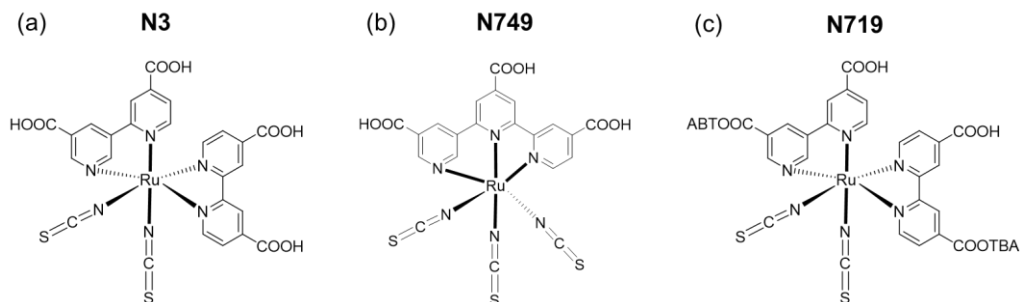


Figure 1.9. Chemical structure of most common and efficient Ru-complexes: (a) N3, (b) N749, and (c) N719.

Ruthenium dyes became very popular among sensitizers after the breakthrough work by Grätzel and O'Regan [12], who revolutionized the field by replacing a compact film of TiO_2 by a mesoporous layer, increasing the internal surface area and significantly enhancing the dye adsorption. The incident light was harvested by a trinuclear ruthenium complex and a PCE of 7.9 % was achieved. Ruthenium sensitizers consist of a central Ru ion with ancillary ligands and anchoring groups. Therefore, when the sensitizer absorbs photons, an electron from the metal d-orbital jumps to the ligand π^* orbital, and thus metal-to-ligand charge transfer (MLCT) is responsible for the light absorption in the visible range of the spectrum [94]. Overall, the HOMO level is attributed to the Ru and electron donating ligands, whereas the LUMO level is localized on the polypyridyl ligand. This distribution enhances the injection of electrons into the semiconductor conduction band through chemical bonding and regeneration of the oxidized state of the sensitizer [9]. In 1993, Nazeeruddin *et al.* [73] introduced another Ru sensitizer, the N3 complex (**Figure 1.9a**), which presents a broad absorption in the visible range of the spectrum, long lifetime of the excited state, its LUMO nearly matches the conduction band of the TiO_2 , and it displays a high thermal stability. Devices

with N3 dye display a PCE over 10 % under 1-sun [73,102] (**Table 1.1**). The N749 (**Figure 1.9b**), also known as “black dye”, possesses three thiocyanate anionic ligands that stabilize the excited states by electron donation to Ru, leading to a red-shift of the MLTC bands [103]. This dye allows efficient sensitization over the whole visible spectrum, even extending to the near-infrared region (ca. 920 nm), culminating in devices with a PCE of 10.4 % [104], further improved to 11.1 % [105] (**Table 1.1**). N719 (**Figure 1.9c**) was also developed from the N3 complex by deprotonation of the carboxylic acid groups, lowering the HOMO-LUMO gap of the dye and resulting in an absorption onset around 1.65 eV (750 nm), which is far from the optimum 1.3–1.4 eV [88,106].

Other successful ruthenium dyes were developed [107–110], but only a few surpass the 10 % threshold. Chang *et al.* reported a PCE of 10.05 % [111]; Ozawa *et al.* achieved a PCE of 11.1 % with TUS-38 dye bearing a *n*-hexylthiophene modified terpyridine derivative ligand and enhanced the PCE of the device to 11.9 % by replacing the 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPII) by 1-ethyl-3-methylimidazolium iodide (EMII) in the electrolyte solution [66]. A remarkable PCE of 12.0 %, certified by the National Measurement Laboratory in Taiwan, was achieved by Chiang *et al.* by employing a Pt₄₉Co₂₃Fe₂₈ nanowire as counter-electrode and sensitizing the photoanode with a Ru-based dye, PRT-22 [112] (**Table 1.1**). The PtCoFe nanowire in combination with the PRT-22 increases the photocurrent and decreases the R_{CT} , a direct result of the exceptional catalytic activity towards the I_3^- reduction. Chiang *et al.* surpassed the 12 % threshold with their champion DSSC, at 12.29 % of PCE, and became the best performing Ru-based device (**Table 1.1**).

Dye N719 is still regarded as the reference ruthenium sensitizer, as evidenced by **Table 1.1**. This sensitizer is almost exclusively employed when modifications are suggested on the photoanode such as: i) doping the titania layer with Cu and N [113,114] or Cu and S [115] to increase the surface area and dye adsorption, delaying charge carrier recombination; ii) including TiO₂

nanorods, which boosts the charge transfer rate of the photogenerated electrons and also enhances the specific surface area [116]; iii) adding nanocomposites of TiO_2 and graphene to improve the photocurrent and the resistance to charge recombination because it provides an effective pathway for electrons to flow within the external circuit [117,118]. N719 is also employed as a reference dye when testing new catalytic materials. A quasi core-shell structure of N-doped graphene/cobalt sulfide demonstrated high conductivity and catalytic activity due to close interactions between the cobalt sulfide core and the N-doped graphene shell. This resulted in high FF due to low resistance for the reduction of I_3^- to I^- on the counter-electrode surface, and increased V_{OC} through lower overpotential in the I_3^- reduction, favoring the regeneration step [119]. CoSe_2 [120] and Co-Cu-WS_x nanospheres [121] also demonstrated excellent capability to accelerate the reduction of I_3^- . Co-Fe-MoS_x [122], CoS nanosheets arrays [123], quaternary porous nanocubes Cu-Ni-CoSe_x [124], porous carbon-cobalt composite [125], $\text{CoSe}_2/\text{graphene}$ [126], Fe_3C with N-doped hollow carbon flower [127], $\text{Co}_9\text{S}_8\text{-Ni}_3\text{S}_2@\text{WS}_2$ [128], and $\text{Bi}_5\text{FeTi}_3\text{O}_{15}@\text{C}_3\text{N}_4$ [129] showed more catalytically active sites, faster electron charge transfer, and higher electrocatalytic activity towards the reduction of I_3^- , decreasing the overpotential and, therefore, increasing the photovoltage.

Some of the drawbacks of ruthenium complexes are low molar extinction coefficients (between 10 000 and 20 000 $\text{M}^{-1} \text{cm}^{-1}$), limited absorption in longer wavelengths (near-IR) of the solar spectrum, and scarcity of the noble metal, entailing an extra recycling fee [6,94,130]. On the other hand, organic dyes are cheaper and more environmentally friendly as they are metal-free. The high molar extinction coefficients (50 000 and 200 000 $\text{M}^{-1} \text{cm}^{-1}$) allow for thinner photoanodes, and the structural design of organic dyes is much more flexible [6,63]. Generally, organic dyes are designed based on the donor- π -bridge-acceptor architecture, or D- π -A (**Figure 1.10**). In this structure, the HOMO band is mainly attributed to the donor and the electron-rich π -bridge, whereas the LUMO is confined to the acceptor and anchoring groups. Hence, it is simple to tune the energy level of the HOMO/LUMO bands by changing the

donor/ π -bridge/ acceptor groups [9]. The D- π -A architecture enables an intramolecular charge transfer complex, resulting in π -orbital overlap and subsequent red-shift in the absorption bands [16].

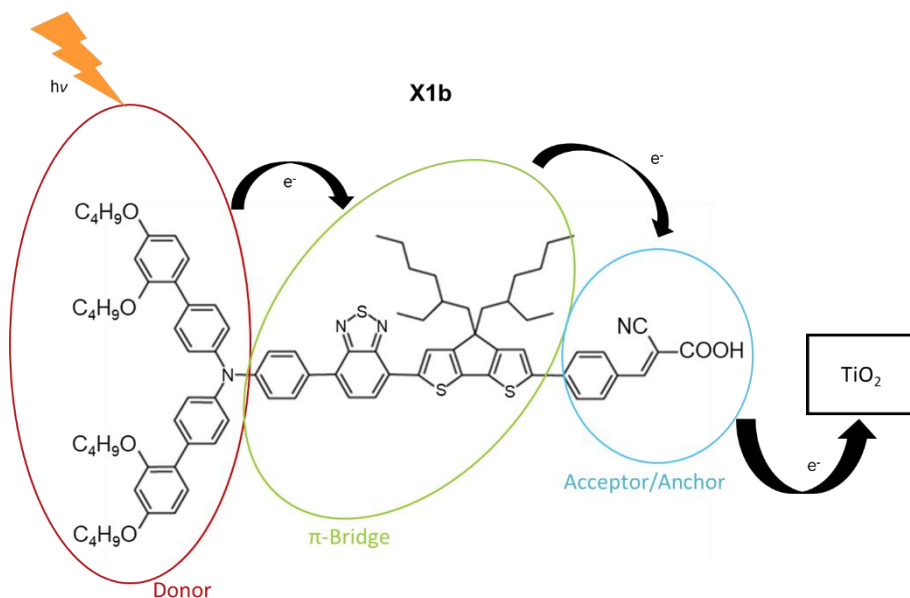


Figure 1.10. Schematic drawing of an organic dye with a D- π -A architecture, using the X1b dye to demonstrate the concept.

In addition to ruthenium sensitizers, organic sensitizers have also been successfully paired with iodine electrolytes. One of the first and most successful attempts was a D- π -A porphyrin sensitizer developed by Bessho *et al.* [131]. A diarylamino group was attached to the porphyrin ring as an electron donor, the porphyrin chromophore was used as π bridge, and an ethynylbenzoic acid moiety as an electron acceptor. A PCE of 11.0 % was reported due to the increased light-harvesting properties of the photoanode, consequence of the addition of a thin layer of larger reflecting particles [131]. Other works showed the versatility of this architecture and achieved overall efficiencies above 10 % [67,132–134] (**Table 1.1**). Zeng *et al.* developed a new sensitizer with a doubled strapped porphyrin framework and a bulky 2,4-bis(hexyloxy)phenyl group incorporated into a phenothiazine donor, coded XW51. This dye contributed to a remarkable V_{OC} of 781 mV because the bulky donor had long alkoxy chains as substituents, forming a compact self-

assembled monolayer to hinder the penetration of the triiodide ion, to culminate in a PCE of 11.1 % [135] (**Table 1.1**).

Achieving panchromaticity when designing a new dye is a big task, thus many researchers have focused on the alternative method of co-sensitization. It is a challenging approach, but when employed correctly, it can enhance light absorption and broaden the spectral range by using two (or more) dyes with complementary absorption spectra. Nonetheless, this is a demanding strategy as the process of anchoring the co-sensitizers onto the semiconductor film is extremely competitive, which can hinder the adsorption of the dye cocktail [136]. The operating principle of a co-sensitized DSSC is similar to a conventional single-dye DSSC, as illustrated in **Figure 1.11** [137]; the main differences are slightly larger electron injection and dye regeneration overpotential. However, proper selection of complementary sensitizers could increase the LHE, leading to higher photocurrent, and minimizing the recombination between e_{CB}^- / oxidized dye A (S_A^+) and e_{CB}^- / oxidized redox shuttle [138]. To ensure maximum light-harvesting efficiency, co-sensitizers should comply with the following guidelines: high molar extinction coefficient to allow the use of a thinner photoanode and recover the loss in IPCE induced by electrolyte absorption; a structure that allows competitive adsorption on the semiconductor surface and suppresses dye aggregation; and compact blocking layer between the TCO and the titania surface to minimize recombination of e_{CB}^- with the redox mediator [139]. Panchromaticity is usually achieved either by dye cocktail [140,141], sequential approach [142,143], or ultrafast co-sensitization [144,145]. Many authors have succeeded in these approaches, namely, Wu *et al.* with a triple dye cocktail of YD2-*o*-C8, CD4 and YDD6, the latter being effectively responsible for the suppression of dye aggregation [146]. Wang *et al.* extended the π -conjugation of the LD31 porphyrin dye to expand the spectral absorption to 800 nm and combined it with an organic sensitizer, coded AN-4 [147]. A similar strategy was employed by Shiu *et al.* by joining a dimeric porphyrin dye, LDD1, and a push-pull Zn(II) porphyrin with extended π -conjugation, LD14, which suppressed dye

aggregation and achieved panchromatic properties from 400 nm to 900 nm, to reach a J_{SC} of $21.3 \text{ mA}\cdot\text{cm}^{-2}$ [148] (**Table 1.1**). Xie *et al.* reported a co-adsorption/co-sensitization strategy that was able to increase the V_{OC} from 645 mV to 760 mV, while synergistically improving the J_{SC} from 18.8 to $20.3 \text{ mA}\cdot\text{cm}^{-2}$, resulting in a PCE of 11.5 % [149] (**Table 1.1**). Zhang *et al.* also proposed a co-sensitization approach to eliminate the trade-off between J_{SC} and V_{OC} repeatedly reported. The authors combined a large sized dye, WS-69, responsible for a broader absorption and high photocurrent, and a small molecularly-sized dye, WS-5, which produced high photovoltage due to lower charge recombination [150]. Kakiage *et al.* achieved an unprecedented breakthrough by designing a high performance co-sensitization strategy with an iodine electrolyte (PCE of 11.2 %) or a cobalt electrolyte (PCE of 14.3 %), combining an alkoxysilyl-anchor dye, ADEKA-1, and a carboxy-anchor organic dye LEG4 [27] (**Table 1.1**). In 2020, Ji *et al.* reported a cocktail approach of two organic chromophores, SGT-149 and SGT-021, with similar results for both electrolytes: a PCE of 11.3 % for I_3^-/I^- and of 13.9 % for $[\text{Co}(\text{bpy})_3]^{3+/2+}$ [16] (**Table 1.1**). In the same year, Zeng *et al.* proposed a novel method for co-sensitization designated “concerted companion dyes” with two complementary dye components linked covalently (Z2 and XW51) and showing complementary absorption spectra. The covalent bond was done through two anchoring carboxyl groups, rendering the XW61 dye. The co-adsorption of XW61 with CDCA resulted in a record PCE of 12.4 % due to high J_{SC} ($21.4 \text{ mA}\cdot\text{cm}^{-2}$) and high photovoltage (775 mV) [151] (**Table 1.1**). The co-sensitization method was also used with Ru-based dyes with different results: a combination of N719 with RK1 [117] and Coomassie 250 [152]. This approach rendered devices with a good absorption range and a PCE of 9.45 % and 10 %, respectively. When mixing the dye N749 with Y1 [153] and U01 [154], the absorption range was extended to 900 nm and photocurrents over $20.5 \text{ mA}\cdot\text{cm}^{-2}$ were reached, achieving PCEs of 11.4 % (certified) and 10.6 % (**Table 1.1**), respectively. For a more extensive review on the development of sensitizers, the reader is referred to the work by Akhtaruzzaman *et al.* [138].

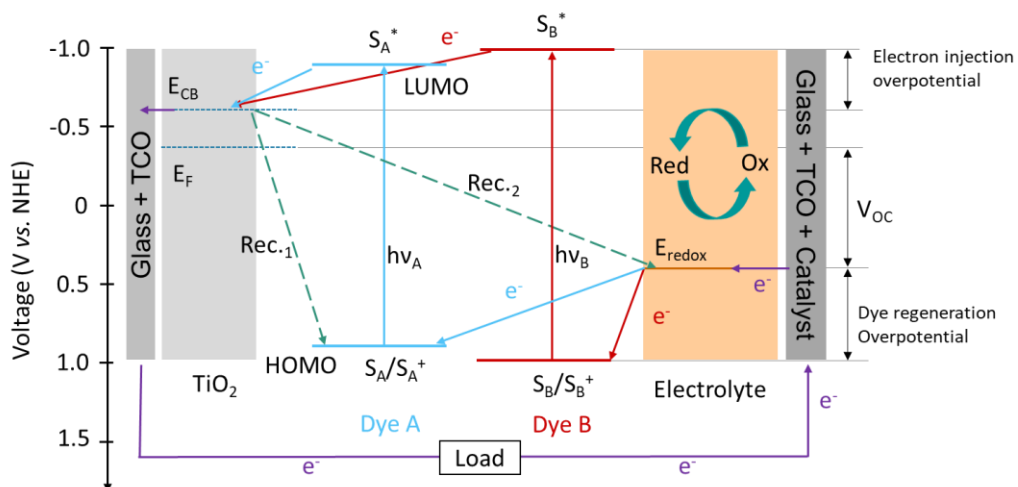


Figure 1.11. Schematic representation of the energy levels in a co-sensitized DSSC, between the semiconductor, dye A and B, electrolyte, and counter-electrode; forward reactions are represented by full arrows and recombination reactions are represented by dashed arrows (adapted from [139]).

In summary, iodine redox systems are the most studied electrolytes, as attested by **Table 1.1**. The stability of these devices has been reported countless times with very successful data. Additionally, iodine-based solar cells are by far the easiest and cheapest system to produce and replicate with excellent reproducibility. However, the corrosive electrolyte, high light absorption between 600 and 800 nm, and the use of noble metals (both in sensitizers and catalysts) are a considerable downside of this redox mediator.

Table 1.1. Photovoltaic Characteristics of iodine-based DSSCs with PCE > 9 % under 1-Sun

Dye	CE	Electrolyte	V_{OC} (mV)	J_{SC} (mA·cm ⁻²)	η_{FF}	η_{PCE} (%)	Year	Ref.
N3	Pt	I ₂ , LiI, tBP	720	18.2	0.73	10.0	1993	[73]
N749	Pt	I ₂ , LiI, DMPII, tBP	720	20.5	0.70	10.4	2001	[104]
N719	Pt	I ₂ , LiI, MBII, tBP	750	17.0	0.72	9.18	2003	[155]
N719	Pt	I ₂ , LiI, GuSCN	796	17.8	0.75	10.6	2003	[102]*
N719	Pt	I ₂ , LiI, DMPII, tBP	764	18.2	0.74	10.2	2004	[156]
N621	Pt	A6141 w/ GuSCN	777	16.8	0.73	9.57	2005	[107]
N719	Pt	A6141 w/ GuSCN	846	17.7	0.75	11.2	2005	[107]
N749	Pt	I ₂ , LiI, DMPII, tBP	736	20.9	0.72	11.1	2006	[105]*
D205	Pt	I ₂ , LiI, BMII, GuSCN, tBP	710	18.7	0.71	9.40	2008	[108]
N719	Pt	I ₂ , LiI, BMII, GuSCN, tBP	789	18.2	0.70	10.1	2008	[157]
CYC-B11	Pt	I ₂ , LiI, DMII, GuSCN, tBP	743	20.1	0.77	11.5	2009	[158]
YD-2	Pt	I ₂ , LiI, DMII, GuSCN, tBP	770	18.6	0.76	11.0	2010	[131]
YDD6+CD4 +YD2-o-C8	Pt	I ₂ , LiI, PMII, tBP	753	18.0	0.72	10.4	2012	[146]

N749	Pt	I ₂ , Lil, DMPII, tBP	727	20.4	0.72	10.8	2012	[159]
N749	Pt	I ₂ , Lil, DMPII, tBP	727	20.5	0.72	10.7	2012	[153]
N749+Y1	Pt	I ₂ , Lil, DMPII, tBP	743	21.3	0.72	11.4	2012	[153]*
N719 (w/ DCA)	Pt	I ₂ , Lil, DMPII, tBP	749	16.9	0.74	9.32	2014	[109]
MH13 (w/ DCA)	Pt	I ₂ , Lil, DMPII, tBP	660	20.6	0.72	9.71	2014	[109]
N719	Pt	I ₂ , Lil, PMII, tBP	806	17.7	0.68	9.63	2014	[160]
TFRS-52	Pt	I ₂ , Lil, DMPII, tBP	850	15.2	0.76	9.90	2014	[110]
LD31	Pt	I ₂ , Lil, PMII, tBP	699	20.0	0.71	9.95	2014	[147]
LD31+AN-4	Pt	I ₂ , Lil, PMII, tBP	704	20.3	0.72	10.3	2014	[147]
XW1+C1	Pt	I ₂ , Lil, PMII, tBP	746	17.5	0.71	9.24	2014	[161]
N719	Pt	TEAI, TMAI, TBAI, NaI, KI, Lil, I ₂ , tBP	779	18.0	0.70	9.86	2014	[161]
XW4+C1	Pt	I ₂ , Lil, PMII, tBP	736	20.2	0.71	10.5	2014	[161]
N749+U01	Pt	I ₂ , Lil, DMPII, tBP	722	20.4	0.72	10.6	2014	[154]
N749	NDG/CoS	I ₂ , Lil, DMPII, tBP	710	20.4	0.74	10.7	2014	[119]
DX3	Pt	I ₂ , Lil, DMPII, tBP	556	30.3	60.5	10.2	2015	[65]
LD14+LDD1	Pt	I ₂ , Lil, PMII, tBP	705	21.3	0.69	10.4	2015	[148]
XW17	Pt	I ₂ , Lil, PMII, tBP	700	18.8	0.72	9.5	2015	[162]
XW16+WS-5	Pt	I ₂ , Lil, PMII, tBP	773	19.0	0.72	10.4	2015	[162]

XW17+WS-5	Pt	I ₂ , Lil, PMII, tBP	748	20.3	0.72	10.9	2015	[162]
ADEKA-1+ LEG4	Pt	I ₂ , Lil, NaI, DMPII, EMII, TBAI, THAI, tBP, MP, GuSCN	783	19.1	0.75	11.2	2015	[27]
XW11+C1	Pt	I ₂ , Lil, PMII, tBP	746	19.5	0.74	10.6	2015	[149]
XW10+WS-5	Pt	I ₂ , Lil, PMII, tBP	765	19.0	0.76	11.0	2015	[149]
XW11+WS-5	Pt	I ₂ , Lil, PMII, tBP	760	20.3	0.74	11.5	2015	[149]
YD23	Pt	I ₂ , Lil, PMII, tBP	740	17.1	0.71	9.00	2016	[163]
YD24	Pt	I ₂ , Lil, PMII, tBP	730	17.3	0.72	9.19	2016	[163]
Y1A1	PVP-Pt	I ₂ , Lil, PMII, tBP	658	18.6	0.75	9.22	2016	[164]
C101		I ₂ , Lil, BMII, tBP, GuSCN	734	19.3	0.72	10.2	2016	[165]
TUS-38	Pt	I ₂ , Lil, EMII, tBP	702	23.4	0.72	11.9	2016	[66]
N719	Pt	I ⁻ / I ₃ ⁻	700	22.6	0.66	11.4	2016	[113]
RK-3	Pt	I ₂ , Lil, DPMII, tBP, GuSCN	750	16.4	0.75	9.30	2017	[166]
N719	Co-Fe-Se	I ₂ , Lil, DPMII, tBP	762	18.4	0.69	9.58	2017	[167]
WS-69	Pt	I ₂ , Lil, DPMII, tBP	696	19.4	0.67	9.03	2017	[150]
WS-5+WS- 69	Pt	I ₂ , Lil, DPMII, tBP	753	19.6	0.68	10.1	2017	[150]
XW11	Pt	I ₂ , Lil, PMII, tBP	727	18.3	0.70	9.30	2017	[132]

XW28	Pt	I ₂ , Lil, PMII, tBP	715	19.4	0.73	10.1	2017	[132]
TF- <i>t</i> Bu_C ₃ F ₇	PVP-Pt	I ₂ , Lil, DPMII, tBP	767	18.5	0.71	10.1	2017	[111]
N719	CoSe ₂ -1.1	I ₂ , NaI, TBAI, tBP	809	17.7	0.71	10.2	2017	[120]
LG6	Pt	I ₂ , Lil, DPMII, tBP	690	19.6	0.71	9.64	2017	[67]
LG5	Pt	I ₂ , Lil, DPMII, tBP	680	21.0	0.71	10.2	2017	[67]
FW-1+WS-5	Pt	I ₂ , Lil, PMII, tBP	761	18.9	0.71	10.2	2017	[168]
MD7	Pt	I ₂ , Lil, DPMII, tBP	753	17.7	0.68	9.03	2018	[169]
N719+RK-1	Pt	Iodolyte	733	25.1	0.51	9.45	2018	[117]
N719	Co-Fe-MoS _x -2	I ₂ , Lil, PMII, tBP	838	18.1	0.64	9.63	2018	[122]
C268+SC-4	Pt	I ₂ , DMII, EMII, Sulfolane, NBB, GuSCN	779	18.1	0.71	10.0	2018	[170]
IQ-4	Pt	I ₂ , Lil, DPMII, tBP,	740	17.5	0.71	9.24	2018	[133]
WS-84	Pt	I ₂ , Lil, DPMII, tBP,	759	19.0	0.70	10.1	2018	[133]
JY53	Pt	I ₂ , Lil, DPMII, tBP, GuSCN	814	18.9	0.61	9.42	2018	[134]
JY55	Pt	I ₂ , Lil, DPMII, tBP, GuSCN	829	19.2	0.63	10.1	2018	[134]
N719	Pt	I ₂ , Lil, DPMII, tBP	700	24.9	0.64	11.3	2018	[171]
N719	Pt	I ₂ , Lil, BMII, tBP	710	23.4	0.67	11.7	2018	[114]
PRT-22	Pt ₄₉ Co ₂₃ Fe	I ₂ , Lil, DPMII, tBP,	741	23.9	0.68	12.0	2018	[112]*

²⁸ nanowire		GuSCN						
N719	Co-N-CNFs	I ₂ , LiI, PMII, tBP, GuSCN	742	18.0	0.68	9.05	2019	[172]
N719	CoS NSAs	I ₂ , LiI, DPMII, tBP	753	16.9	0.74	9.46	2019	[123]
N719	Co-Cu-WS _x	I ₂ , LiI, DPMII, tBP	798	17.7	0.68	9.61	2019	[121]
N719	Pt	I ₂ , LiI, DPMII, tBP	739	17.0	0.77	9.62	2019	[173]
N719	Te-SMC	I ₂ , LiI, DPMII, tBP	733	17.1	0.77	9.67	2019	[173]
N719	Cu-Ni-CoSe _x	I ₂ , LiI, DPMII, tBP	783	17.9	0.69	9.71	2019	[124]
N719	Pt	EL-HPE	735	19.2	0.70	9.84	2019	[59]
N719	CF@PANI@CoSe	I ⁻ / I ₃ ⁻	734	17.7	0.77	10.1	2019	[174]
XW41+Z1	Pt	I ₂ , LiI, PMII, tBP	726	19.6	0.72	10.2	2019	[175]
XW40+Z1	Pt	I ₂ , LiI, PMII, tBP	748	19.6	0.72	10.6	2019	[175]
N719	(SPC-Co)	I ₂ , LiI, DPMII, tBP	730	21.4	0.68	10.6	2019	[125]
XW50	Pt	I ₂ , LiI, PMII, tBP	761	19.0	0.70	10.1	2019	[135]
XW51	Pt	I ₂ , LiI, PMII, tBP	781	20.1	0.70	11.1	2019	[135]
N719	Pt	I ₂ , BMII, tBP, GuSCN	790	21.6	0.65	11.1	2019	[116]
JY57+JY59	Pt	I ₂ , LiI, DPMII, tBP, GuSCN	787	18.2	0.67	9.56	2020	[176]

N719	Ni-MoSex @CoSe ₂	I ₂ , Lil, DPMII, tBP	815	17.3	0.68	9.58	2020	[177]
D2 (w/ CDCA)	Pt	I ₂ , Lil, DPMII, tBP	790	20.0	0.65	10.2	2020	[178]
N719	Pt	I ₂ , Lil, DPMII, C ₉ H ₇ N	710	22.1	0.67	10.4	2020	[115]
SGT-149	Pt	I ₂ , Lil, DPMII, tBP	713	19.3	0.71	9.8	2020	[16]
SGT-149 +SGT-021	Pt	I ₂ , Lil, DPMII, tBP	722	22.1	0.71	11.3	2020	[16]
XW62	Pt	I ₂ , Lil, PMII, tBP	762	20.7	0.74	11.6	2020	[151]
XW61	Pt	I ₂ , Lil, PMII, tBP	775	21.4	0.75	12.4	2020	[151]
N719	GBC	I ⁻ / I ₃ ⁻	700	26.2	0.67	12.4	2020	[179]
CRD-IV	Pt	I ⁻ / I ₃ ⁻ (DHS-Et23)	752	16.4	0.73	9.02	2021	[180]
N719	Cu-MOF/ PEDOT	I ₂ , Lil, LiClO ₄	786	17.5	0.69	9.45	2021	[181]
N719	NiCo ₂ S ₄ NRs/CNFs	I ₂ , Lil, TBAI, tBP	677	23.8	0.59	9.47	2021	[182]
N719	Co ₂ P- NCNTs	I ₂ , Lil, DPMII, tBP	770	18.3	0.69	9.76	2021	[183]
N719	CuTGR	Iodolyte	745	19.9	0.66	9.81	2021	[118]
N719+ Coomassie	Pt	I ₂ , Lil, BMIT, tBP	890	15.9	0.76	10.9	2021	[152]

R-250								
N719	CoSe ₂ /G-1	I ⁻ / I ₃ ⁻	810	22.3	0.71	12.2	2021	[126]
BDTT-im-Cd	Pt	I ₂ , LiI, DPMII, tBP	790	15.6	0.74	9.13	2022	[184]
N719	Fe/Fe ₃ C@ NHCF	I ₂ , LiI, DPMII, tBP	775	18.1	0.67	9.37	2022	[127]
Z907	Pt	I ₂ , LiI, TBAI, tBP	746	19.5	0.65	9.43	2022	[185]
RR14+Y123	Pt	I ₂ , LiI, DMII, tBP, GuSCN	662	20.9	0.61	9.44	2022	[186]
N719	Co ₉ S ₈ - Ni ₃ S ₂ @ WS ₂	I ₂ , LiI, DPMII, tBP	833	17.7	0.66	9.67	2022	[128]
N719	BFTO/CN- 50	I ⁻ / I ₃ ⁻	751	22.9	0.67	11.2	2022	[129]

1.2.2. COBALT SOLAR CELLS

A popular alternative to iodine electrolyte is cobalt-based electrolyte [14–16,27,28], which has contributed to DSSC devices with high PCEs. Co^{3+} complexes have a d^7 electronic configuration, whereas Co^{2+} complexes present a d^6 electronic configuration. In this chemically reversible process, Co^{2+} species regenerate the sensitizer at the photoanode side, while Co^{3+} species are reduced at the counter-electrode and converted to Co^{2+} [187]. Unlike iodine, cobalt complexes do not have an intermediary step in the dye regeneration reaction, so the loss in potential is smaller, thus drastically lowering the dye regeneration overpotential. They show less visible-light absorption and are non-volatile and non-corrosive towards metallic conductors [97,99,188,189].

The energy gap between the quasi-Fermi level of the TiO_2 and the E_{redox} of cobalt-based redox couples is wider, allowing the corresponding DSSC to exhibit higher V_{OC} . These complexes can also be tailored by modifying the ligands on the metal center, enabling adjustments towards the HOMO level of the sensitizer and high photovoltages [27,142,190,191]. However, these one-electron and outer-sphere redox shuttles have shorter electron lifetime and fast interfacial charge recombination from e_{CB}^- to the Co^{3+} species, that can lower the V_{OC} and charge collection [28]. When the charge collection efficiency drops, the attainable photocurrent also drops, leading to a lower PCE. Diffusion of cobalt mediators through the TiO_2 mesoporous layer is slower than iodine redox counterparts due to their larger size and molecular weight, which may also lead to lower charge collection [95]. As a result of the sluggish transport, the concentration of Co^{3+} ions at the interface with photoanode increases, promoting recombination losses [192]. Common strategies to retard recombination involve the deposition of blocking layers between the FTO and the titania layer [42,84], sensitizers bearing sterically bulky groups [15,190,193,194], and the use of additives like *tert*-butylpyridine (tBP) [195]. When the concentration of tBP in the electrolyte increases, the photovoltage

also increases because the tBP molecules adsorb onto the titania layer and suppress the interfacial recombination between e_{CB}^- for the Co^{3+} species [195]. The presence of polarizing ions (*i.e.* Li^+ or Mg^{2+}) close to the TiO_2 surface can also improve photovoltage because they change the local distribution of Co ions and reduce the concentration of Co^{3+} species in the electric double layer at the photoanode surface [192,196].

Early on, it was reported that cobalt electrolytes were not as compatible with ruthenium dyes as iodine electrolytes. Liu *et al.* (2013) reported a PCE of *ca.* 2 % when coupling N719 dye with $[Co(bpy)_3]^{2+/3+}$ redox mediator [197] (**Table 1.2**), since ion pairs can be formed between Co^{3+} and the negatively charged dye molecules, blocking the way for the Co^{2+} , therefore slowing the rate of regeneration. Moreover, N719 and Co^{3+} ion-pair increase the probability of intercepting TiO_2 electrons, thus hindering the charge collection efficiency, photogenerated current and photovoltage [197].

The breakthrough in cobalt-based DSSCs was accomplished in 2011 by Yella *et al.* by combining a porphyrin sensitizer, YD2-o-C8 (**Figure 1.12a**), with a $[Co(bpy)_3]^{3+/2+}$ redox mediator. A PCE of 11.9 % under 1-Sun was reported [28] (**Table 1.2**). With this work, porphyrin sensitizers broke into the spotlight, introducing a push-pull structure and the elongation of the porphyrin π -conjugated system, overcoming the poor light-harvesting ability between 500 and 600 nm and exhibiting high molar extinction coefficients [198]. In a typical absorption spectrum, porphyrins show a strong band between 400 nm and 500 nm and a set of weaker bands in the range of 600 to 750 nm, called Soret and Q bands, respectively. Donor- π bridge-acceptor sensitizers absorb light over the full visible range and have long-chain alkoxy groups that hinder the interfacial back-electron transfer reaction [28].

As previously mentioned, organic dyes usually have high molecular extinction coefficients. Employing these sensitizers allows thinner photoanodes, and thus, mass transport and recombination restrictions associated to cobalt redox mediators can be overcome [199]. In 2014, Yella *et al.* [193] also reported another high-performing porphyrin sensitizer with a D–

π -A structure, introducing a 2,1,3- benzothiadiazole unit as spacer between the anchoring group and the porphyrin core, coded GY50 (**Figure 1.12b**). With this new strategy, the authors succeeded in broadening the absorption spectra and diminished the gap between the Soret and the Q bands. This GY50 dye was used with $[\text{Co}(\text{bpy})_3]^{3+/2+}$, obtaining high photocurrent ($18.5 \text{ mA}\cdot\text{cm}^{-2}$) and a PCE of 12.75 % [193] (**Table 1.2**). In the same year, Mathew *et al.* reengineered the typical D- π -A architecture and introduced a bulky bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amine electron donor group and a benzothiadiazole unit as electron acceptor, naming it SM315 (**Figure 1.12c**). This structure simultaneously maximized the compatibility with the $[\text{Co}(\text{bpy})_3]^{3+/2+}$ shuttle and achieved panchromaticity, exhibiting high J_{SC} ($18 \text{ mA}\cdot\text{cm}^{-2}$) and high V_{OC} (910 mV) that culminated in a PCE of 13.0 % [15] (**Table 1.2**).

Also in 2014, Kakiage *et al.* [190] reported a new organic carbazole-based dye with a trimethoxysilyl group as anchor moiety to the TiO_2 semiconductor, named ADEKA-1 (**Figure 1.13a**). This sensitizer was coupled with a $[\text{Co}(\text{bpy})_3]^{3+/2+}$ and a $[\text{Co}(\text{Cl-phen})_3]^{3+/2+}$ complex (**Figure 1.14**), which show a redox potential of 0.56 V vs. SHE and 0.72 V vs. SHE, respectively [96,200]. The higher redox potential of the $[\text{Co}(\text{Cl-phen})_3]^{3+/2+}$ shuttle increased the photovoltage from 848 mV to 897 mV (with ADEKA-1), thus improving the overall PCE to 10.7 % (vs. 10.4 %). However, the $[\text{Co}(\text{Cl-phen})_3]^{3+/2+}$ presents slower diffusion due to its larger molecular size causing a slight drop in photocurrent. As the authors believed that the $[\text{Co}(\text{Cl-phen})_3]^{3+/2+}$ shuttle promoted a faster recombination reaction between the e_{CB}^- and the Co^{3+} species, they tried to suppress this reaction by blocking the Co^{3+} complex from the titania layer [200,201]. Thus, a multi-capping treatment was applied to the photoanode to form an "alkyl-thicket" structure for effective passivation of the TiO_2 surface, hindering recombination. The treatment was successful and further improved the V_{OC} from 897 mV to 958 mV. In a last effort to improve overall efficiency, Kakiage *et al.* optimized the electrolyte composition and

added an antireflection film on the surface of the photoanode to reach a photovoltage of 1036 mV and a PCE of 12.5 % [190] (**Table 1.2**).

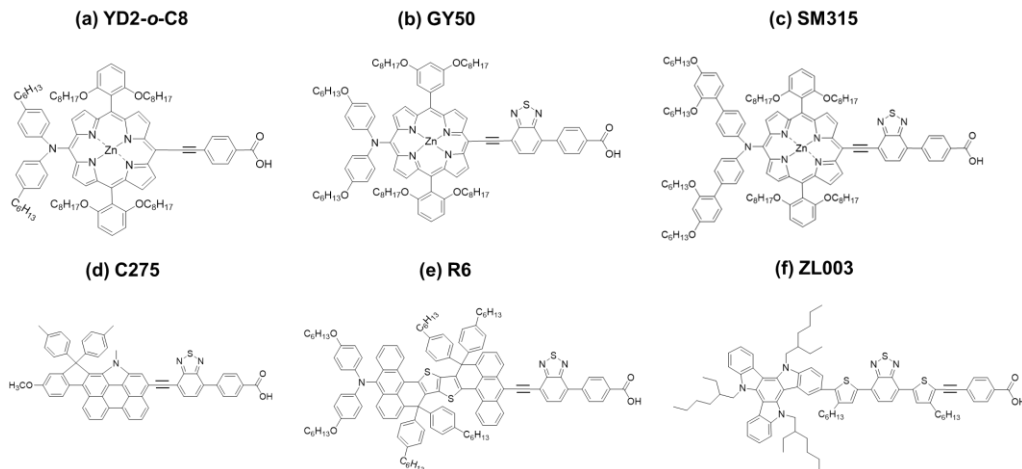


Figure 1.12. Molecular structures of sensitizers in highly performing devices:

(a) YD2-o-C8, (b) GY50, (c) SM315, (d) C275, (e) R6, and (f) ZL003.

In 2015, another successful approach with an organic dye was reported by Yao *et al.* [194], conjugating an indenoperylene electron donor with a benzothiadiazolylbenzoic acid acceptor (C275, **Figure 1.12d**) and a $[\text{Co}(\text{phen})_3]^{2+/3+}$ shuttle (**Figure 1.14c**). This Co complex presents a redox potential of 0.61 V vs. SHE [200] and, in combination with the C275 dye, reached a V_{OC} of 956 mV. The device obtained a 12.5 % PCE under $100 \text{ mW}\cdot\text{cm}^{-2}$ irradiance, without using co-adsorbates [194] (**Table 1.2**).

Hao *et al.* [202] introduced the small organic electron donor tris(p-anisyl)amine (TPAA) in the $[\text{Co}(\text{bpy})_3]^{3+/2+}$ redox shuttle to function as an intermediate redox species. TPAA is a small molecule with reversible electrochemical properties and, in tandem with $[\text{Co}(\text{bpy})_3]^{3+/2+}$, demonstrated ultrafast regeneration kinetics and suppressed recombination between e_{CB}^- and both S^+ and Co^{3+} . This strategy resulted in a significant increase in V_{OC} and J_{SC} , displaying a PCE of 10.5 % (**Table 1.2**). The device maintained 90 % of the initial PCE after 250 h under continuous illumination at 1-Sun and MPP [202]. Later, in 2018, the same authors demonstrated a similar approach by

evaluating the effects of the length and steric hindrance of the tris(4-alkoxyphenyl)-amine (TPA) alkoxy chain. The recombination kinetics demonstrated a clear dependency on the length of the TPA alkoxy chain and, from 1 to 4 carbon atoms, the V_{OC} improved almost linearly from 915 mV to 1030 mV. However, the best overall efficiency was obtained with tris(4-ethoxyphenyl)amine (TPEA), combining high enough V_{OC} (950 mV) and high photocurrent ($15.5 \text{ mA}\cdot\text{cm}^{-2}$) to achieve a PCE of 11.0 % [203] (**Table 1.2**).

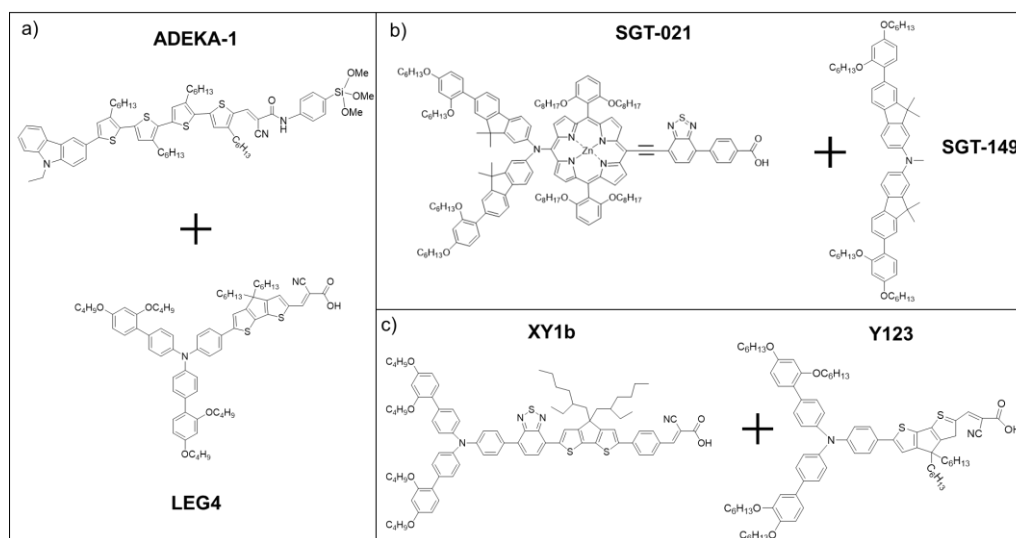


Figure 1.13. Dye molecular structures in most successfully implemented co-sensitization strategies: (a) ADEKA-1+LEG4, (b) SGT-149+SGT021, and (c) MS5+ XY1b.

DSSCs are known for their variety in color, so Ren *et al.* reported a stable and highly-efficient blue sensitizer, coded R6 (**Figure 1.12e**), which features a polycyclic aromatic hydrocarbon, 9,19-dihydrobenzo[1',10']phenanthro[3',4':4,5]thieno[3,2-*b*]benzo-[1,10]phenanthro[3,4-*d*]thiophene, coupled with a diarylamine electron donor and 4-(7-ethynylbenzo[*c*][1,2,5]-thiadiazol-4-yl) benzoic acid acceptor. They combined the R6 dye with a $[\text{Co}(\text{bpy})_3]^{3+/2+}$ electrolyte and, while the V_{OC} was low (850 mV), the superior photocurrent of $19.7 \text{ mA}\cdot\text{cm}^{-2}$ and η_{FF} of 0.75 resulted in a PCE of 12.6 % (**Table 1.2**). The device maintained 90 % of its initial efficiency after 1000 h of continuous full sunlight soaking at 60 °C [204]. In 2019, Zhang *et al.* also used a $[\text{Co}(\text{bpy})_3]^{3+/2+}$

shuttle and investigated electron-injection energy losses in DSSCs using time-resolved laser spectroscopy techniques and two triazatruxene-based sensitizers, with one containing a flexible Z-type double bond (ZL001) and the other a rigid single bond (ZL003, **Figure 1.12f**). The kinetic study revealed that the ZL003 sensitizer injected electrons into the conduction band much faster, minimizing the energy losses on molecular excitation. This resulted in very high photocurrent and photovoltage of $20.7 \text{ mA}\cdot\text{cm}^{-2}$ and 956 mV, respectively; the PCE obtained was 13.6 % under 1-Sun irradiance [209] (**Table 1.2**).

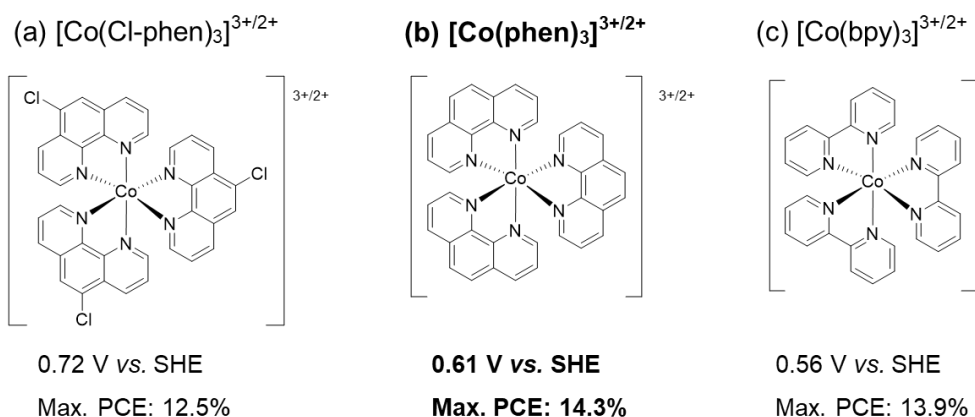


Figure 1.14. Molecular structures of cobalt complexes, with redox potentials and the maximum reported PCE of: (a) $[\text{Co}(\text{Cl-phen})_3]^{3+/2+}$ [193], (b) $[\text{Co}(\text{phen})_3]^{3+/2+}$ [28], and (c) $[\text{Co}(\text{bpy})_3]^{3+/2+}$ [16].

Devices with Co complexes also benefit from a co-sensitization strategy and, in 2011, Yella *et al.* reported one of the earliest and most successful results using a cocktail approach mixing porphyrin YD2-*o*-C8 with organic dye Y123 to achieve a PCE of 12.3 % [28] (**Table 1.2**). In 2015, Kakiage *et al.* reported the most efficient co-sensitization device using ADEKA-1 sensitizer and a carboxy-anchoring organic dye, coded LEG4 (**Figure 1.13b**). The device exhibited a PCE of 14.3 % because the cooperation between dyes improved the electron-injection step from the photoexcited dyes into the TiO_2 conduction band, leading to a $18.3 \text{ mA}\cdot\text{cm}^{-2}$ photocurrent and more than 1 V of photovoltage [27] (**Table 1.2**). The same authors reported another successful

DSSC, this time conjugating ADEKA-1 with a coumarin dye bearing organosilicon tethers as anchoring group (SFD-5) that resulted in a PCE of 12.8 % [142] (Table 1.2).

Figure 1.15 depicts the energy levels of both systems with ADEKA-1, unveiling the importance of a well-chosen co-sensitizer. In any system, dye regeneration is an important step, and when it occurs rapidly, one can successfully prevent charge recombination between the oxidized sensitizer and the injected electrons. The driving force for dye regeneration (ΔG_{reg}) can be approximated as the difference between the HOMO energy level and the E_{redox} . Insufficient ΔG_{reg} will promote faster recombination between the oxidized dye and the injected electrons, causing the J_{SC} to drop. A large dye regeneration overpotential also leads to lower photovoltage and limits PCE [206]. Electron injection can only occur when the LUMO level of the dye (or dyes) is higher than the E_{F} of the semiconductor; this difference between LUMO and E_{F} is usually referred to as electron injection overpotential (ΔG_{inj}). The larger ΔG_{inj} and ΔG_{reg} overpotentials of the SFD-5 dye hinders the photon absorption and lowers the generated photocurrent (**Figure 1.15**).

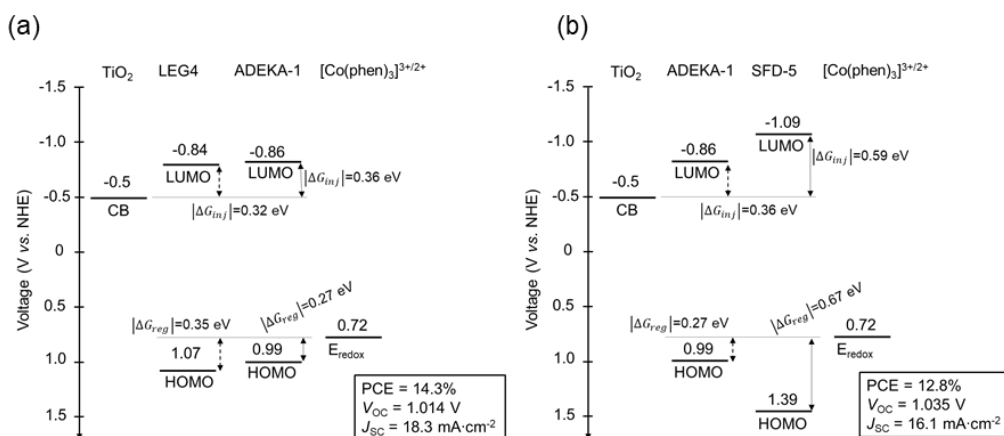


Figure 1.15. Diagram of energy levels of two co-sensitized solar cells (a) LEG4+ADEKA-1 [28]; (b) ADEKA-1+SFD-5 [144].

Ji *et al.* (2020) [16] studied the effect of the electron-donating ability and bulkiness of a new series of fluorenyl moieties in a standard D- π -A structure. These fluorenyl-based donors caused a red-shift of the absorption band, an upshift of the HOMO level, and a reduction in charge recombination. The increase in bulkiness favored the performance of the solar cells, with SGT-149 dye exhibiting the highest V_{OC} and J_{SC} . The co-sensitization of SGT-149 and SGT-021 (**Figure 1.13b**) increased the PCE from 11.4 % to 13.9 % (with $[Co(bpy)_3]^{3+/2+}$), presenting a V_{OC} of 912 mV and a remarkable J_{SC} of 20.9 mA cm⁻² [16] (**Table 1.2**).

Another advantage of cobalt-based cells is the opportunity of using cheaper and widely available materials to replace platinum (Pt) catalyst at the counter-electrode, since Pt is scarce and entails high costs. In fact, several studies have shown that the Pt counter-electrode displays poor electrocatalytic activity towards cobalt complexes and high R_{CT} at the interface between the cobalt electrolyte and the Pt counter-electrode, leading to a lower FF and reduced cell energy performance [199,207]. For a good performing counter-electrode, it is important to ensure: i) high conductivity – to enable fast charge transport; ii) high catalytic activity – to accelerate the regeneration process of the redox couple; iii) high stability – for a long-life device; and iv) low-cost – to ensure commercial attractiveness. [208].

Several successful attempts have been made to replace Pt, such as, carbon-based materials [15,95,219–212], conductive polymers [203,213–225], metal-oxides, as well as composites of those materials [27,177,194,216–218]. Tsao *et al.* demonstrated the effect of R_{CT} on DSSCs performance with a highly porous PEDOT counter-electrode for two Co complexes: $[Co(bpy)_3]^{3+/2+}$ and $[Co(phen)_3]^{3+/2+}$ [213]. Replacing the Pt electrocatalyst with PEDOT significantly improved the FF and lowered the R_{CT} for both cobalt complexes due to the high surface area of the electropolymerized film. However, the pairing with the $[Co(phen)_3]^{3+/2+}$ shuttle limited the photocurrent since it has a bulkier molecular size, which caused diffusion issues. Alternatively, Kakiage *et al.* and Yang *et al.* introduced a gold layer on a graphene nanoparticles (GNP) electrode to

reduce the R_s and enhance the back light reflection from the counter-electrode, thus improving the FF and the J_{sc} , respectively [27,216]. In 2019, Kim *et al.* [173] proposed a novel Pt-free electrochemically stable catalyst based on soft-templated tellurium-doped mesoporous carbon (Te-SMCs). Superior electrocatalytic activity was obtained due to the large specific surface area. Moreover, the mesoporous structure in the carbon network allowed a better electrolyte diffusion and additional contact sites for the Co ions, resulting in a device with a PCE of 11.6 % [173] (**Table 1.2**).

In summary, Co-mediated solar cells have one of the highest performing DSSCs, with a PCE of 14.3 % under 1-Sun (AM1.5G). The three most common Co complexes (**Figure 1.14**) have all showed potential for high performing devices. Co electrolytes are more transparent when compared to iodine and copper counterparts, therefore well-suited for bifacial applications. Some of the best features of these redox mediators are the prospect of reaching higher photovoltages – by modifying the ligands – and higher PCEs under low light intensity or artificial illumination. Additionally, they benefit from the possibility of pairing cobalt electrolytes with organic dyes and of using Pt-free catalysts as counter-electrodes without compromising overall efficiency. However, cobalt complexes are toxic, and further research is required to address the long-term stability of the cobalt mediated devices.

Table 1.2. Photovoltaic Characteristics of Co-mediated DSSCs with PCE > 9 % under 1-Sun

Dye	CE	Electrolyte	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	η_{FF}	η_{PCE} (%)	Year	Ref.
Y123	GnP	Co(bpy) ₃ , LiClO ₄ , tBP	878	14.8	0.72	9.40	2011	[209]
Y123	PEDOT	Co(phen) ₃ , LiClO ₄ , tBP	936	14.8	0.70	9.50	2011	[213]
Y123	PEDOT	Co(bpy) ₃ , LiClO ₄ , tBP	910	15.9	0.71	10.3	2011	[213]
YD2-o-C8	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	965	17.3	0.71	11.9	2011	[28]
YD2-o-C8 + Y123	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	935	17.7	0.74	12.3	2011	[28]
DPP15	Carbon	Co(bpy) ₃ , LiClO ₄ , tBP	745	17.6	0.75	9.81	2013	[210]
DPP17	Carbon	Co(bpy) ₃ , LiClO ₄ , tBP	761	17.9	0.74	10.1	2013	[210]
TFRS-80c	PVP-Pt	Co(phen) ₃ , LiTFSI, tBP	840	14.3	0.75	9.06	2014	[219]
YA422	GnP	Co(bpy) ₃ , LiClO ₄ , tBP	882	15.7	0.69	9.60	2014	[216]
YA422	Au+GnP	Co(bpy) ₃ , LiClO ₄ , tBP	890	16.3	0.74	10.7	2014	[216]
YD2-o-C8	Pt	Co(bpy) ₃ , LiTFSI, tBP	868	16.3	0.74	10.5	2014	[220]
WW-6	Pt	Co(bpy) ₃ , LiTFSI, tBP	809	17.7	0.74	10.5	2014	[220]
ADEKA-1	Pt	Co(bpy) ₃ , LiClO ₄ , Tbp	848	16.1	0.76	10.4	2014	[190]
ADEKA-1	Pt	Co(Cl-phen) ₃ , LiClO ₄ , tBP	958	15.8	0.75	11.3	2014	[190]
ADEKA-1	Pt	Co(Cl-phen) ₃ , LiClO ₄ , tBP, NaClO ₄ , TBAPF ₆ , TBPPF ₆ , HMIPF ₆ ,	1036	15.6	0.77	12.5	2014	[190]

TMSP, MP								
GY50	-	Co(bpy) ₃	885	18.5	0.77	12.8	2014	[193]
SM371	GnP	Co(bpy) ₃ , LiTFSI, tBP	960	15.9	0.79	12.0	2014	[15]
SM315	GnP	Co(bpy) ₃ , LiTFSI, tBP	910	18.1	0.78	13.0	2014	[15]
Y350	Pt	Co(bpy) ₃ , LiTFSI, tBP	942	17.2	0.74	12.0	2014	[221]
M36	Pt	Co(phen) ₃ , LiTFSI, tBP	925	15.0	0.69	9.58	2015	[222]
C272	Au+Cr	Co(phen) ₃ , LiTFSI, tBP	897	15.8	0.74	10.6	2015	[194]
C275	Au+Cr	Co(phen) ₃ , LiTFSI, tBP	956	17.0	0.77	12.5	2015	[194]
YD2-o-C8	Au+Cr	Co(phen) ₃ , LiTFSI, tBP	917	14.4	0.78	10.4	2015	[194]
ADEKA-1+ SFD-5	Pt	Co(Cl-phen) ₃ , LiClO ₄ , tBP, NaClO ₄ , TBAPF ₆ , TBPPF ₆ , HMIPF ₆ , TMSP, MP	1034	16.0	0.77	12.8	2015	[142]
ADEKA-1+ LEG4	Pt	Co(phen) ₃ , LiClO ₄ , tBP, NaClO ₄ , TBAPF ₆ , TBPPF ₆ , HMImPF ₆ , TMSP, MP, CPrBP, CPeBP, COcBP	1018	17.8	0.77	13.8	2015	[27]
ADEKA-1+ LEG4	Au+GnP	Co(phen) ₃ , LiClO ₄ , tBP, NaClO ₄ , TBAPF ₆ , TBPPF ₆ , HMImPF ₆ ,	1014	18.3	0.77	14.3	2015	[27]

TMSP, MP, CPrBP, CPeBP, COcBP								
WW-6	Pt	Co(bpy) ₃ , LiTFSI, tBP	840	17.2	0.74	10.6	2016	[223]
LWP14	Au+Cr	Co(bpy) ₃ , LiTFSI, tBP	805	17.2	0.74	10.3	2016	[217]
SA246	GnP	Co(phen) ₃ , LiTFSI, tBP	845	14.6	0.75	9.40	2016	[211]
51-57dht.1	Carbon	Co(phen) ₃ , LiTFSI, tBP	900	13.9	0.76	9.53	2016	[212]
D35+ DN-F10M	Pt	Co(bpy) ₃ , LiClO ₄ , tBP, TPAA	920	15.5	0.73	10.5	2016	[202]
M42	Pt	Co(phen) ₃ , LiTFSI, tBP	920	15.5	0.68	9.69	2017	[224]
SM342+Y123	GnP	Co(bpy) ₃ , LiTFSI, tBP	941	17.8	0.77	12.8	2017	[95]
FW-1+WS-5	Pt	Co(bpy) ₃ , LiTFSI, tBP	840	18.3	0.68	10.4	2017	[168]
SC-2	Pt	Co(bpy) ₃ , LiTFSI, tBP	856	16.6	0.75	10.6	2017	[225]
SC-3	Pt	Co(bpy) ₃ , LiTFSI, tBP	920	16.5	0.76	11.5	2017	[225]
SM315 (w/ HC-A4)	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	893	16.4	0.79	11.6	2017	[226]
SGT-021(w/ HC-A4)	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	910	17.5	0.75	12.0	2017	[226]
SGT-136	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	804	18.4	0.75	11.0	2017	[227]
SGT-137	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	825	19.4	0.74	11.8	2017	[227]
SGT-137 (w/ HC-A1)	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	884	18.4	0.77	12.5	2017	[227]
WS-70	GnP	Co(bpy) ₃ , LiTFSI, tBP	900	14.1	0.76	9.70	2018	[228]
WS-72	GnP	Co(bpy) ₃ , LiTFSI, tBP	930	14.2	0.77	10.3	2018	[228]
AQ310	PEDOT	Co(bpy) ₃ , LiClO ₄ , TPEA,	950	15.5	0.75	11.0	2018	[203]

tBP								
R4	Pt	Co(bpy) ₃ , LiTFSI, tBP	852	17.3	0.75	11.1	2018	[204]
R6	Pt	Co(bpy) ₃ , LiTFSI, tBP	850	19.7	0.75	12.6	2018	[204]
SGT-021 (w/ CDCA)	Pt	Co(bpy) ₃ , LiTFSI, tBP	848	16.9	0.76	10.8	2019	[229]
SGT-021 (w/ HC-A1)	Pt	Co(bpy) ₃ , LiTFSI, tBP	849	19.2	0.77	12.6	2019	[229]
SGT-021	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	901	16.2	0.79	11.59	2019	[173]
SGT-021	Te-SMC	Co(bpy) ₃ , LiClO ₄ , tBP	893	16.1	0.79	11.64	2019	[173]
H1	Pt	Co(bpy) ₃ , LiTFSI, tBP	931	14.3	0.72	9.70	2019	[230]
H2	Pt	Co(bpy) ₃ , LiTFSI, tBP	903	15.5	0.74	10.3	2019	[230]
DT1	PEDOT:PSS	Co(bpy) ₃ , LiTFSI, tBP	926	16.9	0.75	11.7	2019	[214]
DT2	PEDOT:PSS	Co(bpy) ₃ , LiTFSI, tBP	911	16.0	0.73	10.6	2019	[214]
SGT-030 (w/ HC-A1)	Pt	Co(bpy) ₃ , LiTFSI, tBP	846	16.4	0.77	10.7	2019	[231]
SGT-031 (w/ HC-A1)	Pt	Co(bpy) ₃ , LiTFSI, tBP	847	16.5	0.77	10.8	2019	[231]
ZL001	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	887	20.6	0.70	12.8	2019	[205]
ZL003	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	956	20.7	0.69	13.6	2019	[205]
YD2-o-C8	Co _{0.85} Se/ Gr	Co(bpy) ₃ , LiTFSI, tBP	890	16.5	0.76	11.3	2020	[218]
SGT-148	Pt	Co(bpy) ₃ , LiTFSI, tBP	849	17.1	0.73	10.6	2020	[16]
SGT-149	Pt	Co(bpy) ₃ , LiTFSI, tBP	898	17.5	0.72	11.4	2020	[16]
SGT-149+ SGT021	Pt	Co(bpy) ₃ , LiTFSI, tBP	912	20.9	0.73	13.9	2020	[16]
LS101	Pt	Co(bpy) ₃ , LiTFSI, tBP	966	15.1	0.70	10.2	2020	[191]
YD2-o-C8	Pt	Co(bpy) ₃ , LiTFSI, tBP	858	14.7	0.75	9.44	2021	[232]

bJS2	Pt	Co(bpy) ₃ , LiTFSI, tBP	851	16.4	0.76	10.6	2021	[232]
bJS3	Pt	Co(bpy) ₃ , LiTFSI, tBP	821	16.6	0.75	10.3	2021	[232]
AJ303	Pt	Co(bpy) ₃ , LiTFSI, tBP	914	15.8	0.70	10.2	2021	[233]
XW66	Pt	Co(bpy) ₃ , LiTFSI, tBP	849	14.9	0.74	9.23	2021	[234]
C2+XW66	Pt	Co(bpy) ₃ , LiTFSI, tBP	835	16.4	0.72	9.89	2021	[234]
C3+XW66	Pt	Co(bpy) ₃ , LiTFSI, tBP	853	17.0	0.72	10.2	2021	[234]
YD2-o-C8	PEDOT:PSS	Co(bpy) ₃ , LiClO ₄ , tBP	926	15.5	0.75	10.8	2022	[215]

1.2.3. COPPER SOLAR CELLS

Copper redox mediators are currently very popular because the devices fabricated with these electrolytes routinely surpass the 1000 mV of V_{OC} without significant losses in photocurrent. Additionally, they efficiently regenerate dyes at very small overpotentials (less than 0.2 V) [34,235], therefore allowing DSSCs with higher photovoltages. Compared to Co shuttles, copper-based mediators show slow recombination rates and are environmentally friendly [236]. Similarly to Co complexes, ligands of Cu complexes can be designed to be anchored to the semiconductor surface and stimulate electron transfer between dye and titania layer. Ancillary ligands can be tuned to improve light absorption and enable fast electron transfer between electrolyte and dye [237]. Cu^+ species are tetrahedral while Cu^{2+} cations are usually square-planar. Cu^+ species are unstable, exchange ligands rapidly and they easily oxidize to Cu^{2+} . This phenomenon can be suppressed by employing ligands with moieties that surround the metal and hinder the rearrangement to Cu^{2+} [238].

In 2016, Saygili *et al.* compared three Cu complexes with different ligands and, consequently, different redox potentials: $[Cu(dmby)_2]^{2+/+}$, $[Cu(tmby)_2]^{2+/+}$ and $[Cu(dmp)_2]^{2+/+}$ with redox potentials of 0.97 V vs. SHE, 0.87 V vs. SHE and 0.93 V vs. SHE, respectively [235] (**Figure 1.16**). The authors stated that the internal reorganization energy can be minimized by preserving the coordination geometry around the Cu metal center during the oxidation of Cu^+ to Cu^{2+} , thus enabling a lower driving force in the regeneration step (ca. 0.1 V). The photovoltage of each Cu shuttle exceeded 1 V and it was related to each redox potential, *i.e.*, the V_{OC} of $[Cu(dmby)_2]^{2+/+} > [Cu(dmp)_2]^{2+/+} > [Cu(tmby)_2]^{2+/+}$. However, $[Cu(tmby)_2]^{2+/+}$ exhibited the highest J_{SC} at 15.53 mA·cm⁻² due to the gain in driving force of the dye regeneration [235] (**Table 1.3**). Despite these differences, all Cu-mediated devices achieved similar PCE, with both $[Cu(dmp)_2]^{2+/+}$ and $[Cu(tmby)_2]^{2+/+}$ complexes reaching a PCE of ca. 10.3 % at 1-Sun (**Table 1.3**); so $[Cu(tmby)_2]^{2+/+}$ shuttle became the cornerstone for high performing DSSCs [17,34,36,37,48,228,239–242]. One exception was given by

Yang *et al.* who introduced two novel copper complexes: $[\text{Cu}(\text{mpdt})_2]^{2+/+}$ and $[\text{Cu}(\text{ppdt})_2]^{2+/+}$, with a redox potential of 0.79 V vs. SHE and 0.75 V vs. SHE, respectively. Cu shuttles generally exhibit low diffusion coefficients, which lowers short-circuit currents, yet these two sulfur-copper complexes have smaller ligands that allow high diffusion coefficients [243]. The $[\text{Cu}(\text{mpdt})_2]^{2+/+}$ complex (**Figure 1.16d**) achieved a PCE of 9.9 % under 1-Sun (**Table 1.3**), using a low concentration of Cu^+ (only 0.05 M instead of the standard 0.2 M), which was only possible due to the improved diffusion of this redox shuttle. This small concentration of Cu complex was able to meet the requirements of electron transfer and dye regeneration by reducing the cost and the amount of raw material utilized, avoiding copper precipitation, a great challenge at high electrolyte concentrations [243]. The same authors presented another set of copper complexes: $[\text{Cu}(\text{moby})_2]^{2+/+}$ and $[\text{Cu}(\text{eoby})_2]^{2+/+}$ (**Figure 1.16**) with a redox potential of 0.65 V vs. SHE and 0.70 V vs. SHE, respectively [244]. These complexes had alkoxy chains as ligands, with different sizes, that hindered charge recombination and improved their solubility in acetonitrile. This resulted in an enhancement of J_{SC} and the stability of the assembled devices. Both redox shuttles contributed to a PCE above 10 % under AM1.5G; the device with the smallest size complex, $[\text{Cu}(\text{moby})_2]^{2+/+}$, reached 10.5 % of overall efficiency (**Table 1.3**). This result was only possible due to a high photocurrent ($14.5 \text{ mA}\cdot\text{cm}^{-2}$), consequence of the high diffusion coefficient and high concentration of redox mediator (0.3 M of Cu^+) [244].

Jiang *et al.* proposed a different strategy to increase the photocurrent developing two novel D-A- π -A dyes, HY63 and HY64, bearing a benzothiadiazole or a phenanthrene-fused-quinoxaline as auxiliary electron-withdrawing acceptor moiety, respectively [245]. Both sensitizers present similar HOMO/LUMO levels and absorption spectra. Despite it, HY64 obtained higher photocurrent, which was essentially related to the longer recombination lifetime (τ_{rec}), indicative of improved charge collection efficiency. The photocurrent achieved was $15.76 \text{ mA}\cdot\text{cm}^{-2}$, the highest for a single sensitizer, and the V_{OC} was 1025 mV, leading to a remarkable PCE of 12.5 % [245].

Notable devices were also developed by Liu *et al.* [240] and by Zhang *et al.* [228] with a PCE of 11.2 % and 11.7 %, respectively (**Table 1.3**). Liu *et al.* controlled electron affinity to match the energy levels with a $[\text{Cu}(\text{tmby})_2]^{2+/+}$ redox shuttle, achieving a remarkable photovoltage of 1140 mV while still harvesting a large fraction of photons ($J_{\text{SC}} = 13.0 \text{ mA}\cdot\text{cm}^{-2}$) [240] (**Table 1.3**).

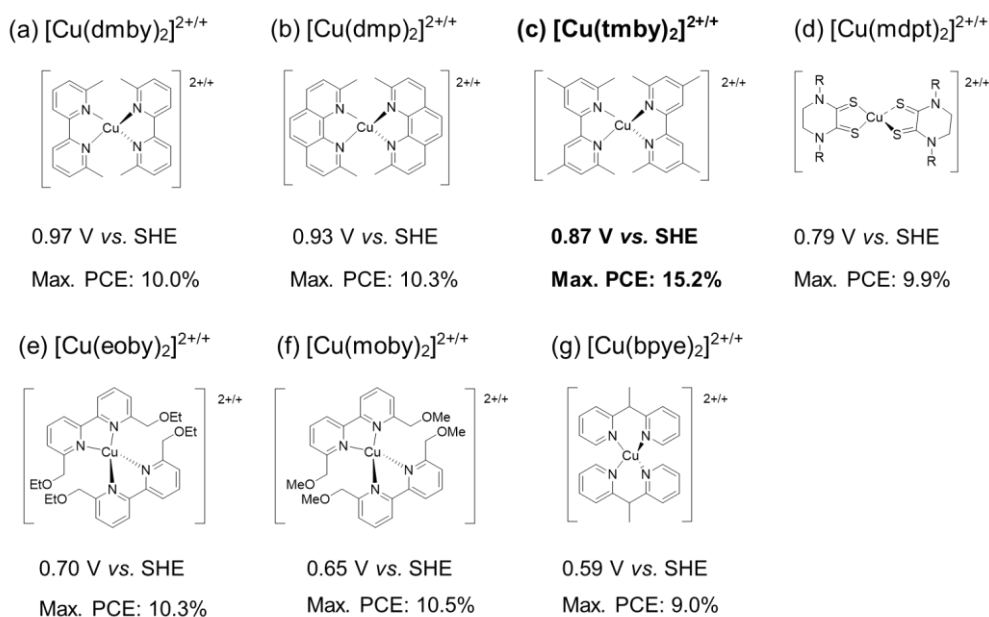


Figure 1.16. Molecular structures of copper complexes, with redox potentials and the best reported PCE of: (a) $[\text{Cu}(\text{dmby})_2]^{2+/+}$ [235], (b) $[\text{Cu}(\text{dmp})_2]^{2+/+}$ [235], (c) $[\text{Cu}(\text{tmby})_2]^{2+/+}$ [13], (d) $[\text{Cu}(\text{mdpt})_2]^{2+/+}$ [243], (e) $[\text{Cu}(\text{eoby})_2]^{2+/+}$ [244], (f) $[\text{Cu}(\text{moby})_2]^{2+/+}$ [244], and (g) $[\text{Cu}(\text{bpye})_2]^{2+/+}$ [246].

In 2018, Cao *et al.* introduced a novel DSSC architecture considering the direct contact between the TiO_2 photoanode and a p-type semiconducting polymer (PEDOT) working as a hole-selective electron-blocking layer, without spacer [48]. This device structure decreased the Warburg resistance, related to the electrolyte diffusion. This new architecture co-sensitized with dyes Y123 and XY1b resulted in an improved PCE of 13.1 %, mainly due to a V_{OC} of 1050 mV [48] (**Table 1.3**). Other successful co-sensitized systems were developed in recent years. For example, Freitag *et al.* combined D35 and XY1

dyes to attain a PCE of 11.3 %, mainly due to high V_{OC} (1030 mV) and good J_{SC} ($16.2 \text{ mA}\cdot\text{cm}^{-2}$) [34] (**Table 1.3**). Tanaka *et al.* combined a D-A- π -A dye XY1 with the less-expensive π -A 5T dye to reach a PCE of 9.1 % under 1-Sun (**Table 1.3**), reducing the cost of the dye by ca. 30 % and improving the cost-performance 1.4 times [37]. The improved performance was essentially related with the increase in photocurrent, mainly because the voids left by the bulky XY1 dye were occupied by the compact I-shape 5T dye and this led to enhanced dye adsorption [37]. In 2020, Michaels *et al.* compared the XY1/D35 to the XY1/L1 system. The latter system also exhibited complementary dye adsorption because the smaller L1 dye and the larger XY1 created a dense dye monolayer, passivating the TiO_2 surface and suppressing electron back-transfer [36]. The introduction of the L1 sensitizer in the dye cocktail enhanced the photovoltage to 1080 mV (**Table 1.3**), as L1 dye has high electronic transition energy. Therefore, higher-energy electrons are injected into the TiO_2 conduction band, which raised the Fermi level. The final device exhibited a PCE of 11.5 % under 1-Sun [36] (**Table 1.3**). More recently, in 2021, Zhang *et al.* [17] developed a new dye, MS5, with a long *n*-dodecyl chain as a bulky donor that was coupled with a copper redox mediator. It raised the V_{OC} up to 1240 mV due to a favorable ground state oxidation potential towards $[\text{Cu}(\text{tmbpy})_2]^{2+/+}$. The MS5 sensitizer was also combined with the wide spectral-range XY1b dye (**Figure 1.13c**) to achieve a PCE of 13.5 % (**Table 1.3**). The devices retained 93 % of the initial efficiency after 1000 h of soaking under 1-Sun illumination and 45 °C. Furthermore, they hold the record of the highest certified DSSC at 13 %.

Very recently, Ren *et al.* developed a new strategy to control the assembly of the dye molecules on the surface of the semiconductor that favors charge regeneration. The authors proposed pre-adsorbing a monolayer of hydroxamic acid on the surface of the TiO_2 to improve dye molecular packing. The photocurrent collection was also enhanced using two newly designed sensitizers with better light harvesting across the entire visible spectrum. The authors reported a record PCE of 15.2 %, with $17.5 \text{ mA}\cdot\text{cm}^{-2}$ of J_{SC} and 1040 mV of V_{OC} [13].

An interesting property of copper complexes was discovered by Freitag *et al.* in 2015: if the solvent of copper-based DSSCs is slowly evaporated through the pre-drilled holes of the counter-electrode substrate, the copper redox shuttle and related additives will act as hole-transporting material (HTM), typically used in solid-state DSSCs (ssDSSCs) [247]. Against all logic, the apparently dead and dried-out cells still generated electricity, hence called “Zombie Cells”. This new type of ssDSSCs achieved a PCE of 8.2 % under 1-Sun, later surpassed by Cao *et al.* in 2017 [239], Zhang *et al.* in 2018 [228], and Michaels *et al.* in 2020 [36]. Cao *et al.* achieved simultaneously high J_{sc} ($13.87 \text{ mA}\cdot\text{cm}^{-2}$) and high V_{oc} (1080 mV), resulting in a PCE of 11 % under 1-Sun (**Table 1.3**). This enhanced performance was a direct result of efficient photon harvesting by using a $6.5 \text{ }\mu\text{m}$ thick mesoscopic TiO_2 layer, favorable energy alignment, efficient charge separation between $\text{TiO}_2/\text{Y123}/\text{HTM}$, and rapid hole hopping in the amorphous Cu-based HTM [239]. Zhang *et al.* outperformed the PCE reported previously by reducing the driving force of electron injection, decreasing the dye regeneration overpotential, and suppressing interfacial electron recombination. These features were accomplished modulating the energy levels of the sensitizers and of the redox mediators, as well as the dye adsorption onto the TiO_2 layers. The optimized device yielded a liquid-junction device with a remarkable V_{oc} (1100 mV), resulting in a PCE of 11.6 % under AM1.5G [228] (**Table 1.3**). Furthermore, Zhang *et al.* evaporated the solvent to produce a ssDSSC, obtaining a PCE of 11.7 %, which remained stable for 1000 h [228]. Despite these achievements, Zombie Cells are impractical for rapid batch production because the solvent of the copper electrolyte must be evaporated slowly, which takes between 72-96 h. Only this slow evaporation allows suppressing the formation of grain boundaries, so that fewer carriers are trapped at the interfaces, leading to an increase in the conductivity of the HTM [36,239,247].

In conclusion, Cu complexes have the highest redox potential of the three systems herein reviewed and, therefore, can reach the highest photovoltages (even surpassing 1200 mV) and very high PCE (**Table 1.3**). The possibility of

producing ssDSSCs is another significant advantage of these complexes. However, Cu-based devices are a relatively new technology, insufficiently studied, and with low reproducibility. In fact, only few laboratories have reported high performing devices. Moreover, despite all the different Cu complexes reported, only two contributed to surpass the 13 % PCE threshold (**Figure 1.16**) [13,239]. Cu complexes are also extremely expensive since Cu(I) is thermodynamically unstable and sophisticated molecular design should be employed to hinder the deep oxidation of Cu(I).

Table 1.3. Photovoltaic Characteristics of Cu-based DSSCs with PCE > 9 % under 1-Sun

Dye	CE	Electrolyte	V _{oc} (mV)	J _{sc} (mA cm ⁻²)	η _{FF}	η _{PCE} (%)	Year	Ref.
LEG4	PEDOT	Cu(bpye) ₂ , LiClO ₄ , tBP	895	14.1	0.71	9.00	2016	[246]
Y123	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	1040	15.5	0.64	10.3	2016	[235]
Y123	PEDOT	Cu(dmby) ₂ , LiTFSI, tBP	1070	14.2	0.69	10.0	2016	[235]
Y123	PEDOT	Cu(dmb) ₂ , LiTFSI, tBP	1060	13.6	0.69	10.3	2016	[235]
Y123	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	1070	13.2	0.66	9.30	2017	[239]
D35	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	1100	12.5	0.72	9.90	2017	[34]
XY1	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	1020	14.6	0.67	10.2	2017	[34]
D35+XY1	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	1030	16.2	0.68	11.3	2017	[34]
Y123	PEDOT	Cu(tmby) ₂ , LiTFSI, MBI	1090	13.7	0.78	11.6	2018	[48]
XY1b	PEDOT	Cu(tmby) ₂ , LiTFSI, MBI	1010	15.0	0.76	11.5	2018	[48]
XY1b+Y123	PEDOT	Cu(tmby) ₂ , LiTFSI, MBI	1050	15.7	0.79	13.1	2018	[48]
L350	PEDOT	Cu(tmby) ₂ , LiTFSI	1140	13.0	0.76	11.2	2018	[240]
WS-70	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	1060	13.2	0.77	11.0	2018	[228]
WS-72	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	1070	13.8	0.79	11.7	2018	[228]
L156	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	1096	12.2	0.69	9.26	2019	[241]
XY1+5T	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	1040	11.8	0.74	9.10	2020	[37]
AJ206	Pt	Cu(tmby) ₂ , LiTFSI, tBP	1020	14.5	0.73	10.6	2020	[242]

XY1+D35	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	1070	15.3	0.67	11.0	2020	[36]
XY1+L1	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	1080	15.9	0.67	11.5	2020	[36]
Y123	PEDOT	Cu(tmby) ₂ , LiTFSI, NBB	1028	13.3	0.75	10.3	2020	[245]
HY63 (w/ CDCA)	PEDOT	Cu(tmby) ₂ , LiTFSI, NBB	986	13.7	0.76	10.3	2020	[245]
HY64	PEDOT	Cu(tmby) ₂ , LiTFSI, NBB	1025	15.8	0.77	12.5	2020	[245]
Y123	PEDOT	Cu(mpdt) ₂ , LiTFSI, tBP	953	14.2	0.73	9.90	2021	[243]
Y123	PEDOT	Cu(eoby) ₂ , LiTFSI, tBP	1029	14.4	0.69	10.3	2021	[244]
Y123	PEDOT	Cu(moby) ₂ , LiTFSI, tBP	1022	14.5	0.71	10.5	2021	[244]
XY1b	PEDOT	Cu(tmby) ₂ , LiTFSI, NMB	1010	15.3	0.76	11.8	2021	[17]
MS5+XY1b	PEDOT	Cu(tmby) ₂ , LiTFSI, NMB	1050	15.8	0.81	13.5	2021	[17]
SL9	PEDOT	Cu(tmby) ₂ , NaTFSI, NMB	1040	16.5	0.78	13.9	2022	[13]
SL9+SL10 (w/ BPHA)	PEDOT	Cu(tmby) ₂ , NaTFSI, CEMI	1040	17.5	0.82	15.2	2022	[13]

1.2.4. OTHER REDOX MEDIATORS

In search of iodine free devices, other redox complexes have been reported; **Table 1.4** summarizes the best performing devices produced using those alternative redox mediators. In 2011, Daeneke *et al.* proposed a ferrocene/ferrocenium (Fc/Fc^+) redox shuttle combined with a novel organic donor-acceptor dye, Carbz-PAHTDIT, which achieved a rather high PCE of 7.5 % under 1-Sun (**Table 1.4**). This result was mainly ascribed to the favorable matching of the E_{redox} of Fc/Fc^+ (0.62 V vs. SHE) to the HOMO/LUMO levels (0.91 V / -1.20 V vs. SHE) of the sensitizer, leading to high V_{OC} (842 mV) and η_{FF} of 0.73 [248]. In the following year, Kato *et al.* reported a DSSC with the 2-azaadamantan-*N*-oxyl (AZA) radical. This redox shuttle has an appropriate E_{redox} (0.63 V vs. SHE), high diffusion coefficient ($12 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$), high heterogenous transfer-rate ($1.6 \text{ cm} \cdot \text{s}^{-1}$), and high electron self-exchange reaction rate ($33 \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$) [249]. The AZA redox shuttle was paired with two indoline dyes, D205 and D131, and a PCE of 8.6 % was obtained mostly due to the high V_{OC} (850 mV) and high η_{FF} (0.75) [249]. In the same year, Burschka *et al.* proposed a disulfide/thiolate-based redox electrolyte (T^-/T_2) to replace the iodine electrolyte. The authors evaluated different counter-electrode materials based on their electrocatalytic activity and surface area. Using a PEDOT counter-electrode with high porosity and surface area, a PCE of 7.9 % was obtained [250]. Another interesting work with a T^-/T_2 redox mediator was developed by Hasin *et al.* in 2017, who evaluated the electrocatalytic properties of *N*-doped mesoporous carbon with nanocomposites of cobalt or nickel [251]. The authors concluded that nickel *N*-doped mesoporous carbon exhibited high electrocatalytic activity towards the reduction of T_2 , obtaining a device with 6.95 % of PCE, 710 mV of photovoltage and $16.0 \text{ mA} \cdot \text{cm}^2$ of photocurrent (**Table 1.4**).

Table 1.4. Photovoltaic characteristics of DSSCs employing alternative redox mediators under 1-Sun

Dye	CE	Electrolyte	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	η_{FF}	η_{PCE} (%)	Year	Ref.
Carbz-PAHTDTT	Pt	Fc, FcPF ₆ , tBP, CDCA	842	12.2	0.73	7.5	2011	[248]
Z907	PEDOT	T ⁻ , T ₂	687	15.9	0.72	7.90	2012	[250]
N719	PEDOT	AT ⁻ , BAT	670	13.8	0.68	6.27	2012	[252]
D205+D131	Pt	TEMPO, NOBF ₄ , LiTFSI, CDCA	780	13.5	0.66	7.00	2012	[249]
D205	Pt	AZA, NOBF ₄ , LiTFSI, CDCA	820	12.9	0.76	8.10	2012	[249]
D205+D131	Pt	AZA, NOBF ₄ , LiTFSI, CDCA	850	13.3	0.75	8.60	2012	[249]
D205	CB	TMTU, NOBF ₄ , LiClO ₄ , tBP	777	16.6	0.49	6.32	2013	[253]
CM309	PEDOT	HQ, BQ, LiTFSI, tBP	755	12.1	0.68	6.20	2013	[254]
N719	Ni-N-MC	NMe ₄ ⁺ T ⁻ , T ₂ , LiClO ₄ , tBP	710	16.0	0.62	6.95	2017	[251]

1.3. INDOOR SOLAR CELLS

Many authors have written about the advantages of DSSCs since they came into the spotlight in 1991, namely their ability to harvest diffuse light or low power light. However, the first articles studying the performance of DSSCs under artificial illumination were only published in 2016, by Liu *et al.* They proposed a new porphyrin dye (Y1A1) tailored for the I^-/I_3^- redox mediator and evaluated the device under three artificial light sources: two fluorescent lamps and one LED planar light, both with variable light intensities. The emission spectrum of the LED demonstrated a better match with the absorption spectrum of the Y1A1 dye and it resulted in a PCE of 19.5 % under 350 lx ($104.3 \mu\text{W}\cdot\text{cm}^{-2}$) with an output power (P_{out}) of $20.3 \mu\text{W}\cdot\text{cm}^{-2}$ [164] (**Table 1.5**). Interestingly, at higher photon flux (1200 lx), the overall efficiency was lower (15.7 %), yet there was a linear correlation between P_{out} and P_{in} with a slope of ~ 0.18 [164]. The superior spectral overlap of artificial light sources over simulated sunlight explains the greater efficiency of DSSCs under indoor light.

In the following years, more articles evaluating indoor performance of DSSCs were published. In 2017, Tingare *et al.* developed a new based-anthracene sensitizer replacing the alkyl group with variable lengths of alkoxy chains, incorporating electron deficient groups, and combining it with iodine electrolyte. The device with TY6 dye was evaluated under fluorescent (T5) and LED light, achieving a PCE of 24.4 % and 17.0 % under 1200 lx, respectively [255] (**Table 1.5**). The emission spectrum of a standard fluorescent lamp presents three narrow, but very sharp, peaks at 440, 550 and 610 nm, whereas LED lamp shows a wide emission peak at 450 nm and a broad band from 500 to 700 nm (with a peak at 600 nm) (**Figure 1.17**). The PCE under fluorescent light outperformed the LED lamp because almost the entire current generated by the TY6 device occurred between 400 and 650 nm, thus displaying a superior match [255]. Later, other works reported PCEs of iodine-based devices exceeding the 20 % threshold [43,59,169]. Jiang *et al.* proposed, in

2019, a novel Y-shaped sensitizer incorporating quinoxalinoid moieties, and an extra acceptor group between the donor and π -bridge to form a D-A- π -A structure that enhanced the absorption extinction coefficients. The co-sensitization of two complementary dyes, MM-6+MM-3, resulted in improved dye coverage on the titania surface and led to a PCE of 27.8 % under fluorescent illumination ($1000 \text{ lx} / 185 \mu\text{W}\cdot\text{cm}^{-2}$) [256]. Other authors have also employed the co-sensitization strategy to achieve high performing DSSCs under indoor light [257–259]. In 2021, Haridas *et al.* achieved a remarkable PCE of 28.7 % under cool fluorescent tube using a carbazole-based D- π -A dye (YK8) without co-adsorbents [260].

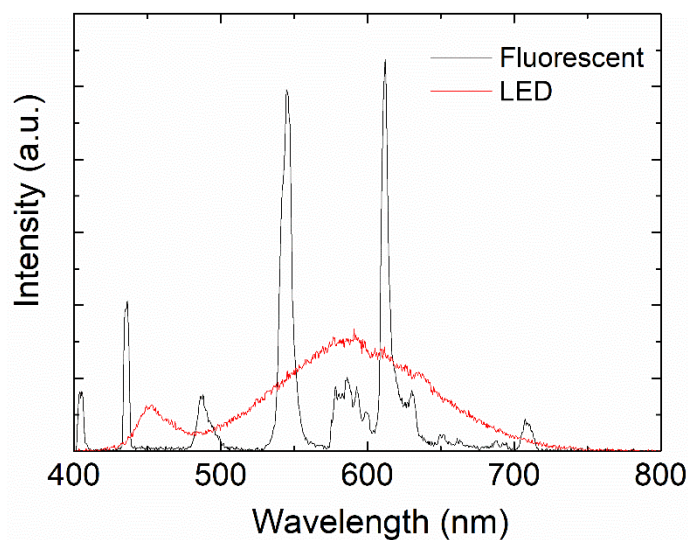


Figure 1.17. Emission spectra of fluorescent (black) and LED (red) lamps.

DSSCs with cobalt redox shuttles have also been analyzed under indoor illumination, and it was observed that the diffusion restrictions of the bulkier cobalt complexes no longer were responsible for limiting the observed photocurrent; this pointed out for a likely superior performance of Co-based DSSCs under low light conditions [95,203]. Some examples of these devices are presented in **Table 1.6**; the most efficient devices were reported by Venkatesan *et al.* [261,262] and Hora *et al.* [215] (see **Chapter 3**). In 2019, Venkatesan *et al.* carefully optimized the three main components of a DSSC

with the specific objective of increasing indoor performance. After optimizing the electrolyte composition, the thickness of counter-electrode catalyst, the photoanode structure and the sensitizer, the obtained optimum conditions were: electrolyte with a ratio of 0.11/0.025 M of Co(II)/Co(III) and 1.2 M of TBP; 0.16 nm Pt layer as counter-electrode; photoanode structure of 6 μm of mesoporous layer, and 4 μm of scattering layer sensitized with Y123 dye. These devices displayed high R_k , between photoanode and redox mediator and low R_{CT} at the counter-electrode/electrolyte interface, resulting in high J_{SC} and V_{OC} , which contributed to a PCE of 24.5 % with an output power of $76.39 \mu\text{W}\cdot\text{cm}^{-2}$ under fluorescent illumination (1000 lx/ $311.5 \mu\text{W}\cdot\text{cm}^{-2}$) [261](**Table 1.6**). Later in 2021, the same authors introduced a new device structure by sandwiching a TiO_2 scattering layer between two TiO_2 mesoporous layers and co-sensitizing the photoanode with dyes D35 and XY1b. This device attained a PCE of 25.0 % and a P_{out} of $85.13 \mu\text{W}\cdot\text{cm}^{-2}$ under fluorescent illumination (1000 lx/ $337.6 \mu\text{W}\cdot\text{cm}^{-2}$) [262] (**Table 1.6**). More recently, Hora *et al.* reported a remarkable PCE of 29.7 % and a P_{out} of $82.0 \mu\text{W}\cdot\text{cm}^{-2}$ under LED illumination (1000 lx/ $275 \mu\text{W}\cdot\text{cm}^{-2}$) incorporating a PEDOT:PSS and graphene nanoplatelets (GNPs) composite as counter-electrode. In fact, GNPs protruded from the PEDOT:PSS film and shortened the effective diffusion path for the Co ions, decreasing the device resistance, as evidenced by the higher η_{FF} and J_{SC} values [215] (see **Chapter 3**).

Cu complexes have collectively shown the highest overall efficiencies under typical indoor light sources [17,34,36,37,48,240]. In 2017, Freitag *et al.* reported an impressive PCE of 28.9 % and an output power of $88.5 \mu\text{W}\cdot\text{cm}^{-2}$ under fluorescent illumination (1000 lx/ $307 \mu\text{W}\cdot\text{cm}^{-2}$) [34] (**Table 1.7**). Several factors were responsible for this rather good performance under indoor light, namely: i) the judicious engineering of dyes that minimized the energy loss related to the interfacial electron-injection; ii) co-sensitization of two dyes with complementary absorption spectra, which formed a compact monolayer at the semiconductor surface and suppressed the back-electron transfer from the TiO_2 conduction band to the Cu(II/I) shuttle; iii) high V_{OC} due to close matching

of the redox potentials of the dyes and Cu complexes [34]. Liu *et al.* also reached a similar result, using only one D- π -A organic sensitizer [240]. Later, Cao *et al.* accomplished a record 31.8 % PCE and a $101.2 \mu\text{W}\cdot\text{cm}^{-2}$ of output power under 1000 lx ($318 \mu\text{W}\cdot\text{cm}^{-2}$) from a fluorescent lamp (**Table 1.7**). In that study, two dyes (Y123 and XY1b) were used to broaden the photocurrent action spectrum and the titania layer was composed of 18 nm particles (instead of the typical 30 nm), which increased the dye uptake. Moreover, Cu(II) concentration was reduced to delay interfacial charge recombination, as indoor conditions are less demanding on the diffusion flux of the redox shuttle [48]. In 2020, Michaels *et al.* broke another record reporting a Cu-based device with 34.0 % of PCE and a P_{out} of $103.1 \mu\text{W}\cdot\text{cm}^{-2}$ under 1000 lx ($303 \mu\text{W}\cdot\text{cm}^{-2}$) from a fluorescent lamp, employing a “Zombie Cell” co-sensitized with XY1 and L1 dyes [36]. Lastly, in 2021, Zhang *et al.* established the PCE record under fluorescent illumination of 34.5 % at 1000 lx ($318 \mu\text{W}\cdot\text{cm}^{-2}$) [17] (**Table 1.7**).

After reviewing the performance of DSSCs under indoor illumination, and analyzing **Table 1.5**, **Table 1.6** and **Table 1.7**, it can be concluded that the field lacks a standard testing protocol. Different studies use different illumination sources and different light intensities, and there are even discrepancies between the conversion of radiometric and illuminance units. As Kokkonen *et al.* mentioned in their review article, the next logical step must be standardizing the evaluation and characterization of DSSCs under indoor illumination [11]. This will be crucial to allow the entrance of DSSCs in the IPV market.

Table 1.5. Photovoltaic characteristics of iodine-based DSSCs under ambient light

Dye	CE	Electrolyte	Lamp	P_{in} (lx)	P_{in} ($\mu W \cdot cm^{-2}$)	V_{oc} (mV)	J_{sc} ($\mu A \cdot cm^{-2}$)	η_{FF}	P_{out} ($\mu W \cdot cm^{-2}$)	η_{PCE} (%)	Year	Ref.
Y1A1	PVP-Pt	I_2 , LiI, PMII, tBP	LED 40 W	350	104	476	56.6	0.76	20.3	19.5	2016	[164]
				1200	358	510	144	0.77	56.3	15.7		
GJ-BP	PVP-Pt	I_2 , LiI, PMII, tBP	T5 (fluorescent)	600	176	487	62.0	0.68	20.7	11.8	2017	[263]
				6000	1751	567	640	0.76	276	15.8		
TF- tBu_C3 F7	PVP-Pt	I_2 , LiI, DPMII, tBP	T5 (fluorescent)	600	176	540	81.3	0.73	-	16.7	2017	[111]
				1200	344	570	161	0.73	-	19.1		
TY6	PVP-Pt	I_2 , LiI, PMII, tBP	T5 (fluorescent)	600	175	649	77.0	0.77	-	21.9	2017	[111]
				1200	345	671	164	0.78	-	24.4		
TKU-4	Pt	EL-201 (Everlight)	T5 (fluorescent)	600	174	600	59.0	0.70	-	13.4	2018	[255]
SK7	PVP-Pt	I_2 , LiI, PMII, tBP	T5 (fluorescent)	600	174	493	60.0	0.74	21.9	12.6	2018	[264]
				1200	340	527	133	0.76	53.4	15.7		
SK6+C W10	PVP-capped Pt	I_2 , LiI, PMII, TBAI, tBP	T5 (fluorescent)	600	195	552	65.0	0.73	26.9	13.8	2018	[43]
				6000	1860	646	883	0.75	419	22.9		
MD7	Pt	I_2 , LiI, DPMII, tBP	T5 (fluorescent)	600	180	597	81.8	0.77	-	20.2	2018	[169]
				6000	1700	676	914	0.76	-	27.2		
N719	Pt	EL-HPE (GreatCell Solar)	Osram 60 W warm white (LED)	-	224	564	112	0.83	52.2	23.3	2019	[59]
				-	1577	640	911	0.78	452	28.7		
MM-6+MM-3	Pt	I_2 , LiI, tBP	TL84, cool white (fluorescent)	600	110	537	84.5	0.68	-	27.8	2019	[256]
				1000	185	598	137	0.65	-	28.7		

N749+ N719	Pt	I ₂ , Lil, PMII, GuSCN, tBP	LED, warm white	500	150	533	81.2	0.72	-	20.7	2021	[257]
N719	Cu-MOF/ PEDOT	I ₂ , Lil, LiClO ₄	Philip T5 (fluorescent)	1000	320	620	130	0.71	-	17.4	2021	[181]
				3000	970	676	4610	0.67	-	21.6		
N719+ YS-2	Pt	I ₂ , Lil, tBP	TL84 (fluorescent)	2500	462	636	234	0.74	-	23.8	2021	[258]
N719+ RY3	Pt	I ₂ , Lil, tBP	TL84, cool white (fluorescent)	1000	185	569	120	0.66	-	24.5	2021	[259]
				2500	462	628	278	0.69	-	26.2		
YK8	Pt	EL-HPE (GreatCell Solar)	Osram 14 W T2, cool white (fluorescent)	700	160	649	90	0.61	35.4	22.2	2021	[260]
				1000	240	669	141	0.72	68.9	28.7		
N719	PEDOT/P t	I ₂ , Lil, DMPH, tBP, GuSCN		200	-	583	24.9	0.76	11.0	15.7	2022	[266]

Table 1.6. Photovoltaic characteristics of cobalt-based DSSCs under ambient light

Dye	CE	Electrolyte	Lamp	P_{in} (lx)	P_{in} ($\mu W \cdot cm^{-2}$)	V_{oc} (mV)	J_{sc} ($\mu A \cdot cm^{-2}$)	η_{FF}	P_{out} ($\mu W \cdot cm^{-2}$)	η_{PCE} (%)	Year	Ref.
Y123	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	Philip T5 (fluorescent)	251	79	712	25.6	0.77	14.0	17.8	2018	[42]
				1002	320	766	95.1	0.79	57.6	18.0		
MK-2	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	Philip T5 (fluorescent)	200	-	638	23.3	0.67	10.0	15.4	2019	[267]
Y123	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	Philip T5 (fluorescent)	202	63.8	785	25.8	0.71	14.5	22.7	2019	[261]
				1000	311	846	124	0.73	76.4	24.5		
TPAA8	PEDOT	Co(bpy) ₃ , LiTFSI, tBP	LED	1000	-	684	70	0.73	-	11.0	2021	[268]
D35+ XY1b	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	Philip T5 (fluorescent)	200	69.6	773	27.6	0.74	15.9	22.7	2021	[262]
				1000	338	831	139	0.73	85.1	25.0		
YD2-o-C8	PEDOT:P SS+GNP	Co(bpy) ₃ , LiClO ₄ , tBP	Osram, warm white (LED)	1000	275	724	146	0.80	82.0	29.7	2022	[215]

Table 1.7. Photovoltaic characteristics of copper-based DSSCs under ambient light

Dye	CE	Electrolyte	Lamp	P_{in} (lx)	P_{in} ($\mu W \cdot cm^{-2}$)	V_{oc} (mV)	J_{sc} ($\mu A \cdot cm^{-2}$)	η_{FF}	P_{out} ($\mu W \cdot cm^{-2}$)	η_{PCE} (%)	Year	Ref.
D35+ XY1	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	Osram 930, warm white (fluorescent)	200	61.3	732	27.2	0.79	15.6	25.5	2017	[34]
				1000	307	797	138.0	0.80	88.5	28.9		
L350	PEDOT	Cu(tmby) ₂ , LiTFSI	Osram 930 warm white (fluoresce.)	1000	-	837	132.9	0.78	-	28.4	2018	[240]
XY1b+ Y123	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	Osram 930, warm white (fluorescent)	200	63.6	808	29.6	0.72	17.5	27.5	2018	[48]
				1000	318	878	149.3	0.77	101.1	31.8		
L156	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	Osram 930, warm white (fluorescent)	200	61.3	763	17.0	0.82	10.7	16.8	2019	[241]
				1000	307	939	103	0.69	67.3	21.9		
XY1+ L1	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP	Osram 930, warm white (fluorescent)	200	60.6	840	29.0	0.78	19.0	31.4	2020	[36]
				1000	303	910	147.0	0.77	103.1	34.0		
XY1+ 5T	PEDOT	Cu(tmby) ₂ , LiTFSI, tBP		1000	303	860	131	0.78	-	29.2	2020	[37]
MS5+ XY1b	PEDOT	Cu(tmby) ₂ , LiTFSI, NMB	Osram 930, warm white (fluorescent)	200	63.6	920	27.1	0.83	20.3	32.4	2021	[17]
				1000	318	980	138.2	0.82	109.8	34.5		

1.4. BIFACIAL SOLAR CELLS

In 2008, Ito *et al.* [269] introduced the novel concept of bifacial solar cells (Bi-DSSCs), which can provide photogenerated power when illuminated from the front- (photoanode side) and the rear-side (counter-electrode side). Compared to one-sided counterparts, Bi-DSSCs can generate ca. 20-40% more power, which is critical in addressing output power density in low light environments [270].

Ideally, a Bi-DSSC should have a transparent counter-electrode to allow light to reach the photoanode. The transparent counter-electrode should maintain high electrocatalytic activity for the reduction of the oxidized species of the redox mediator [215,218,271,272]. Materials such as conductive polymers [215,271–275], metal composites [218,276,277] and platinum [262,269,278–282] are the most studied catalysts in DSSCs. Enhancing the performance of Bi-DSSCs can be achieved by i) optimizing the titania mesoporous layer thickness and including SiO_2 , to prevent the generation of unwanted back-current [269]; ii) changing the architecture of the titania layers [262]; and iii) improving the scattering properties of the semiconductor surface using different size TiO_2 particles [278] or increasing the surface roughness through the inclusion of ZnO microflowers [280,282].

Several authors, such as Wu *et al.*, Zhang *et al.*, and Yao *et al.*, have reported different characterization methods of Bi-DSSCs by simultaneously illuminating the device from front- and rear-sides. Wu *et al.* achieved a PCE of 8.35 %, with a V_{OC} of 730 mV and a J_{SC} of $17.5 \text{ mA}\cdot\text{cm}^{-2}$ [271]. Zhang *et al.* developed a device that produced a photocurrent of $22.3 \text{ mA}\cdot\text{cm}^{-2}$, photovoltage of 691 mV and a PCE of 9.24 % [273]. Finally, Yao *et al.* added a mirror as a sunlight reflector to secure irradiation from both sides (**Figure 1.18**) and obtained a J_{SC} of $20.3 \text{ mA}\cdot\text{cm}^{-2}$, a V_{OC} of 725 mV and a PCE of 9.48 % [275] (**Table 1.8**).

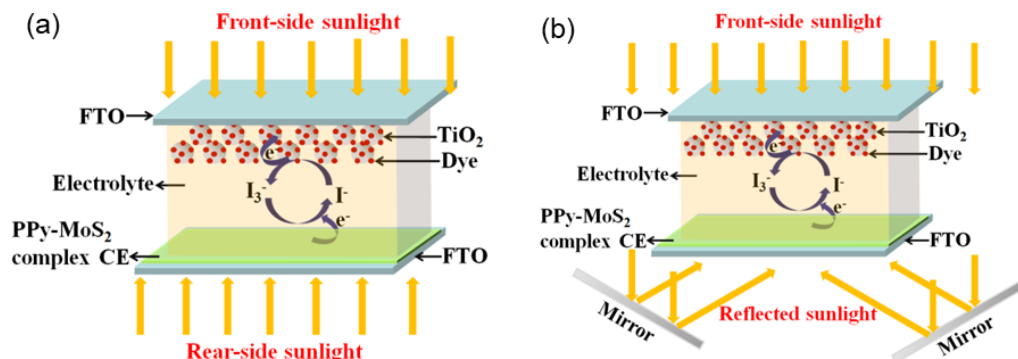


Figure 1.18. Schematic illustration of **(a)** a conventional Bi-DSSC, and **(b)** a Bi-DSSC with a mirror as an incident light reflector. Reproduced with permission of Elsevier, from [275], copyright 2022.

Furthermore, one of the most successful bifacial devices under 1-Sun was developed by Peng *et al.*, who proposed a composite counter-electrode of cobalt selenide/graphene ($\text{Co}_{0.85}\text{Se}/\text{Gr}$). This electrode combined the high electrochemical surface area of $\text{Co}_{0.85}\text{Se}$ and the straight paths for electron transfer from graphene, resulting in a PCE of 11.3 % and 9.43 % from the front- and rear-sides, respectively [218] (**Table 1.8**). Additionally, Venkatesan *et al.* introduced a novel concept for semiconductor architecture by sandwiching a scattering layer between two mesoporous layers (**Figure 1.19**). This novel architecture allowed the light to first be absorbed by the mesoporous layer before being reflected on the scattering layer, regardless of the side of illumination. PCEs of 25.04 % and 23.7 % (**Table 1.9**) were obtained for front- and rear-side illumination ($1000 \text{ lx} / 337.6 \mu\text{W}\cdot\text{cm}^2$), respectively [262].

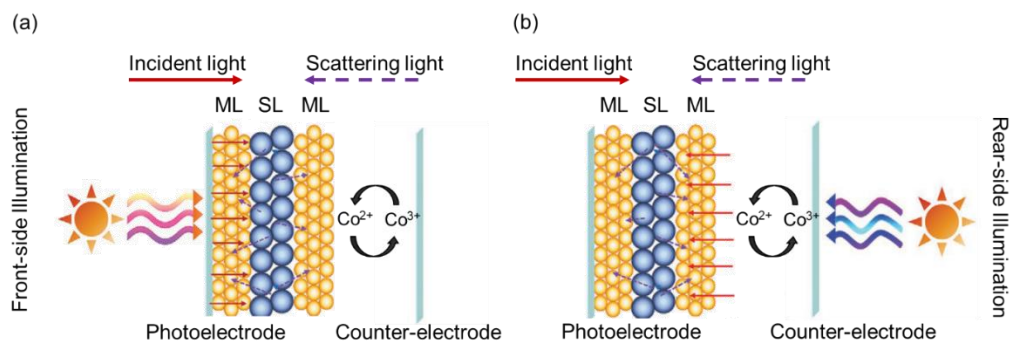


Figure 1.19. Bi-DSSC fabricated using a sandwich architecture of two mesoporous layer (ML) and one scattering layer (SL), under front- (**a**) and rear-side illumination (**b**). Reproduced with permission of Wiley, from [262], copyright 2022.

Table 1.8. Photovoltaic characteristics of Bi-DSSCs under 1-Sun

Dye	CE	Electrolyte	Side	V_{oc} (mV)	J_{sc} (mA·cm ⁻²)	η_{FF}	η_{PCE} (%)	Year	Ref.
Z907Na	Pt	I ₂ , BMII, PMII, GuSCN, tBP	Front	730	13.1	0.69	6.54	2008	[269]
			Back	728	11.6	0.71	5.96		
N719	4-ATP/ PANI(CD)	I ₂ , Lil, TBAI, tBP	Front	709	13.7	0.69	6.70	2014	[271]
			Back	682	8.34	0.73	4.15		
N719	PANI@ 8 wt% MWCNT	I ₂ , Lil, TMAI, TBAI, KI, NaI, tBP	Front	675	18.0	0.65	7.91	2015	[273]
			Back	622	4.30	0.64	1.72		
N719	Ni ₃ S ₄	I ₂ , BMII, tBP, GuSCN	Front	690	15.4	0.63	7.06	2015	[276]
			Back	690	11.1	0.68	5.52		
N719	Co _{0.85} Se	I ₂ , Lil, TEAI, TMAI, TBAI, KI, NaI, tBP	Front	742	16.8	0.67	8.30	2015	[277]
			Back	721	9.90	0.65	4.63		
N719	Pt	I ₂ , BMII, GuSCN, tBP	Front	769	13.5	0.64	6.70	2016	[278]
			Back	766	10.4	0.68	5.40		
N719	Pt	I ⁻ / I ₃ ⁻	Front	810	13.5	0.67	7.29	2018	[279]
			Back	802	10.9	0.67	5.85		
Y123	PEDOT	Co(bpy) ₃ , LiClO ₄ , tBP,	Front	872	14.5	0.68	8.65	2018	[272]
			Back	876	11.9	0.72	7.48		
N719	Pt	I ₂ , Lil, BMII, GuSCN, tBP	Front	739	14.0	0.66	6.82	2020	[280]
			Back	720	9.48	0.69	4.71		
N719	MoS ₂ (2L)/ PEDOT	I ₂ , Lil, BMII, GuSCN, tBP	Front	743	13.7	0.69	7.00	2020	[274]
			Back	730	8.75	0.76	4.82		
N719	PtNPs- ITO PED	I ₂ , Lil, TBAI, NMB, tBP	Front	720	17.2	0.60	7.62	2020	[281]
			Back	730	13.7	0.68	6.83		

YD2-o-C8	Co _{0.85} Se/ Gr	Co(bpy) ₃ , LiTFSI, tBP	Front	890	16.5	0.76	11.3	2020	[218]
			Back	890	13.8	0.77	9.43		
N719	Pt	I ⁻ / I ₃ ⁻ (HPE)	Front	765	14.6	0.64	7.13	2021	[282]
			Back	749	9.55	0.70	5.03		
Y123	Pt	Co(bpy) ₃ , LiClO ₄ , tBP, TPAA	Front	982	13.8	0.70	9.52	2021	[252]
			Back	992	11.3	0.74	8.33		
N719	PPy@ 4 wt% MoS ₂	I ₂ , LiI, TMAI, TEAI, KI, NaI, tBP	Front	707	16.5	0.67	7.80	2022	[275]
			Back	678	7.03	0.66	3.13		
YD2-o-C8	PEDOT:P SS+GNP	Co(bpy) ₃ , LiClO ₄ , tBP	Front	927	15.7	0.67	9.80	2022	[215]
			Back	928	12.9	0.68	8.20		

Table 1.9. Photovoltaic characteristics of Bi-DSSCs under ambient light

Dye	CE	Electrolyte	Lamp	P _{in} (lx)	P _{in} ($\mu\text{W}\cdot\text{cm}^{-2}$)	Side	V _{oc} (mV)	J _{sc} ($\mu\text{A}\cdot\text{cm}^{-2}$)	η_{FF}	P _{out} ($\mu\text{W}\cdot\text{cm}^{-2}$)	η_{PCE} (%)	Year	Ref.
Y123	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	T5 (fl.)	202	63.8	Front	750	23.5	0.76	13.5	20.7	2019	[261]
						Back	747	19.5	0.78	11.3	17.3		
N719	Pt	I ⁻ /I ₃ ⁻ (HPE)	CFL	1000	230	Front	543	94.0	0.69	-	15.5	2021	[282]
						Back	519	64.0	0.59	-	8.50		
D35+ XY1b	Pt	Co(bpy) ₃ , LiClO ₄ , tBP	T5 (fl.)	1000	338	Front	831	139	0.73	85.1	25.0	2021	[262]
						Back	832	127	0.76	80.6	23.7		
YD2-o- C8	PEDOT :PSS+ GNP	Co(bpy) ₃ , LiClO ₄ , tBP	Osram , warm white (LED)	1000	275	Front	719	110	0.77	60.6	21.9	2022	[215]
						Back	721	91.0	0.81	50.4	18.2		

1.5. MONOLITHIC SOLAR CELLS

The monolithic configuration of DSSCs (M-DSSCs) was proposed in 1996 by Kay and Grätzel [283]. These authors applied the mesoporous titania photoanode and the carbon-based counter-electrode onto the same conductive substrate, physically separating the electrodes by scribing a line in the TCO glass. Furthermore, an insulator/spacer layer was deposited between the photoanode and the counter-electrode to ensure electrical separation and to avoid short-circuiting the solar cell. A comparative sketch of conventional and monolithic structures is displayed on **Figure 1.20**.

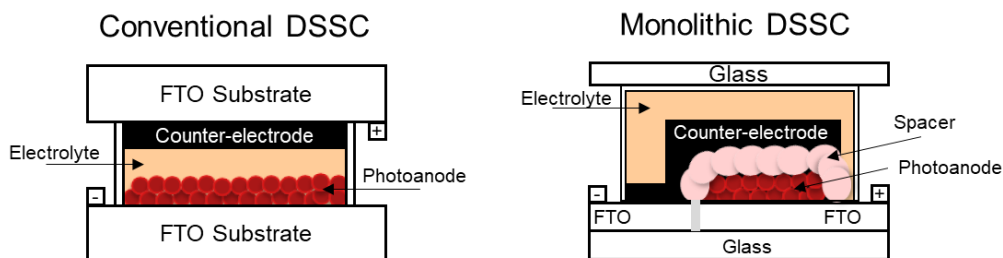


Figure 1.20. Comparative sketch between conventional (left) and monolithic (right) configuration of DSSCs (adapted from [284]).

As it is apparent from **Figure 1.20**, the monolithic configuration can significantly reduce the overall costs of materials used in production, because there is only one FTO substrate, instead of the standard two substrates of the conventional solar cells [12]. Employing the monolithic configuration simplifies the scale up process [285,286] and allows a more straightforward production, especially when using flexible substrates [287,288]. These features account for the main appeal of M-DSSCs. However, monolithic cells are not as efficient as the n-type DSSCs, as the records for highest PCE under 1-Sun show: 9.5 % [289] and 15.2 % [13] for monolithic and conventional DSSCs, respectively. This lower efficiency is partially responsible for the lack of M-DSSCs research articles when compared to their conventional counterparts.

There are several factors that hinder the overall efficiency of M-DSSCs: i) poor light harvesting capacity since the insulator/spacer layer has low reflectivity; ii) increased mass transport and diffusion resistance of the electrolyte due to the second porous layer; and iii) insufficient reduction of the redox mediator by the counter-electrode catalyst layer, resulting in larger R_{CT} [290,291]. Besides, the electrochemical activity and lateral conductivity of the carbon-based counter-electrodes normally used in M-DSSCs are lower when compared with conventional cells, resulting in low η_{FF} and R_s [292,293]. Therefore, replacing the counter-electrode catalyst layer is a usual strategy to improve the overall efficiency of M-DSSCs.

In monolithic solar cells the counter-electrode employed should not only have high electrochemical activity and conductivity, but it should also have a sufficiently large porous network to enable the easy diffusion of the electrolyte species through the whole device (including triple layer structure and the adsorbed dye) [290]. The seminal work by Kay and Grätzel proposed a carbon-based counter-electrode, mixing graphite powder with carbon-black particles, to improve the electrochemical activity and the conductivity, resulting in a PCE of 6.67 % under 1-Sun illumination [283]. Following this trend, Liu *et al.* (2012) suggested a platinized graphite/carbon-black catalyst that improved the catalytic activity and the charge transfer rate when compared with pure carbon; the reported 0.5 % Pt load was, however, sufficient to enhance the electrochemical activity of the counter-electrode, resulting in a PCE of 7.61 % [292].

In 2013, Kwon *et al.* proposed a different approach and combined a highly conductive polymer (PEDOT) as counter-electrode catalyst with macroporous polymer spacer layers (Poly ethylene); this structure resulted in a PCE of 7.73 % under AM1.5G and showed promise when applied to flexible substrates [291]. Years later, in 2018, Behrouznejad *et al.* [293] replaced the carbon counter-electrode and electrodeposited a Cr film and Pt nanoparticles onto a metal foil substrate, which decreased the series resistance of the device and achieved a PCE of 8.0 % (9.5 % unmasked). These authors also evaluated

different insulator/spacer layers; comparing SiO_2 , TiO_2 , and Al_2O_3 they found that a mixture of rutile TiO_2 and SiO_2 (300 nm of average particle size) displayed a better performance. The high refractive index of rutile and the excellent insulating feature of silica shell particles were accountable for the increase in photocurrent. In the following year, using a similar strategy, Santos *et al.* [294] achieved a PCE of 8.3 % employing a SiO_2 - TiO_2 composite as insulating layer. In 2021, these same authors achieved a new record for M-DSSCs by replacing the standard ruthenium dye and iodine electrolyte with a porphyrin sensitizer (YD2-o-C8) and a cobalt redox mediator [289]. The authors studied the impact of ZrO_2 and rutile TiO_2 spacer layers, as well as the concentration of TBP in the electrolyte; the increased light harvesting and the suppression of recombination resulted in a PCE of 9.5 % and 21.9 % under 1-Sun and 1000 lx (LED), respectively. This was also the first time M-DSSCs were evaluated under artificial illumination.

1.6. APPLICATIONS

Over the years, DSSCs have been steadily breaking into the photovoltaic market due to their unique advantages, such as transparency, colorfulness, the use of safe and environmentally friendly materials, low EROI, and their attractive price perspective for mass production. Aesthetic properties make DSSCs perfect candidates for applications such as building integrated photovoltaics (BIPV) [295–297], automotive integrated photovoltaics (AIPV), or outdoor advertising. Noteworthy examples of DSSCs as BIPV are the SwissTech Convention Center at EPFL in Lausanne, Switzerland, the Science Tower in Graz, Austria, and the Solar Pavilion at Roskilde University in Denmark as shown in **Figure 1.21**.

The SwissTech Convention Center (**Figure 1.21a**) was developed by Solaronix and displays a total of 1400 modules in a 300 m² installation varying in color and size to accommodate the roof slope. Instead of a conventional photovoltaic chain installation, this photovoltaic grid was built to fit different panel sizes, exposure angles and different electrical output, as each panel has

a single micro-converter that powers the main circuit [298]. Similarly, the Science Tower (**Figure 1.21b**), which was included in a case study for a Smart City, was manufactured by H. Glass and consists of 896 W-connected DSSCs resulting in an installation of ca. 500 m² [299]. Finally, the Solar Pavilion (**Figure 1.21c**) constructed by the Dongjin Semichem company, implements a design concept by architect Jane Ostermann-Petersen, which comprehends 192 semi-transparent DSSCs over a total area of ca. 180 m². This set-up produces enough power to illuminate the Pavilion all year round and enough surplus power to fuel charging stations for small electronic devices, such as mobile phones and tablets [300].

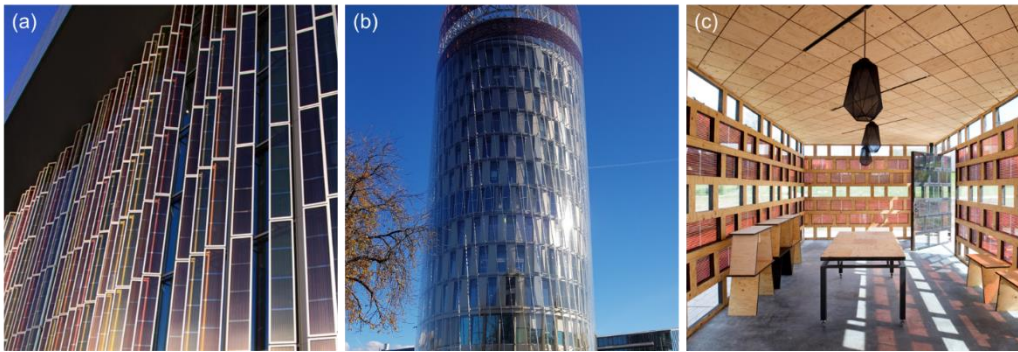


Figure 1.21. Examples of DSSCs as BIPV: **(a)** SwissTech Convention Centre at EPFL in Lausanne, Switzerland, built by Solaronix; reproduced with permission of Solaronix S.A., copyright 2022. **(b)** Science Tower in Graz, Austria, manufactured by H. Glass; reproduced with permission of Hechenblaickner, copyright 2022. **(c)** Solar Pavilion at Roskilde University, Denmark, design concept by Jane Ostermann-Petersen, manufactured by Dongjin Semichem (South Korea), and photograph by Karina Tengberg in 2018; reproduced with permission of Jane Ostermann-Petersen, copyright 2022.

New requirements for DSSCs drove researchers to develop devices on flexible substrates, such as textiles [33] or paper [301], leading to new applications in the field of wearable electronics and even military equipment, such as tents with lightweight DSSCs, capable of powering small portable

devices. They present high performance under low light conditions, namely under indoor illumination, which is increasingly beneficial given the rise of the Internet of Things (IoT) and the forecasted of billions of small devices requiring low power supply. Most smart devices connected via IoT technology are expected to be installed indoors, and while battery technology is constantly advancing, there will be an upsurge in recharging or replacement. Indeed, some companies have already integrated DSSCs to power various types of products. For example, 3G Solar, in Israel, has developed various niche applications such as medical and sports monitors, wireless sensor networks, security sensors and cameras, wearable electronics, among others (). Similarly, Exeger, operating out of Sweden, has developed the Powerfoyle solar cell that can be seamlessly integrated into a wide range of appliances from IoT devices to wearable electronics, bags, furniture, vehicles, among others (**Figure 1.23**). Also, Japanese company Ricoh, developed several products integrating ssDSSCs (**Figure 1.24**). Moreover, UK company G24 Power launched the DSSC GCell technology implemented in a myriad of different products such as keyboards, eReaders, washroom fragrance dispensers, smart cards, and electronic price labels (**Figure 1.25**).



Figure 1.22. Examples of products developed by 3GSolar (Israel): **(a)** temperature sensor, **(b)** security camera, **(c)** smoke alarm, and **(d)** security alarm; reproduced with permission of 3GSolar, copyright 2022.



Figure 1.23. Examples of products developed by Exeger (Sweden): **(a)** Powerfoyle solar cell and Powerfoyle integrated devices: **(b)** headphones, **(c)** safety helmet, **(d)** handbag, wallet, and tablet case, and **(e)** IoT device.

Reproduced with permission of Exeger, copyright 2022.



Figure 1.24. Examples of products developed by Ricoh (Japan): **(a)** environment sensor, **(b)** loopline T1 (the desk is equipped with a strip of DSSCs which can recharge laptop batteries), **(c)** remote controller, and **(d)** smart R mouse; reproduced with permission of Ricoh, copyright 2022.



Figure 1.25. Examples of products developed by GCell by G24 Power (UK): (a) backpack, (b) beacon, (c) iPad case, and (d) keyboard; reproduced with permission of GCell, copyright 2022.

1.6.1. MEDICAL APPLICATIONS

Autonomous devices, which are powered by their own solar cells, can be used in medical applications such as point-of-care diagnostic to detect cancer or degenerative diseases [302–307]. Biosensors are popular devices in point-of-care detection and have two main components: a bioreceptor (or biorecognition element) and a transducer. The bioreceptor can be of a biological nature (*i.e.*, antibodies, enzymes, sugars, nucleic acids, etc.) or of a synthetic one (aptamers or plastic antibodies). The biological bioreceptors are widely established, but have complex production methods, entail higher costs, and lack stability, whereas synthetic counterparts are robust, have high shelf-life and much lower costs [308,309].

Among synthetic bioreceptors, the use of molecularly imprinted polymers (MIPs) is widely popular. MIPs are polymeric matrices that selectively bind to specific molecules, and the technique involves the polymerization of monomers in the presence of a target molecule, *i.e.*, the template compound [310]. After the template is removed, the polymer matrix preserves recognition cavities that are complementary to that template in size, shape, and functionality [309].

In the biosensor, the interaction between the target molecule and the biorecognition compound is monitored by the transducer, which then translates the information into an electrical signal. Photovoltaic cells can be used as electrochemical transducers because they convert photons into electrical energy while being electrically independent. Moreira *et al.* [303] developed a biosensor using a biomimetic material with carcinoembryonic antigen (CEA) as the target protein, which is a cancer biomarker with clinical relevance in the diagnosis of colorectal cancer [311]. The authors proposed the integration of the biosensor in a DSSC, thus paving the way for autonomous screening devices that are fully independent of any electrical reading apparatus or power source. The device was calibrated in urine samples, resulting in a limit of detection (LOD) of $0.0832 \text{ pg}\cdot\text{mL}^{-1}$, with the minimum concentration of the linear range of $0.125 \text{ pg}\cdot\text{mL}^{-1}$, and a sensitivity of $0.89 \text{ }\Omega\cdot\text{mL}\cdot\text{pg}^{-1}$ [303]. Later, Truta *et al.* [304] proposed an electrically autonomous electrochemical immunosensing device powered by a DSSC; the immunosensor was also designed to target CEA detection but using a biological biorecognition element – a natural antibody. J_{sc} was the photovoltaic property that showed the most reliable concentration dependency, and the final device exhibited a linear response within the concentration range of clinical interest: $0.25 \text{ ng}\cdot\text{mL}^{-1}$ to $183.5 \text{ ng}\cdot\text{mL}^{-1}$ [304].

Tavares *et al.* [305,306] proposed two self-powered and self-signaling electrochemical biosensors by merging a biomimetic biosensor, a DSSC and an electrochromic cell into a single device. To build such device, the authors started by assembling the biosensor tailoring a MIP layer to the target analyte (CEA) on the counter-electrode of a DSSC; the electrochromic cell was interfaced in the external circuit and connected the electrodes of the DSSC (**Figure 1.26**). When the DSSC in the hybrid device is illuminated, the generated current flowing through the electrochromic cell promoted a color change as evidenced in **Figure 1.26c** [306]. The hybrid device achieved a LOD of $0.14 \text{ ng}\cdot\text{mL}^{-1}$ and a linear concentration range from $0.1 \text{ ng}\cdot\text{mL}^{-1}$ to $100 \text{ }\mu\text{g}\cdot\text{mL}^{-1}$ [306], a range with clinical relevance. A healthy individual has a

concentration below $2.5 \text{ ng}\cdot\text{mL}^{-1}$ and the presence of oncological disease increases the CEA concentration to values above $10 \text{ ng}\cdot\text{mL}^{-1}$ [312]. Furthermore, the hybrid device successfully produced a gradient of color dependent on the increasing CEA concentration (**Figure 1.27**).

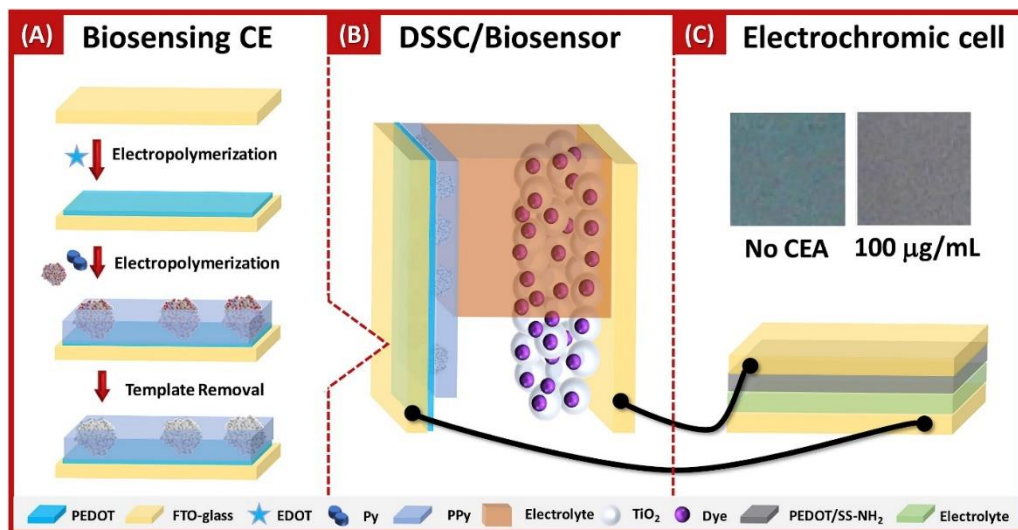


Figure 1.26. Schematic representation of (a) the various stages of the biosensing film assembly on the counter-electrode, (b) the integration of the counter-electrode in the DSSC to produce the hybrid biosensing device, and (c) the interface of the external circuit with the electrochromic cell. Reproduced with permission of Elsevier, from [306], copyright 2022.

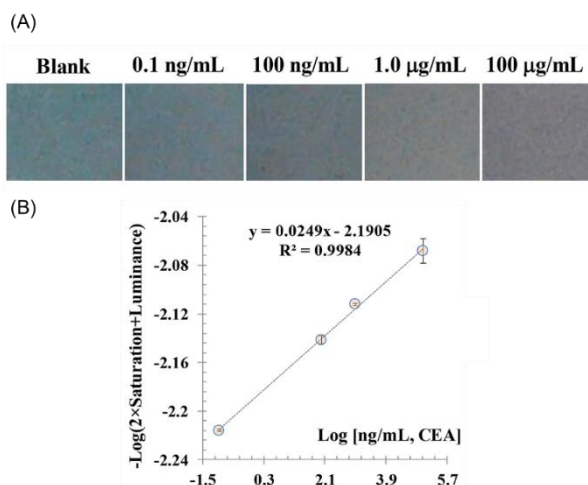


Figure 1.27. (a) Color behavior of electrochromic material when interfaced in the external circuit of the hybrid DSSC/biosensor; (b) Calibration plot, generated by designating the color coordinates of the HSL (Hue, Saturation and Lightness) system to the logarithm of CEA concentration. Republished with permission of Elsevier, from ref. [306], copyright 2022.

1.7. SCOPE OF THE THESIS

After 30 years of research, the initial boost on Dye-sensitized Solar Cells (DSSCs) research has declined, aided by the exponential interest on the development of a similar but more efficient technology, the Perovskite Solar Cells (PSCs). It is common knowledge that DSSCs can also absorb diffuse light more efficiently than many technologies, but it was the indoor potential that has given them a new purpose. The simple fabrication, appealing aesthetics, mechanical flexibility, and sustainability of the materials used to produce the DSSCs are just a few key features that drive the research and development of this photovoltaic technology. The eruption of wireless sensors connected through the Internet of Things (IoT) and the increasing need for swift and dependable sensing devices operating in point-of-care, are great examples of devices that can be suitably powered by DSSCs. This thesis aimed at the development of high-performing DSSCs capable of powering

several small and low-power devices. To achieve this goal, DSSCs with various dye/electrolyte systems will be developed and optimized in search for the best performing cell under solar and artificial light.

This thesis is divided into 6 chapters. **Chapter 1** examines the working principle of a n-type DSSC as well as the characterization methodologies used throughout this thesis. It also overviews the most researched redox couples under both solar and artificial illumination, centering on the key features and weak points of each system. Focusing on the state-of-the-art of the best performing DSSCs with each electrolyte, the role of each DSSC component is thoroughly discussed. Furthermore, bifacial devices are also reviewed, and several approaches for preparing them discussed. Lastly, emerging applications of DSSCs in several fields are reviewed, with a special focus on medical devices, such as biosensors.

Record-achieving DSSCs are nowadays rare and, typically, use sophisticated approaches to achieve high performance. **Chapter 2** reports efficient DSSCs assembled from commercially available materials. The power conversion efficiency of DSSCs was improved by tuning the light absorption layers and minimizing electron recombination with electrolyte. Devices routinely displaying a PCE of 9.84 % at simulated AM 1.5G solar light were obtained. For the first time ever a high PCE of ca. 29 % under artificial room light was attained using DSSCs sensitized with N719 dye.

Chapter 3 presents the development of a PEDOT:PSS (PP) / graphene nanoplatelets (GNPs) composite cathode (PP:GNP) for cobalt-mediated DSSCs, using FTO and non-FTO glass substrates. The optimized devices were also tested for back illumination. Conventional DSSCs using either PP or PP:GNP cathodes showed high average PCE of 10.8 % and 10.4 %, respectively, while the champion cell displayed a PCE of 11 % with a PP cathode under 1-Sun. The main advantage of the developed PP:GNP cathode layer was observed for artificial light conversion; the great energy performance under weak light was unexpectedly derived from the better performance of the counter-electrode for small current densities, which was reported in this thesis

for the first time. The deposition of composite PP:GNP cathodes in FTO-less bifacial DSSCs allowed a PCE of ca. 22 % and 18 % (1000 lx), respectively for front and rear illumination, making them particularly attractive for the use under artificial illumination.

Chapter 4 studies the impact of photoanode architecture, namely, the light-scattering properties, dye loading, and electrolyte layer thickness on key parameters such as photogeneration, recombination, and overall PCE of DSSCs under solar and artificial light. The most common and versatile types of devices were considered: iodine and cobalt, mediated with benchmark N719 and YD2-*o*-C8 dyes, respectively. The champion cobalt device displayed a PCE of 11.0 % and 32.0 % under AM1.5 G and 1000 lx, respectively. The best iodine cells yielded 9.0 % 1-Sun PCE and 23.1 % of PCE under 1000 lx. Capitalizing on the optimized architecture of conventional devices, it is reported on the highest efficiency for back-illuminated cobalt cells under 1000 lx light, with a PCE of 32.0 % and 27.3 % for front and backside illumination, respectively.

Chapter 5 addresses the development of an autonomous and self-powered biosensor using DSSCs to power the device. The need for fast and reliable sensors operating in point-of-care is continually rising and after assessing the best dye/electrolyte system, the DSSC was successfully merged with a biosensor. This biosensor was tailored to a sarcosine molecule, which is a potential biomarker for prostate cancer. The biosensor was constructed on the counter-electrode of the DSSC, with PEDOT as electrocatalyst and modified with an antibody-like film by polymerizing EDOT and pyrrole with sarcosine. The biosensor was coupled with a DSSC, and the characterization included the standard *J-V* curves and electrochemical impedance spectra (EIS). The device could detect the analyte in a 1 ng/mL to 10 µg/mL concentration range (within the range of clinical interest), with a limit of detection (LOD) of 0.33 ng/mL and a sensitivity of 0.47 Ω/decade of sarcosine concentration in spiked urine. The biosensor was also successfully coupled with an electrochromic device, examining its color in the presence of increasing

concentrations of sarcosine. The related color coordinates were extracted and a linear regression between the color saturation and the logarithm of sarcosine concentration was obtained.

Lastly, **Chapter 6** offers the main conclusions of the work developed in this dissertation, along with guidelines and suggestions for future studies.

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CHAPTER 2

DYE-SENSITIZED SOLAR CELLS FOR EFFICIENT
SOLAR AND ARTIFICIAL LIGHT CONVERSION

Adapted from the peer-reviewed article

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DYE-SENSITIZED SOLAR CELLS FOR EFFICIENT SOLAR AND ARTIFICIAL LIGHT CONVERSION

2.1 ABSTRACT

Progresses in dye-sensitized solar cells (DSSCs) have been benchmarked with N719 dye-based devices. However, power conversion efficiency (PCE) improvements performed in low energy performing devices cannot be extrapolated to high performing ones. This points to the need of using a high PCE reference DSSC device, which preferably should be produced using readily available commercial reactants and parts. This study reports an optimized DSSC prepared with commercial reactants, displaying a PCE of 9.84 % under simulated solar light and of 28.7 % under artificial room-light.

The efficient light harvesting at the photoanode and electron recombination suppression at the photoanode/electrolyte interface were systematically optimized; the thickness and light scattering ability of the photoanode mesoporous layers were tuned to maximize light harvesting and minimize the recombination losses. Electron back recombination with electrolyte was minimized using a TiO_2 blocking layer and treating the mesoporous layer of TiO_2 with TiCl_4 , to increase its electronic conductivity. Finally, despite the use of a light scattering over the mesoporous layer, the use of a light reflection layer applied to the back of the devices proved to further improve the PCE.

2.2 INTRODUCTION

Dye-sensitized solar cells (DSSCs) have recently broken into the market with devices that merge good power conversion efficiency (PCE) with low-cost production [1,2]. Since the seminal work by O'Regan and Grätzel in 1991 [3], the PCE of DSSCs has gradually progressed from 7.1 % to ca. 14 % [4]. The best performing DSSCs utilize Co(III)/Co(II) redox shuttle to generate high open circuit voltage; PCEs above 13 % with porphyrin dyes [5] and even above 14 % with metal-free organic dyes were reported [4].

In the past few years, DSSCs were tested and optimized for working under room light [6-9]. The photocurrent response of DSSCs is much higher for the visible spectrum rather than the solar spectrum, allowing efficiencies ca. 30 % under artificial light, though, using very untrivial sensitizers and unstable Cu(II)/Cu(I) redox shuttle [7,8].

Nevertheless, the highest to date certified PCE of DSSCs under standardized solar light is still 11.9 % [10]. The record belongs to the cells sensitized with ruthenium dye and utilizing the iodide/tri-iodide redox electrolyte [11]. Among numerous Ru-complexes tested as sensitizers in DSSCs [12], di-tetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II), also known as N719, is definitely the most reported and one of the most efficient. It was introduced in 2002 [13] and became the "standard dye" for comparing and selecting new sensitizers. This sensitizer (N719) requires reference DSSCs with high performance to use as benchmark. Typical PCE of the cells with N719 dye is ca. 8.3 %, yet few studies report on PCEs above this value, as **Figure 2.1** attests.

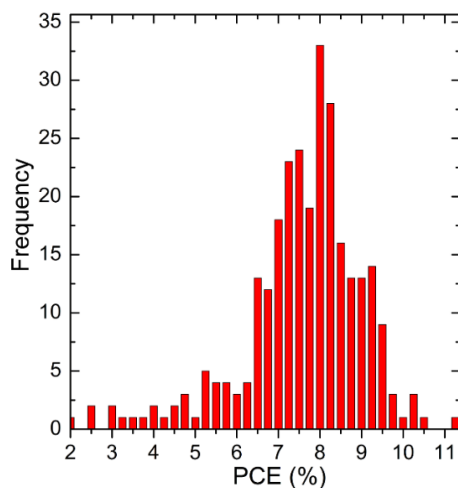


Figure 2.1. Distribution of the DSSCs efficiencies in ca. 300 cases encountered in DSSCs database [14].

Nazeeruddin *et al.* presented a swift self-assembled procedure for N719 dye uptake that yielded 9.18 % of PCE [15]; a purification procedure was developed to obtain pure *N*-bonded isomers originated from N3 dye and resulted in a PCE of 11.18 % [16]. In 2007, Nazeeruddin *et al.* presented a new sensitizer with similar structure to the N719 dye and the PCE of the reference herein reported was 9.3 % [17]. Wang *et al.* used a multilayered photoanode with an optical scattering gradient for enhancing light harvesting reporting a PCE of 10.2 % [18]. Hu *et al.* focused on gel-hydrothermal synthesis of mesoporous TiO₂ photoanode and reported a PCE of 9.86 % [19]. Impressing 11.3 % of PCE was demonstrated implementing a rather complicated blocking layer; W-doped TiO₂ film was prepared to form intermediate bands in the bandgap of semiconductor which improved the electron transport and generated high photocurrent [20].

Record-achieving DSSCs are nowadays rare and, typically, use sophisticated approaches to achieve high performance. In this study, efficient DSSCs assembled from commercially available materials are reported. The power conversion efficiency of DSSCs was improved by tuning the incident light harvesting and minimizing electron recombination with electrolyte.

Devices routinely displaying PCE of 9.84 % at simulated AM1.5G solar light were obtained. For the first time ever a rather high PCE of ca. 29 % under artificial room light was attained using DSSCs sensitized with N719 dye.

2.3 EXPERIMENTAL SECTION

2.3.1 MATERIALS AND REAGENTS

Fluorine-doped tin oxide (FTO)-coated glasses (TEC-7; 7 Ω /sq), screen-printable TiO₂ pastes (30NR-D and 18NR-AO), EL-HPE electrolyte were acquired from GreatCell Solar®. Absolute ethanol, titanium diisopropoxide bis(acetylacetonate), anhydrous isopropyl alcohol and acetylacetone were purchased from Sigma Aldrich®. Dye N719 (ruthenizer 525-bisTBA), platinum paste (Platisol T/SP), chenodeoxycholic acid (CDA) and hot melt sealant (Meltonix 1170-60, 60 μ m Surlyn®) were ordered from Solaronix®. TiCl₄ (99.90%) from Acros Organics was used.

2.3.2 DEVICE ASSEMBLY

The working and counter electrodes were prepared on pieces of FTO-coated glasses with sizes of 2×2 cm². In the substrates for the counter-electrodes, two holes were drilled for the injection of electrolyte. Substrates were cleaned in an ethanol solution of KOH (30 g of KOH dissolved in 200 mL of 70 wt.% EtOH) in an ultrasonic bath, washed with distilled water and dried.

Platinum-activated counter-electrodes were prepared by doctor blading the Platisol T/SP on predrilled FTO-glasses and sintering the substrates at 460 °C for 30 min; 5-10 nm Pt particles were formed homogeneously on the FTO surface (**Figure A1**).

Cells with and without compact TiO₂ blocking layer between photoanode and FTO layer were prepared. Blocking layer with a thickness of 80±5 nm was deposited by spraying a TiO₂ precursor solution (7.0 mL of anhydrous *i*-PrOH + 0.6 mL titanium diisopropoxide bis(acetylacetonate) + 0.4 mL of acetylacetone)

on substrates heated up to 450 °C. The deposited TiO₂ layer was annealed at this temperature for 45 min.

Circular shaped photoanodes (0.13 cm²) were formed on FTO-glasses by screen printing. Pastes 30NR-D and 18NR-AO were used for the deposition of transparent mesoporous TiO₂ (denoted as *Tr*-TiO₂) and scattering opaque TiO₂ (denoted as *Op*-TiO₂) layers, respectively. The thickness of the TiO₂ photoanode layer was controlled by the number of screen-printing cycles; each cycle deposited 7±0.5 μm after sintering. Each printed layer was dried at 120 °C for 10 min before the deposition of the next layer. Printed TiO₂ films were then heated up to 500 °C (2 °C/min) and sintered for 1 h. According to the supplier, the *Tr*-TiO₂ film comprises 30 nm anatase particles while the *Op*-TiO₂ is a mixture of 20 nm anatase particles and ca. 30 wt.% of ≤ 450 nm anatase particles. Typical SEM images of the assembled layers are presented in **Figure A2**. Optical transmittance and reflectance spectra of the *Tr*- and *Op*-TiO₂ films deposited on FTO-glasses are shown in **Figure A3**. The spectra were collected using Shimadzu UV-3600 spectrophotometer equipped with LISR-3100 integrating sphere. Reflectance from BaSO₄ powder compact was used as baseline in reflectance spectrum.

After sintering, TiO₂ films, when necessary, were treated in a 40 mM TiCl₄ aqueous solution for 20 min. at 70 °C, dried and annealed at 500 °C for 1 h. The sensitization was performed dipping the photoelectrodes in a fresh solution of 0.5 mM N719 dye + 5 mM CDA in absolute ethanol for 20±1 hours (for details consult [21]). After sensitization, the cells were rinsed with absolute ethanol, dried in N₂ flow, and immediately sandwiched, like shown in **Figure A4**, with counter-electrode using a hot-pressed thermoplastic gasket. Electrolyte was injected through the holes in the counter-electrode; these holes were then sealed with thermoplastic film and a lamella glass atop.

2.3.3 DEVICE CHARACTERIZATION

For the electrochemical characterization an Autolab, PGSTAT302N electrochemical station was used. Current vs. applied potential (*I*-*V*) response

of the cells was obtained under simulated solar light (AM1.5G, 100 mW/cm²) using a Solar Simulator MiniSol (LSH-7320, Newport). A LED lamp (Osram, Class A+, 60 W, 2700 K) and a fluorescent lamp (Osram, Class A, 86 W, 2700 K) were used to simulate the interior artificial light. The power radiation of the lamps was measured using a radiometer Delta Ohm HD 2102.2 and their emission spectra were obtained using a Getspec 2048 spectrometer. The electrochemical impedance spectra were collected in dark conditions at 20 mV below the open-circuit potential; a sinusoidal perturbation with an amplitude of 10 mV and a frequency range of 100 kHz-0.1 Hz was applied. The impedance spectra were analyzed using the ZView[®] software. The incident photon to current conversion efficiency (IPCE) was recorded using a semi-automatic station (Newport).

2.4 RESULTS AND DISCUSSION

The thickness and light scattering capacity of the mesoporous TiO₂ layer are critical for the photocurrent generation and PCE of the cells [22,23]. For a particular dye-electrolyte system, the photoanode should be tuned to obtain the optimal balance between photogeneration and recombination [24].

A bilayer film of TiO₂ was used for preparing the photoanodes; it was made of a transparent mesoporous titania layer (*Tr*-TiO₂) overcoated with an opaque (*Op*-TiO₂) layer with a higher light scattering capacity (**Figure A3**); both are commercial titania pastes. The optimum thickness of *Tr*-TiO₂ layer in the bilayer structure was optimized based on the photocurrent-potential response of the cells and their impedance spectra. *J-V* curves for the cells with photoanodes made of *Tr*-TiO₂ of different thicknesses are presented in **Figure 2.2a**; **Table 2.1** summarizes the derived photovoltaic parameters.

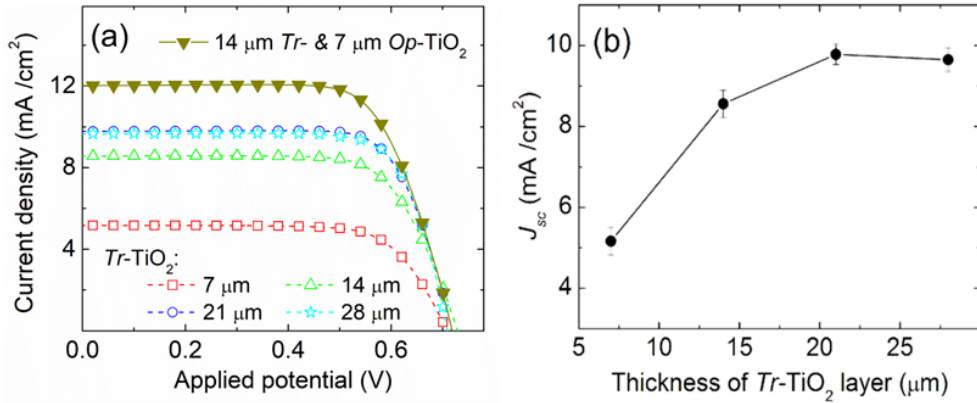


Figure 2.2. (a) Photocurrent vs. applied potential for DSSCs with photoanodes made from Tr -TiO₂ (outlines) and 14 μm Tr -TiO₂ with Op -TiO₂ overlayer (solid symbols); (b) J_{sc} vs. Tr -TiO₂ layer thickness.

Table 2.1. Photovoltaic metrics of the DSSCs with photoanodes made from solely Tr -TiO₂ and $Tr\&Op$ -TiO₂ bi-layer; resistances (Ω·cm²) of the DSSCs obtained by fitting the model (**Figure 2.3b**) to the impedance spectra in **Figure 2.3a**.

TiO ₂ layer	η_{PCE} (%)	V_{OC} (mV)	J_{SC} (mA·cm ⁻²)	η_{FF}	R_s (Ω·cm ²)	R_{CE} (Ω·cm ²)	R_K (Ω·cm ²)
7 μm Tr -TiO ₂	2.64	707	5.16	0.72	1.4	10.1	48.4
14 μm Tr -TiO ₂	4.44	728	8.56	0.71	1.5	13.1	33.4
21 μm Tr -TiO ₂	5.22	717	9.78	0.74	1.6	6.8	18.4
28 μm Tr -TiO ₂	5.17	709	9.65	0.74	1.4	5.3	15.5
14 μm Tr -TiO ₂ & 7 μm Op -TiO ₂	6.12	718	12.02	0.71	1.6	7.3	23.3

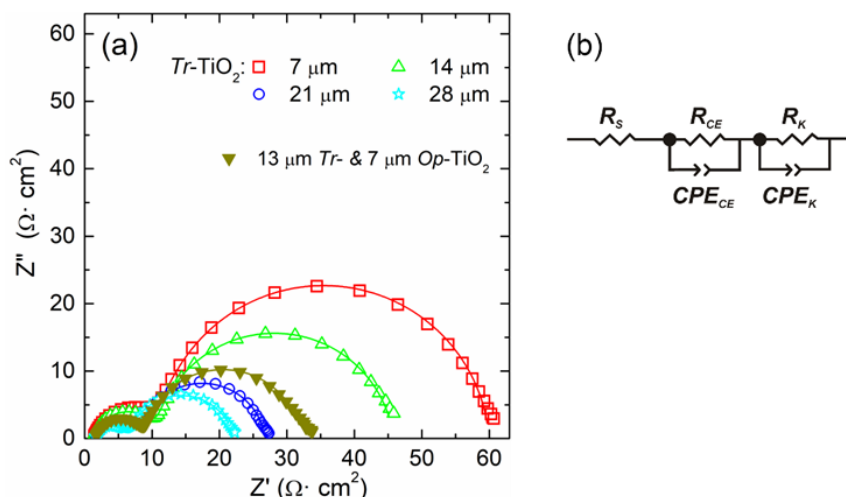


Figure 2.3. (a) Nyquist plots of DSSCs with photoanodes made from Tr-TiO_2 (outlines) and 13 μm Tr-TiO_2 with Op-TiO_2 overlayer (solid symbols). Solid lines stand for the fits to spectra of the equivalent circuit model; (b) Equivalent electrical circuit used for fitting the spectra.

Regardless of the thickness of the Tr-TiO_2 layer, the open circuit potential and the FF of the cells remained almost the same - ca. 710 mV and 0.72, respectively, while the J_{SC} gradually rose with TiO_2 thickness and saturated at a layer thickness of ca. 21 μm (**Figure 2.2b**), resulting in a PCE of ca. 5.2 %. As the thickness of the TiO_2 increases, the loading of the dye increases too, more electrons from the dye are injected into the TiO_2 scaffold, leading to the increase of J_{SC} until an optimal mesoporous layer is achieved. Although rather thick, the Tr-TiO_2 films loaded with dye display transparency in the red-NIR range (**Figure A5**), allowing photogeneration in the deep layers in the path of the light; these layers, however, display much higher ohmic resistances. EIS response of the cells corroborates this assumption (**Figure 2.3**).

Two capacitive semi-circles are observed in the Nyquist plots of the DSSCs. The small and large semi-circles are associated with electron transport at the interfaces between counter-electrode/electrolyte and photoanode/electrolyte, respectively. The spectra were fitted using an equivalent electrical circuit presented in **Figure 2.3b**. In the model, the constant phase elements CPE_{CE} and CPE_K are related to the interfaces

counter-electrode/electrolyte and photoanode/electrolyte, respectively, while the charge transfer resistances R_K , R_{CE} and R_S are related to photoanode/electrolyte interface, counter-electrode/electrolyte interface, and series resistance of the DSSCs, respectively. The fitting parameters of the electric equivalent model is given in **Table 2.1**. In dark conditions, at potential close to V_{OC} , the depletion layer in the TiO_2 is practically absent (flat-band potential) and resistance R_K is ascribed to the electrochemical reaction of electron recombination with electrolyte.

As the TiO_2 mesoporous layer thickness increases, R_S and R_{CE} remain practically the same, while R_K drops because of the larger TiO_2 surface in contact with electrolyte; R_K drops from 33.4 to 18.4 $\Omega \cdot cm^2$ when the thickness of the photoanode increases from 14 to 21 μm . At the same time, the photocurrent rises slightly from 8.6 to 9.8 mA/cm^2 (**Figure 2.2b**, **Table 2.1**) originating a gain in J_{SC} of ca. 14 % and in PCE of 17.6 % (**Table 2.1**). This suggests that the thickness increase of $Tr-TiO_2$ to approx. 21 μm brings significant recombination losses. Increasing further the $Tr-TiO_2$ layer thickness to ca. 28 μm results in a PCE drop.

Photocurrent boosts 30 % when an opaque titania light scattering film ($Op-TiO_2$) is used as the last layer in the path of the incident light (**Figure 2.2**, solid triangles). The $Op-TiO_2$ layer has lower specific surface area than the $Tr-TiO_2$ and offers higher recombination resistance (**Figure 2.3a**). However, a more significant advantage of $Op-TiO_2$ is its reflectivity, which allows scattering of unabsorbed light back to the transparent layer thus benefiting the photocurrent quantum yield in the action spectrum (**Figure 2.4**). This is evidenced by a “shoulder” in the IPCE plot at 580-730 nm originated from the scattering of light on large particles of titanium dioxide (≤ 450 nm) in the $Op-TiO_2$ layer [25].

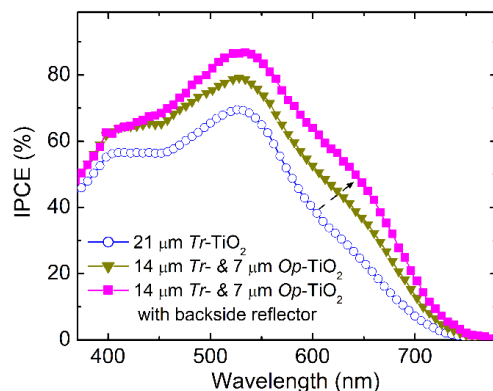


Figure 2.4. IPCE spectra of DSSCs with photoanodes composed from different TiO_2 layers (circles, triangles) and with light reflector on the backside of the DSSCs (squares).

Further improvement of light harvesting was reached by implementation of a light reflector made from self-adhesive polyvinyl chloride (PVC) white tape to the backside of the DSSC. PVC film evenly increases the reflectivity of the counter-electrode (**Figure A6**). When the incident light hits the reflective material in the counter-electrode, it is reflected and travels through the electrolyte to the photoanode, enhancing the light adsorption by the dye [26]. This causes a rise in the IPCE spectra (**Figure 2.4**), especially at longer wavelengths (**Figure A7**).

Reflecting and scattering layers bring the photocurrent to 14.7 mA/cm^2 , resulting in the overall PCE of 7.5 % (**Figure 2.5, Table 2.2**).

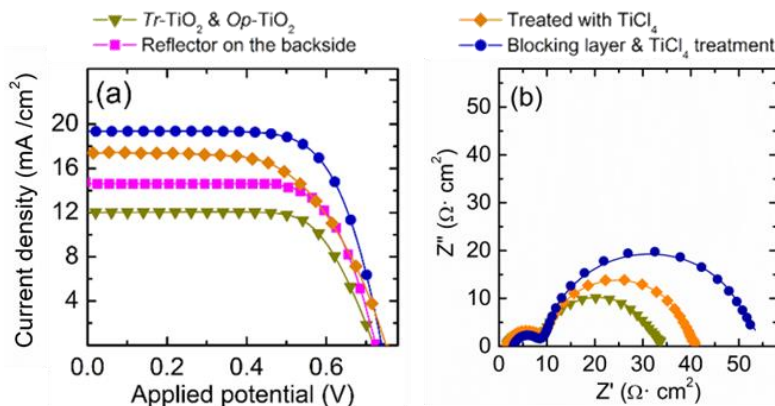


Figure 2.5. J-V curves (a) and Nyquist plots (b) of the DSSCs with different implementations for PCE improvement

Table 2.2. Photovoltaic metrics of the DSSCs with different implementations for the PCE advance; resistances ($\Omega \cdot \text{cm}^2$) of the DSSCs obtained by fitting the model (**Figure 2.3b**) to the impedance spectra in **Figure 2.5**.

Implementation for PCE improvement	η_{PCE} (%)	V_{oc} (mV)	J_{sc} ($\text{mA} \cdot \text{cm}^{-2}$)	η_{FF}	R_{s} ($\Omega \cdot \text{cm}^2$)	R_{CE} ($\Omega \cdot \text{cm}^2$)	R_{K} ($\Omega \cdot \text{cm}^2$)
Light reflector in the backside of the cells	7.54	730	14.67	0.70	1.6	7.3	23.3
TiCl ₄ treatment; backside light reflector	7.84	744	17.44	0.60	1.6	8.0	30.3
TiO ₂ blocking layer; TiCl ₄ treatment; backside light reflector	9.84 (9.92*)	735	19.2 (19.35*)	0.70	3.0	6.1	44.7

A PCE close to the average from **Figure 2.1** was achieved by managing the incident light harvesting and without reducing the electron recombination with electrolyte in the FTO and TiO₂ interfaces. Treating the mesoporous TiO₂ layer at the photoanode with TiCl₄ and the addition of a blocking layer to FTO/photoanode interface are two traditional strategies for suppressing recombination losses [27,28]. The first one downward shifts the conduction band edge of TiO₂ originating a higher quantum efficiency of electron injection from dye to TiO₂ and thus a higher photocurrent; improves the interconnectivity of the TiO₂ nanocrystals in the polycrystalline layer giving better electron transport through photoanode; brings slightly higher surface area allowing more dye to be absorbed and partially blocks FTO surface, suppressing electron recombination at FTO/electrolyte interface [27]. After this treatment, the recombination resistance R_{K} was improved up to $30.3 \Omega \cdot \text{cm}^2$; J_{sc} and V_{oc}

were raised up to $17.44 \text{ mA}\cdot\text{cm}^{-2}$ and 0.74 V , respectively, yielding the PCE of 7.84% (**Table 2.2**). The second strategy, adding a blocking layer, greatly suppresses the recombination at the FTO/electrolyte interface and promotes better electrical contact between the mesoporous TiO_2 layer and the FTO-glass substrate [28]. Blocking layer shifts the recombination resistance R_K up to $44.7 \Omega\cdot\text{cm}^2$ and pushes the J_{SC} up to $19.2 \text{ mA}\cdot\text{cm}^{-2}$, resulting in the typical PCE of the cell of 9.84% ; the best performing device displayed the PCE as high as 9.92% (**Table 2.2**)

Figure 2.6 summarizes the impact of all the aforementioned strategies on the photovoltaic performance of the DSSCs.

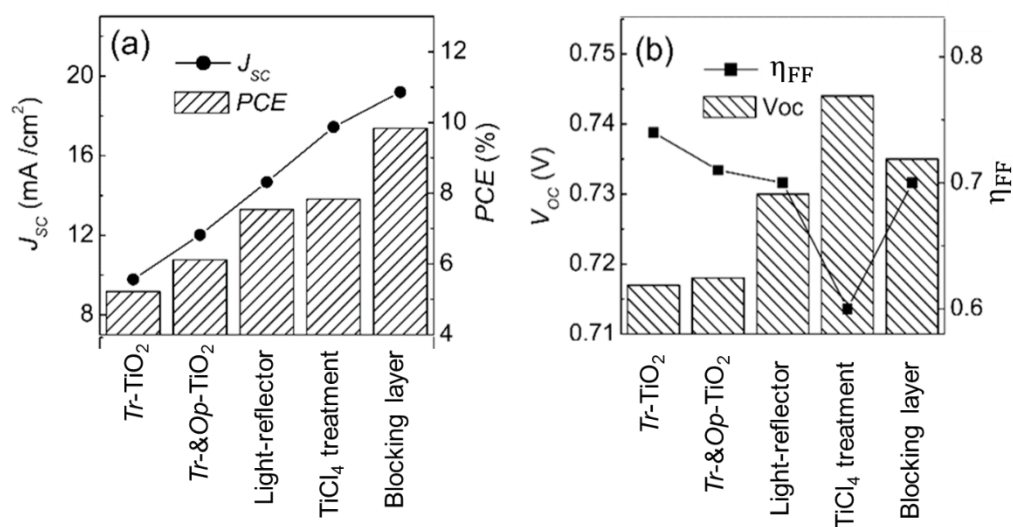


Figure 2.6. Photovoltaic metrics of DSSCs in step-by-step improvement of PCE.

All strategies for improving the PCE discussed above tangibly enhance J_{SC} , allowing to attain ca. 90 % of the theoretical current delivered by a hypothetical “ideal DSSC” with N719 dye [29]. The FF of the cells is satisfactory (0.6-0.74) regardless of the efforts made to ameliorate the PCE. However, due to high overpotentials for the dye regeneration (ca. 0.6 V [30]) and triiodide reduction (ca. 0.3 V [31]), the V_{OC} is much below of the theoretical limit for N719 derived from its optical bandgap (1.6 V [29]). The challenges for

minimizing losses-in-potential are currently being addressed by using new sensitizers and single-electron redox shuttles [32]. These allow to attain a PCE above 13 % under solar light [8] and above 20 % under indoor-light conditions [9,10].

Figure 2.7a presents J - V response of the DSSCs prepared in this work, under artificial light. The use of DSSCs for power generation under indoor light is a relatively new trend and no standard indoor-light source has been established so far [33]. We used two typical sources of artificial light: a LED lamp and a fluorescent lamp. The illumination intensity was varied by changing the distance between the DSSCs and the lamps; the PCE of the cells was derived from the ratio of the maximum power produced by the cells (P_{out}) to the power of the incident light (P_{in}).

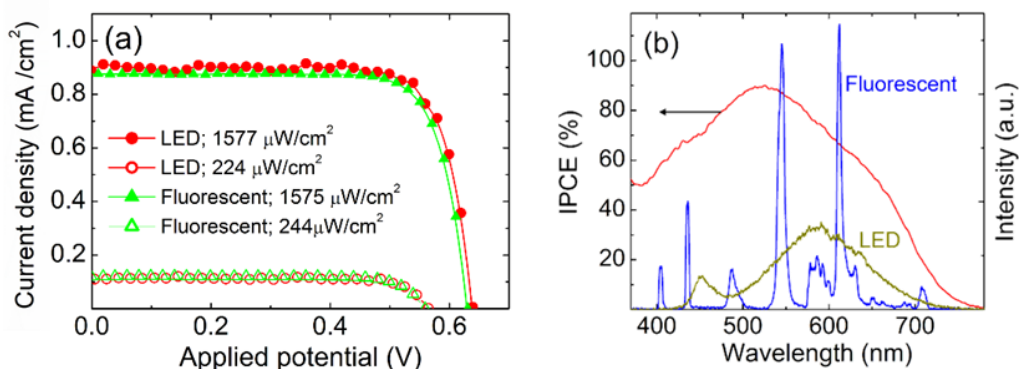


Figure 2.7. (a) J - V curves of the DSSCs under artificial light delivered by LED (**red circles**) and fluorescent lamps (**green triangles**); (b) typical IPCE spectra of a DSSC sensitized with N719 dye (**red curve**) and spectral output from LED and Fluorescent artificial light sources (**green** and **blue** curves respectively).

The photocurrent response from the DSSC depends only on the incident light power and is not sensitive to the type of the artificial light source (a). The reason for this comes from the fact that the emission spectra of both lamps cover the absorption spectrum of DSSC where the highest IPCE values are found (**Figure 2.7b**). **Table 2.3** shows that the PCE increases with the irradiance; such behavior is due to the filling of trap states in TiO_2 with increase of incident light flux [34,35], which in turn originates higher IPCE [36].

For an incident irradiance of 1.5 mW/cm^2 the PCE under artificial light conditions is 28.7 %, the highest to date reported efficiency under artificial light for the DSSCs sensitized with N719 dye. It is noteworthy that properly constructed simple DSSCs system with iodide electrolyte and N719 dye display as good indoor-light conversion efficiency as more complex DSSCs [7-9]. Venkatesan *et al.* reported 18.91 % of PCE with MK-2 dye using Co(III/II) redox shuttle and 3.8 % with N719 dye; a PCE of 28.9 % was achieved by co-sensitizing TiO_2 with XY1&D35 dyes and using untrivial Cu(II/I)(tmby)_2 redox mediator [7]; recently, a PCE of 32 % was reported for XY1b/Y123 co-sensitized TiO_2 and Cu(II/I) redox shuttle [8] with maximum output of $101.2 \text{ } \mu\text{W/cm}^2$, much less, however, than DSSCs with N719 dye and iodide electrolyte performed herein, $452.5 \text{ } \mu\text{W/cm}^2$.

Table 2.3. Photovoltaic metrics of the DSSCs for indoor-light sources

Lamp	P_{in} ($\mu\text{W/cm}^2$)	η_{PCE} (%)	V_{oc} (mV)	J_{sc} ($\mu\text{A}\cdot\text{cm}^{-2}$)	η_{FF}	P_{out} ($\mu\text{W}\cdot\text{cm}^{-2}$)
LED	1577	28.7	640	910.8	0.78	452.5
LED	224	23.3	564	112.3	0.83	52.2
Fluorescent	1575	27.2	630	896.2	0.78	428.3
Fluorescent	244	21.7	558	121.1	0.79	53.0

2.5 CONCLUSIONS

Conventional DSSCs sensitized with N719 dye and assembled using just commercial materials were tuned for effective electricity production under solar and artificial room light. Optimized balance between photocurrent generation and electron recombination versus the thickness of the mesoporous TiO_2 layer was determined based on J - V and EIS responses. The determined optimal thickness of the photoelectrode is ca. $21 \text{ } \mu\text{m}$; increasing the mesoporous TiO_2 thickness the photocurrent remains the same, but the recombination losses

increased tremendously. In 21 μm thick photoanode light harvesting was pushed up using 7 μm of active scattering layer. It improved IPCE at wavelengths above 580 nm. The light unabsorbed by the photoanode was reutilized with the help of a reflector on the backside of the cells, which promotes a response from photoanode layers placed closer to counter-electrode, increasing IPCE at longer wavelengths.

Electron back-recombination reaction at the photoanode/electrolyte interface was suppressed by treating the mesoporous TiO_2 layer with TiCl_4 and inserting TiO_2 blocking layer at the FTO-glass/mesoporous TiO_2 interface; ca. 90 % of the theoretically possible current density in N719-sensitized cells was reached rendering devices routinely displaying a PCE of 9.84 % under simulated solar light. Perfect match of the spectral response from N719-sensitized cells with the emission spectra of typical daylight sources translates to high PCE of 28.7 % under artificial room-light, showing the great potential of conventional DSSCs for the indoor light harvesting. This work should allow researchers to routinely prepare DSSCs displaying 10 % of PCE, useful for benchmarking new developments.

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CHAPTER 3

HIGHLY CATALYTICALLY ACTIVE PEDOT-
GRAPHENE COMPOSITE COUNTER
ELECTRODE FOR SOLAR AND IMPROVED
ARTIFICIAL LIGHT CONVERSION IN REGULAR,
BI-FACIAL AND FTO-LESS COBALT(III/II)
MEDIATED DSSCs

Adapted from the peer-reviewed article

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PEDOT-GRAPHENE COUNTER-ELECTRODE FOR SOLAR AND IMPROVED ARTIFICIAL LIGHT CONVERSION IN REGULAR, BIFACIAL AND FTO-LESS COBALT MEDIATED DSSCs

ABSTRACT

Dye-sensitized solar cells (DSSC) are emerging as an attractive indoor photovoltaic technology to address the challenge of sustainable powering wireless sensor nodes for Internet of Things (IoT) and low power consuming electronics. This study reports on new highly electrochemically active PEDOT:PSS (PP) and graphene nanoplatelets (GNP) composite layer with protruding morphology as counter-electrode for Co(III/II) mediated DSSCs. The PP:GNP counter-electrode layer displays an apparent activation energy (E_a) for charge transfer with $\text{Co}(\text{bpy})^{3+/2+}$ ions of $6.2 \text{ kJ}\cdot\text{mol}^{-1}$, almost twofold lower than pristine PP. The fraction of oxidized EDOT units in the polymer increased upon graphene nanoplatelets doping; the work function of PP:GNP catalyst was best suited to the $\text{Co}(\text{bpy})^{3+/2+}$ redox potential than pristine PP. Despite the significant difference in the catalytic activity, conventional DSSCs with PP and PP:GNP counter-electrodes display similar power conversion efficiency (PCE) of 11.0 % and 10.7 %, respectively, under 1-Sun illumination. A considerable advantage of the PP:GNP counter-electrode layer emerges under artificial

light; DSSCs with PP:GNP cathode render PCE of 29.7 % at 1000 lx, surpassing the counterparts with PP counter-electrode. Protruding from the PP matrix film, GNPs particles shorten the effective diffusion path for Cobalt ions and decrease the device resistance; higher photocurrent is possible under low power illumination. Transparency of ca. 65 % in the visible region and superior electrical conductivity of the PP:GNP films allow using them in FTO-less bifacial devices; DSSCs with bare soda-lime glass substrates for the cathode displayed a PCE of 9.4 % under 1-Sun and 21.9 % and 18.7 % under 1000 lx, for front and back illumination respectively. This makes PP:GNP counter-electrode very attractive for the cost-effective DSSCs targeting indoor light conversion.

3.1 INTRODUCTION

With the rapidly increasing number of indoor, low-power, wireless communication devices, the development of sustainable cordless powering became imperative [1,2]. Indoor photovoltaic devices are considered one of the most promising approaches to address the Internet of Things (IoT) powering [3]. Among the PV technologies, dye sensitized solar cells (DSSCs) have been recognized as the best one to convert indoor artificial light into power [4–8]. On the one hand, DSSCs are perfectly fitted for indoor use [8,9], showing incredibly high and stable power conversion efficiencies (PCE), reaching the 34 % of PCE under 1000 lx [4,5,10]. On the other hand, they are safe for residential use since they do not contain toxic components such as soluble Sn or Pb compounds, and show a very attractive appearance – display true colors, can be produced with flexible and semi-transparent features, being easy to integrate harmonically indoor [9]. DSSCs are rapidly entering the market of indoor photovoltaics [3,6].

The best performing DSSCs to date use Co(III)/Co(II) and Cu(II)/Cu(I) redox shuttles to yield an output voltage above 1.0 V [9]. Bipyridine complexes of cobalt and Zn-porphyrin dyes allow rendering 13 % of PCE under standard AM1.5G illumination, when the photoanode is sensitized with just one dye [11,12], and over 14 % of PCE when implementing a strategy of co-sensitization [13,14]. First reported in 2005 [15], state-of-the-art DSSCs with Cu(II/I) complexes show a landmark PCE of ca. 13.5 % [10] and the highest to date certified PCE of 13 % [16]; amazingly, they display a very high open circuit potential (V_{oc}) of 1.24 V [10]. Copper-mediated DSSCs also hold the record of 34.5 % PCE under indoor 1000 lx light [10].

The indoor irradiance is ca. $100\times$ - $1000\times$ smaller than sunlight, and the maximum power delivered by conventional DSSCs hardly reaches tenths of a milliwatt per cm^2 [4–8]. DSSCs can easily be made bifacial [17], displaying 20–40 % more power generation [17–19]. When the conventional redox mediators for bifacial devices are concerned, the obvious choice favors Co(III/II)

complexes as they allow transparent electrolyte and lead to high PCE when illuminated from the rear side [20–23]. For bifacial devices, it is critical to have a counter-electrode as transparent as possible and at the same time with excellent ability to reduce the oxidized species of the redox mediator [18,20,22].

With the advent of the Co(III/II) shuttles, it soon became apparent that conventional Pt cathodes, typically used in iodine DSSCs, display poor charge transfer with cobalt complexes; research efforts were focused on developing alternatives to Pt catalyzer [24–31]. Carbon materials [12,24,25,32], conductive polymers [22,26–28,33,34] and composites of graphene [20,29–31] have been reported as efficient cathodes for Co(III/II) devices. Kavan et al. [24] showed that graphene nanoplatelets (GNP) are efficient for $\text{Co}(\text{bpy})_3^{3+}$ reduction and allow producing a semi-transparent cathode; 1-Sun PCE of 9.40 % was attained. Tsao et al. [26] assessed the use of PEDOT as counter-electrode reporting a mass transport improvement for the Co ions due to highly porous PEDOT layer and reported on 1-Sun PCE of 10.3 %. Kim et al. [31] assessed a graphene/PEDOT composite cathode layer, which combines the enhanced adhesion and electrical conductivity of PEDOT with the catalytic activity and stability of graphene; these authors reported a device displaying 8.3 % of PCE under 1-Sun. Most studies on counter-electrodes for DSSCs using cobalt electrolytes assess the catalytic activity of the material based on the charge transfer resistance or exchange current density [20–22,25–30]. However, both parameters depend on the effective surface area. They reflect only indirectly the efficacy of the catalyzer to reduce the apparent activation energy (E_a) for the charge transfer, which is a thermodynamically grounded argument for comparing and ranking electrocatalyzers [35].

This work reports a new PEDOT:PSS (PP) / GNP composite cathode (PP:GNP) for DSSCs, FTO-less glass substrate and bifacial cobalt mediated DSSCs. An almost twofold decrease of E_a for charge transfer reaction with $\text{Co}(\text{bpy})_3^{3+/2+}$ ions was observed when using the developed counter-electrode layer. This decrease was assigned to the high catalytic activity of the graphene

nanoplatelets and increase of oxidized EDOT units in the PP, when graphene is added. Conventional DSSCs using either PP or PP:GNP cathodes showed high PCE under 1-Sun, respectively 10.8 % and 10.4 %; the champion cell displayed a PCE of 11 % with a PP cathode. The great advantage of the developed PP:GNP cathode layer was observed for artificial light conversion. To the best of our knowledge, we are reporting for the first time on the impact of this counter-electrode on the device performance under indoor illumination. Due to the morphology of the PP:GNP cathode layer, the electrical resistance of the cell at small currents is substantially lower and led to ca. 13 % more photocurrent under indoor illumination when compared with a device using a counter-electrode layer of just PP. The implementation of composite PP:GNP cathodes in FTO-less bifacial DSSCs allowed 1000 lx PCE of ca. 22 % and 18 %, respectively for front and rear illumination, making them particularly attractive to prepare DSSCs with the improved PCE under weak artificial light.

3.2 EXPERIMENTAL SECTION

3.2.1 MATERIALS AND REAGENTS

Fluorine-doped tin oxide (FTO)-coated glasses (TEC-7; 2.2 mm thick, 7 Ω /sq) and screen-printable TiO₂ pastes (18NR-T and WER2-O) were acquired from GreatCell Solar[®]. Absolute ethanol, titanium diisopropoxide bis(acetylacetonate), tert-butyl pyridine, lithium perchlorate, anhydrous isopropyl alcohol and dimethyl sulfoxide (DMSO) were purchased from Sigma Aldrich[®]; thermoplastic sealant (Meltonix 1170-25, 25 μ m Surlyn[®] and Meltonix 1170-60, 60 μ m Surlyn[®]) were ordered from Solaronix[®]. TiCl₄ (99.90 %) from Acros Organics was used. Porphyrin dye [5,15-bis(2,6-dioctoxyphenyl)-10-(bis(4-hexylphenyl)amino)-20-(4-carboxyphenyl ethynyl)porphyrinato] Zinc(II), also known as YD2-o-C8, and cobalt complexes tris-(2,2'-bipyridine)cobalt(II) di(tetracyanoborate) and tris-(2,2'-bipyridine)cobalt(III) tri(tetracyanoborate), as also known as Co(bpy)₃(B(CN)₄)₂ and Co(bpy)₃(B(CN)₄)₃ respectively, were purchased from Everlight Chemical. Aqueous 1.3 wt.% PEDOT:PSS dispersion

(CLEVIOS™ PH 1000) was purchased from Heraeus Epurio. Polydispersed 6-8 nm thick graphene nanoplatelets were acquired from abcr GmbH (product ID AB304023); the width of graphene plates ranges from ca. 2 to 65 μm (**Figure B1**) with an average of 15 μm , according to the supplier specification.

3.2.2 PREPARATION OF COUNTER-ELECTRODES

FTO-coated glass and bare soda-lime glass served as substrates for the counter-electrodes. PEDOT:PSS and composite PEDOT:PSS-Graphene nanoplatelets counter-electrodes (denoted as PP and PP:GNP, respectively) were deposited from the precursor dispersion by spin coating at 3000 rpm for 45 s. A commercial solution, CLEVIOS™ PH 1000 (1.3 wt.% of PEDOT:PSS in water), was mixed with 5 % (V/V) of DMSO and used to deposit the PP films. The number of spin coating steps dictated the thickness of the films; three layers were deposited sequentially, one on top of the other. Between each deposition step, the films were dried at 120 °C for 15 min. The thickness of PP film was ca. 300 nm, as determined from cross-sectional SEM images (**Figure B2a**). For the preparation of the PP:GNP films, graphene nanoplatelets were first dispersed in isopropanol (5 mg/ml). One milliliter of isopropanol-GNP dispersion was added to one milliliter of the PEDOT:PSS solution with DMSO and homogenized by sonification for 10 min. Three layers of PP:GNP were spin-coated sequentially; cross-sectional SEM images (**Figure B2b**) allowed to obtain the thickness of the composite PP:GNP layer, which was determined to be of ca. 17-31 μm . GNP concentration of 5 mg/mL in the added isopropanol suspension leads to the most efficient devices in the batch, as shown in **Figure B3**.

3.2.3 DSSCs PREPARATION

The working and counter-electrodes were prepared on pieces of FTO-coated glasses with sizes of 2×2 cm². The substrates were cleaned in an ethanol solution of KOH (100 g of KOH dissolved in 500 mL of 70 wt.% EtOH)

in an ultrasonic bath, washed with distilled water and dried. A blocking layer with a thickness of 80 ± 5 nm was deposited spraying a TiO_2 precursor solution (7.0 mL of anhydrous i-PrOH + 0.6 mL titanium diisopropoxide bis(acetylacetonate) + 0.4 mL of acetylacetone) on substrates heated up to 450°C , for 45 min. The photoanode of the DSSCs comprehended a TiO_2 mesoporous layer with thickness of $6\ \mu\text{m}$ and prepared using commercial paste 18NR-T, and a TiO_2 reflecting layer with a thickness of $6\ \mu\text{m}$ and prepared using a commercial paste WER2-O. For the bifacial DSSC devices, the photoanode was prepared from two layers of a mesoporous paste (18NR-T) with a total thickness of $12\ \mu\text{m}$. The photoanodes were screen printed using two commercially available titanium dioxide pastes (from Greatcell Solar) in a circular shape of $0.126\ \text{cm}^2$ and sintered at 500°C for 1 h. After, they were treated with 40 mM TiCl_4 aqueous solution, sintered again (500°C for 1 h), and finally immersed in a solution of YD2-o-C8 in ethanol:toluene (3:1) for 16 h. The counter-electrodes were drilled with two holes ($0.75\ \text{mm}$ diameter). The working and counter-electrodes were sealed with $25\ \mu\text{m}$ thick thermoplastic sealant (Meltonix 1170-25) in a hot-press at 160°C for 15 s. The cobalt electrolyte contains: 0.165 M of $\text{Co}(\text{bpy})_3(\text{B}(\text{CN})_4)_2$, 0.045 M of $\text{Co}(\text{bpy})_3(\text{B}(\text{CN})_4)_3$, 1.0 M of tert-butyl pyridine (TBP) and 0.1 M of lithium perchlorate (LiClO_4) in acetonitrile [36]. After cooling, the DSSC was injected with the electrolyte, the injection holes sealed with Surlyn[®] and a circular cover glass.

3.2.4 CHARACTERIZATION

PP and PP:GNP films were deposited onto FTO glasses to prepare the symmetrical dummy cells; the active area of the dummy cells was $1.0 \times 0.5\ \text{cm}^2$ and they were sealed with a $60\ \mu\text{m}$ thick Meltonix 1170-60 sealant. For the electrochemical characterization of the dummy cells, it was used an Autolab, PGSTAT302N station. Current vs. applied potential (I - V) responses of the prepared cells was obtained under simulated solar light (AM1.5G, $100\ \text{mW}/\text{cm}^2$) using a Solar Simulator MiniSol (LSH-7320, Newport). For I - V

characterization under artificial light, a LED lamp (Osram, Class A+, 2700 K, 60 W) with emission spectra presented in **Figure B4** was used as the light source; the incident light intensity from the LED was calibrated using a radiometer Delta Ohm HD 2102.2. Each testing condition was performed in the batch of 5 devices.

The electrochemical impedance spectra (EIS) were collected in dark conditions at -850 mV; a sinusoidal perturbation with an amplitude of 10 mV and a frequency range of 100 kHz-0.1 Hz was applied. The impedance spectra were analyzed using the ZView[®] software. A UV-Vis-NIR Spectrophotometer from Shimadzu (UV-3600) was used to determine the transmittance spectra of the counter-electrodes. The surface morphology of the catalytic materials was analyzed by scanning electron microscopy (FEI Quanta 400FEG ESEM provided with EDAX Genesis X4M spectroscope). The Raman spectra were obtained using a Raman spectrometer (DXR Raman Microscope, Thermo Scientific) equipped with 532 nm laser. The work function of the films was determined by Kelvin Probe (UHVKP020, KP Technology). The sheet resistance was determined by a four-probe method, using a Keithley 2425-C 100 W Sourcemeter[®].

3.3 RESULTS AND DISCUSSION

3.3.1 STRUCTURAL CHARACTERIZATION OF PP AND PP:GNP FILMS

The counter-electrode in liquid junction DSSCs must ensure efficient Co(III) reduction to provide electrolyte regeneration for the sustainable functioning of the device. Besides, electrocatalytic activity towards the reduction of the oxidized form of the redox mediator, a large specific surface area of the counter-electrode interface with electrolyte is crucial for reducing area-normalized charge transfer and polarization resistances [26]. **Figure 3.1** shows typical SEM images obtained from PP and PP:GNP films deposited on FTO-glass.

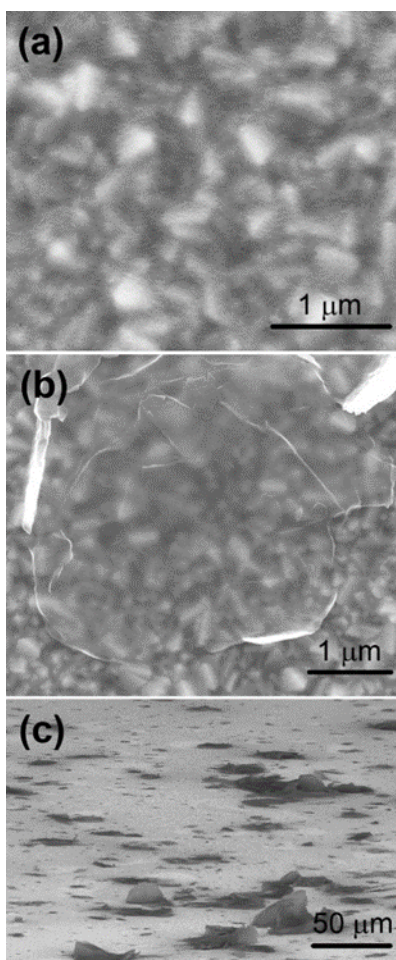


Figure 3.1. SEM patterns of FTO-supported PP (a), PP-GNP (b) counter-electrodes from the top-view, and PP:GNP electrode at sample tilt of 30° (c).

The PP film on FTO shows a homogeneous surface (**Figure 3.1a**) with a thickness of ca. 0.3 μm (**Figure B2a**); this full coverage of the PP film over the FTO is responsible for the blurred effect of the image. In the PP:GNP electrode, most graphene nanoplatelets are conformally immobilized into the thin PP film (**Figure 3.1b**). Some of the graphene sheets are tilted and, to a great extent, protrude from the PP matrix film (**Figure 3.1c**), allowing direct contact of graphene nanoplatelets with the electrolyte; when the GNP protrude from the film, the thickness of the layer reaches ca. 30 μm (**Figure B2b**). For effective reduction of Co(III) at the graphene particles, the latter must have

good contact and exchange charges efficiently with conducting polymer to ensure electronic flow from the electrode to electrolyte. Intermolecular interaction of PP and graphene was characterized by Raman spectroscopy (**Figure 3.2**).

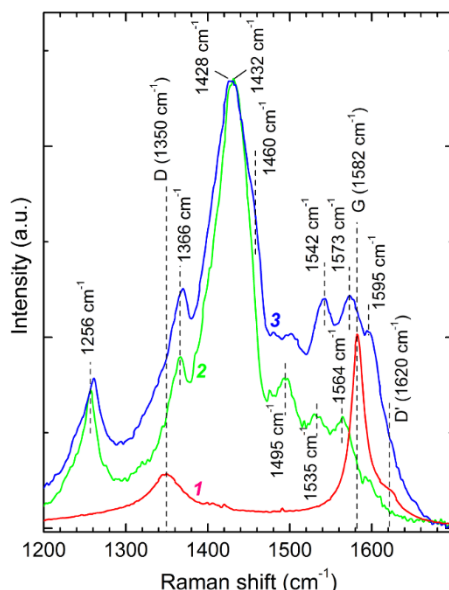


Figure 3.2. Raman spectra of GNP powder (**1**), PP (**2**), and PP:GNP (**3**) films.

Raman spectrum of GNP showed a typical pattern within the frequency range 1200 – 1700 cm^{-1} ; dominant G band at 1582 cm^{-1} is related to a primary in-plane vibrational mode of sp^2 bonded carbons and D band centered at 1350 cm^{-1} corresponds to the breathing vibrations of the sp^2 rings and induced by disorder in graphene layer [37].

Raman spectrum of the undoped PP film showed bands corresponding to $\text{C}_\alpha - \text{C}_\alpha$ inter-ring stretching at 1256 cm^{-1} , the $\text{C}_\beta - \text{C}_\beta$ stretching at 1366 cm^{-1} , a dominant band at 1432 cm^{-1} due to the symmetric $\text{C}_\alpha=\text{C}_\beta$ stretching [38], the band at 1495 cm^{-1} is due to antisymmetric $\text{C}_\alpha=\text{C}_\beta$ stretching of the reduced species in the polymer chain, bands at 1535 cm^{-1} and 1564 cm^{-1} are due to antisymmetric $\text{C}_\alpha=\text{C}_\beta$ stretching of oxidized and reduced ethylenedioxythiophene units in the polymer chains, respectively [39].

The addition of graphene nanoplatelets to the polymer led to a change in the characteristic Raman bands of the polymer. The dominant band of the

symmetric $C_{\alpha}C_{\beta}$ stretching became slightly (4 cm^{-1}) red-shifted to 1428 cm^{-1} ; this is commonly observed in PP-graphene composites, being assigned to the transition from benzoid to quinoid resonant structure in the PEDOT chain caused by π -stacking interaction between PEDOT and the basal plane of graphene [31,40]. A noticeable shoulder appeared on the dominant band at 1460 cm^{-1} , which is related to $C_{\alpha}C_{\beta}$ bond in the oxidized units of the polymer chain [39]. The intensity of the band at 1495 cm^{-1} due to $C_{\alpha}C_{\beta}$ antisymmetric stretching in the reduced polymer units was lower wherein vibrational modes of antisymmetric $C_{\alpha}C_{\beta}$ stretching in the oxidized (1535 cm^{-1}) and reduced (1564 cm^{-1}) EDOT units noticeably increased and blue-shifted to 1542 cm^{-1} and 1573 cm^{-1} , respectively. In addition, a vibration mode at 1595 cm^{-1} due to an antisymmetric stretching of $C_{\alpha}C_{\beta}$ bond of the oxidized species, became pronounced. The spectral changes indicated an increased fraction of the oxidized polymer units at the PP:GNP film. Kelvin probe measurements of the work function of PP and PP:GNP, additionally supported the previous observation. PP loaded with GNP had a work function higher ca. 0.15 eV than the pristine polymer; the determined work function values are 4.62 and 4.47 eV for PP:GNP and PP, respectively.

The changes in the morphology, structure, and fraction of oxidized units in the polymer upon being loaded with GNP affected the electrochemical behavior of the counter-electrode. Electrocatalytic and electrochemical performance of PP and PP:GNP electrodes with the Co-based electrolyte were studied using thin symmetrical half-cells (dummy cells) [24,35,41].

3.3.2 ELECTROCHEMICAL PROPERTIES OF PP AND PP:GNP FILM ELECTRODES IN Co(III/II) ELECTROLYTE

An efficient counter-electrode must display a high electrocatalytic activity to Co(III) reduction and a high electrical conductivity. Overall, the electrochemical activity means the ability of the electrode to yield high currents at minimal losses of the applied potential. The most common approach to assess these losses is based on the charge transfer resistance (R_{CT}) or

exchange current density (J_0) [20–22,25–30], both dependent on the interfacial electrode/electrolyte area, meaning that the same material prepared with a higher specific surface area will allow lower R_{CT} and higher J_0 .

The electrocatalytic activity implies the ability to facilitate the electrochemical reaction. Electrocatalytic activity is fairly and straightly assessed from the apparent activation energy (E_a) of the charge transfer reaction. The Arrhenius equation (**Eq. 3.1**) allows computing E_a using the temperature dependence of exchange current density, J_0 [42]:

$$J_0 = J_{inf} \cdot \exp\left(-\frac{E_a}{\mathcal{R} \cdot T}\right) \quad (\text{Eq. 3.1})$$

where T is absolute temperature, $\mathcal{R}$ is the gas constant, J_{inf} is the J_0 at infinite temperature. In its turn, J_0 can be obtained from R_{CT} following (**Eq. 3.2**) [24,42]:

$$J_0 = \frac{\mathcal{R} \cdot T}{nFR_{CT}} \quad (\text{Eq. 3.2})$$

where n is the number of electrons and F is the Faraday's constant.

Temperature-dependent EIS response (**Figure 3.3**) of the symmetrical half-cells at zero potential bias was used to determine R_{CT} , J_0 and E_a . The Nyquist plots of the dummy-cells with PP and PP:GNP electrodes show two distinct regions for the frequency response. The higher-frequency semicircle is related to the R_{CT} at the electrode/electrolyte interface. A typical equivalent circuit [24,31,35] (**Figure 3.3c**) was used to fit the EIS response. In the equivalent circuit R_s and R_{CT} stand for series and charge transfer resistances, respectively; W_s is the finite-length Warburg element, CPE is a constant phase element associated with electrode/electrolyte interface. From the model, R_{CT} was extracted and J_0 was computed according to (**Eq. 3.2**). **Figure 3.4** shows the Arrhenius plots for J_0 in the case of PP and PP:GNP electrodes.

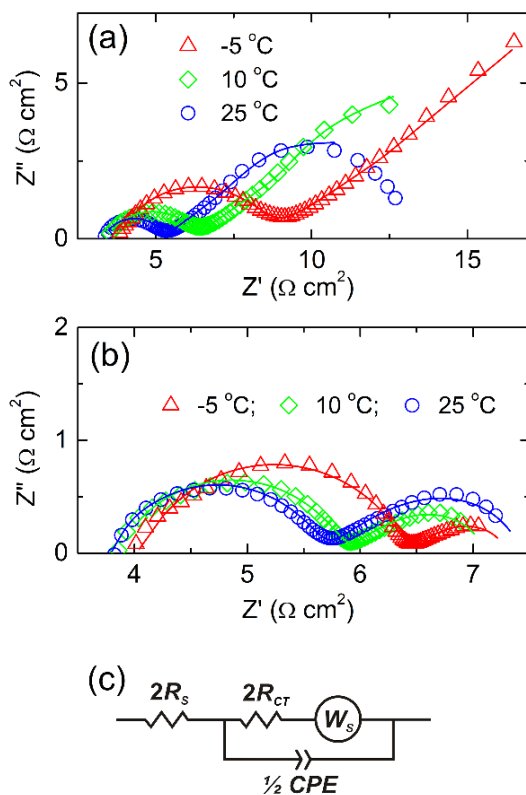


Figure 3.3. Typical Nyquist diagrams at selected temperatures obtained from the EIS response of the symmetrical dummy-cells with PP **(a)** and PP:GNP **(b)** electrodes and Co(III/II) electrolyte. Solid lines stand for fittings of the spectra to the equivalent circuit **(c)**.

Both PP and PP:GNP electrodes display typical Arrhenius behavior at temperatures from -5 to 40 °C. The linear regression slope for the $\ln(J_0)$ vs. $1/T$ fitting allowed to compute E_a which was 17.5 and 6.2 $\text{kJ} \cdot \text{mol}^{-1}$ for the electronic transfer with PP and PP:GNP electrodes, respectively. Almost trifold decrease of the E_a for charge transport in Co(III/II) electrolyte was observed when GNP were incorporated into the PP film.

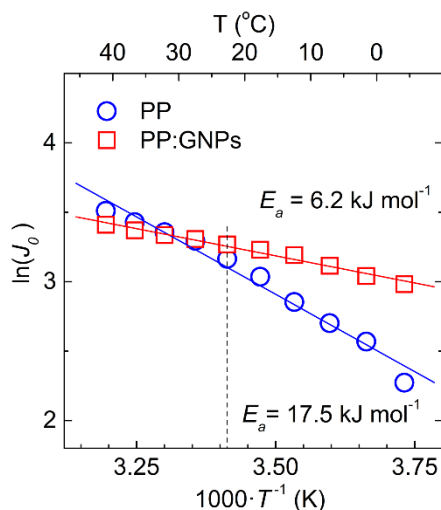


Figure 3.4. $\ln(J_0)$ vs. $1/T$ obtained for PP (**circles**) and PP:GNP (**squares**) electrodes. A vertical dashed line marks room temperature of 20 °C.

The authors suggest at least three reasons for such an intense drop in the E_a . The first one should be related to the high activity of graphene nanoplatelets in reducing Co(III) [24,25,29–31], which has been thoroughly reported, though omitting the determination of E_a . The second one should be related to the increase of the oxidized polymer units in the PP:GNP, which are known to play a crucial role in the cathodic catalysis [43–45]; electrons are trapped on them, leading to the unstable intermediate state of reduced PEDOT, which is then re-oxidized transferring an electron into the electrolyte [44,45]. Thirdly, a close match between the work function of the counter-electrode and redox potential of the mediator leads to lower R_{CT} , allowing a good electrocatalytic activity of the counter-electrode catalyst [46–48]. The redox potential of $[\text{Co}(\text{bpy})_3]^{3+/2+}$ is 0.57 V vs. NHE [35], *i.e.*, 5.01 eV in the absolute scale. The PP:GNP composite displays a work function of 4.62 eV - more approximate to the Co(III/II) redox potential if compared to pristine PP with the work function of the 4.47 eV. Quantifying these three contributions for the electrocatalytic activity of PP:GNP is challenging, as described next.

Despite the considerable difference in E_a , both PP and PP:GNP electrodes at room temperature generate almost similar J_0 (**Figure 3.4**). Still,

the addition of GNP into PEDOT:PSS improves the overall electrochemical activity of the composite, rendering higher current densities in the dummy cells (**Figure 3.5**).

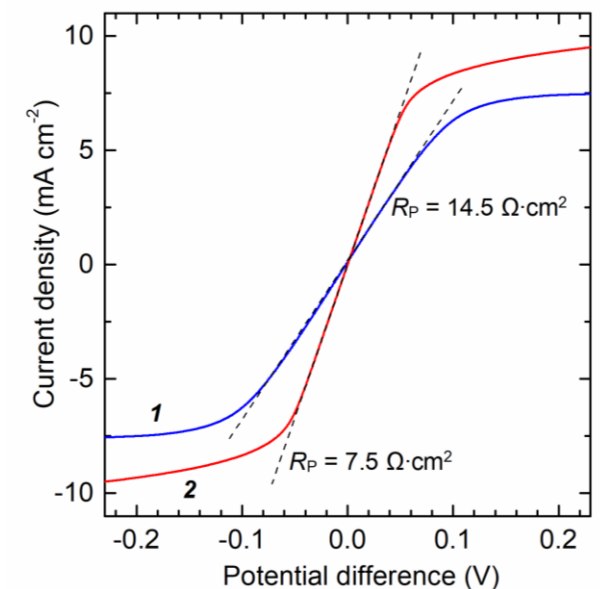


Figure 3.5. Current vs. applied potential curves for the dummy cells with PP (**1**) and PP:GNP (**2**) electrodes. The sweep rate of potential is $10 \text{ mV}\cdot\text{s}^{-1}$; temperature – 20°C .

The current-potential response of the dummy cells displayed a typical sigmoidal curve with three distinct zones: i) polarization zone at low potentials, up to ca. 0.08 V for PP and up to ca. 0.04 V for PP:GNP, with a linear current response vs. applied potential; ii) a transient region, ranging from 0.08 V to 0.14 V for PP and from 0.04 V to 0.08 V for PP:GNP, which was related to the charge transfer at the electrode/electrolyte interface; and iii) diffusion zone, where the current started to saturate with the potential, which happened above 0.14 V for PP and 0.08 V for PP:GNP [49]. I - V curves of the dummy cell with PP:GNP electrodes indicated much higher current densities for the potential difference in the polarization zone; they also indicate much lower polarization resistance at lower currents, R_P . The inverse of the slope in the polarization zone gives the resistance R_P , overall resistance of the device at small currents

[41], which was 7.5 and 14.5 $\Omega\cdot\text{cm}^2$ for the cells with PP:GNP and PP electrodes, respectively. These values agree with the total impedance at the lowest frequencies (**Figure 3.3**). Another relevant feature is the limiting current density for the PP:GNP dummy cell, which is higher compared with the PP dummy cell. These differences in the electrochemical behavior of the films should be assigned to the morphology of the electrodes rather than to their electrocatalytic activity. The nanoplatelets of GNP protrude from the surface of the PP matrix film (**Figure 3.1c**) and reduce the effective distance between the electrodes, besides originating a larger active surface area. It shortened the diffusion path for Co(III/II) species, leading to low device resistance at small currents and ca. 30 % higher diffusion-limited currents.

3.3.3 CONVENTIONAL DSSCs WITH PP AND PP:GNP COUNTER-ELECTRODES

Performance of the PP and PP:GNP films as counter-electrodes were first assessed in conventional DSSCs operating under standard AM1.5G illumination and artificial light (**Figure 3.6**).

Conversion of artificial light is a recent trend, and there is no established standard indoor light source so far [50]. As the share of LEDs in the market for indoor lighting is increasing, we used a LED lamp. The PCE of the devices was calculated as the ratio of the maximum power produced by the cell to the power of incident light.

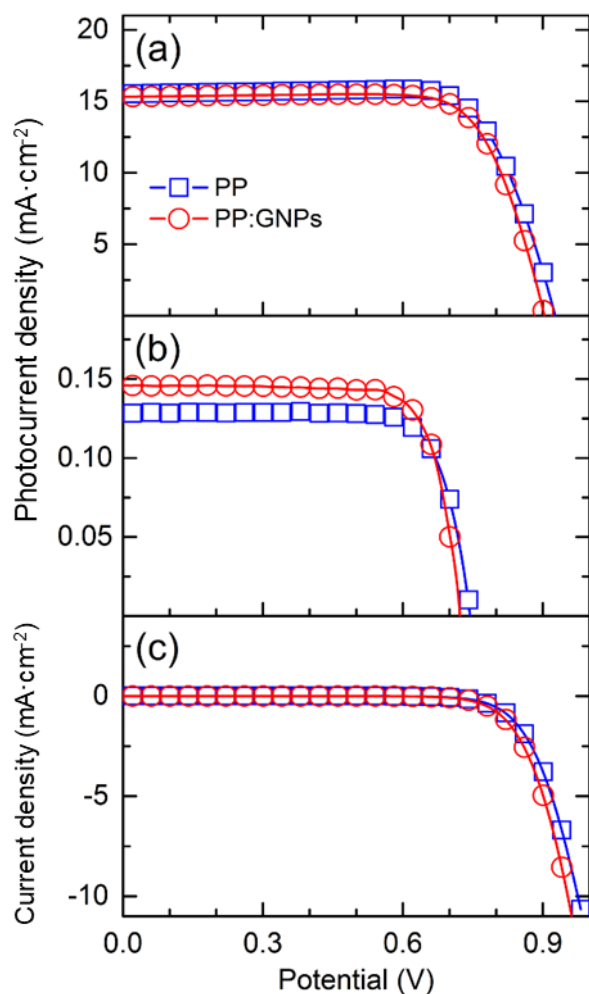


Figure 3.6. *I*-*V* curves of the DSSCs with PP (**squares**) and PP:GNP (**circles**) counter-electrodes, illuminated at standard AM1.5G light (**a**), artificial 1000 lx light (**b**), and recorded in the dark (**c**).

The photovoltaic parameters of the devices were extracted from the *I*-*V* plots and are summarized in **Table 3.1**.

Table 3.1. Photovoltaic metrics of the DSSCs under standard AM1.5G and artificial 1000 lx LED light (average of 5 identical devices).

Counter-electrode; Illumination	η_{PCE} (%)	V_{OC} (mV)	J_{SC} (mA·cm ⁻²)	η_{FF}
PP; AM1.5G	10.8 ± 0.2 (11.04*)	926 ± 5 (915*)	15.53 ± 0.4 (15.87*)	0.75 ± 0.006 (0.76*)
PP:GNP; AM1.5G	10.4 ± 0.2	902 ± 13	15.32 ± 0.6	0.75 ± 0.004
PP; 1000 lx	26.8 ± 0.1	730 ± 4	0.129 ± 0.003	0.8 ± 0.002
PP:GNP; 1000 lx	29.7 ± 0.2	724 ± 9	0.146 ± 0.005	0.8 ± 0.001

*metrics for the best performing device.

Under 1-Sun illumination, devices with PP and PP:GNP counter-electrodes showed almost identical photoresponse (**Figure 3.6a**). The similar *I*-*V* response of both types of cells is related to good electrochemical activity of both materials. The counter-electrode must display a J_0 above the limiting current at the photoanode to minimize possible potential losses in the device [51]. Both, PP and PP:GNP cathode layer generate at room temperature almost the same exchange current density, J_0 (**Figure 3.4**), of 24.2 and 26.3 mA·cm⁻², respectively. These values are higher than the theoretically possible photocurrent of 23 mA·cm⁻², assuming 100 % photon conversion over the entire range of the dye absorption 370-750 nm [52]. However, the performance of DSSCs with the highly catalytically active counter-electrode made of PP:GNP was routinely slightly lower than for devices with blank PP – 10.4 % vs. 10.8 % for the cells with PP electrode (**Table 3.1**). The smaller PCE of PP:GNP cells was assigned to the lower short-circuit current densities (J_{SC}) and V_{OC} than the PP cathode achieved. Lower V_{OC} of the cells with PP:GNP agrees with slightly higher dark currents above 0.8 V (**Figure 3.6c**).

Completely different behavior of the DSSCs with PP and PP:GNP electrodes was observed under artificial light (**Figure 3.6b**). Under weak

illumination, *i.e.*, at small currents passing through the cells, the devices with PP:GNP counter-electrode consistently outperformed the devices with PP counter-electrode. Electrodes made from PP:GNP led to noticeably higher limiting current densities and J_{SC} of $146 \text{ mA}\cdot\text{cm}^{-2}$ vs. $129 \text{ mA}\cdot\text{cm}^{-2}$ in the cells with PP cathode.

This opposite behavior in the PCE when using AM1.5G and artificial light is due to different limiting factors that determine the overall device performance under a certain light intensity. Under weak light, currents below $0.15 \text{ mA}\cdot\text{cm}^{-2}$ pass through the device. At such small currents, the counter-electrode works at low overpotentials - polarization zone in **Figure 3.5**. The PP:GNP films allow much higher polarization currents at low overpotentials than PP (**Figure 3.5**); higher current densities and PCE are observed. Under high light intensity (AM1.5G) *ca.* 100 times higher currents pass through the cell – $15 \text{ mA}\cdot\text{cm}^{-2}$ (**Figure 3.6a**); counter-electrode operates at higher overpotentials corresponding to charge and diffusion-limited zones in **Figure 3.5**. PP and PP:GNP electrodes have an exchange current density, J_0 , of 24.2 and $26.3 \text{ mA}\cdot\text{cm}^{-2}$, respectively, which is sufficient to maintain a photocurrent of $15 \text{ mA}\cdot\text{cm}^{-2}$; thus, neither counter-electrode catalyst will impair the overall performance of the device. At a high light intensity, the PCE limiting factor becomes the charge recombination at the photoanode, which strongly increases with the incident light [53]. EIS further assesses recombination at the photoanode and charge transfer in the cells.

Nyquist plots of both devices show a typical pattern with two capacitive semicircles (**Figure 3.7**).

The smaller and larger semicircles are related to the charge transfer at the interface of the counter-electrode/electrolyte and photoanode/electrolyte, respectively. In the equivalent circuit presented in **Figure 3.7**, constant phase elements CPE_{CE} and CPE_K simulate interfaces counter-electrode/electrolyte and photoanode/electrolyte, respectively. The series resistance of the device is R_S ; R_{CE} and R_K stand for charge transfer resistance at counter-electrode/electrolyte and photoanode/electrolyte interfaces, respectively.

Resistance R_K is related to the back-electron recombination with electrolyte [54].

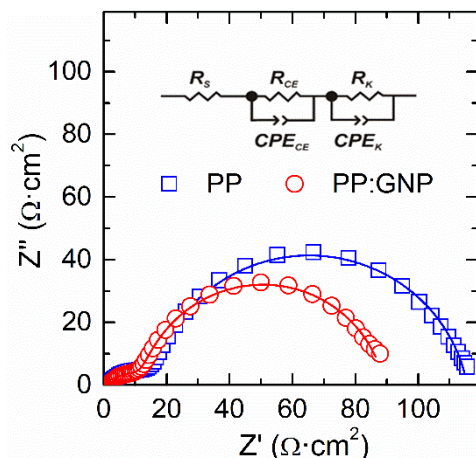


Figure 3.7. Nyquist diagrams of DSSCs with PP (**squares**) and PP:GNP (**circles**) counter-electrodes and equivalent circuit used to fit the spectra. Solid lines correspond to the fitting of the equivalent circuit.

Fittings of the equivalent circuit model to EIS data suggested that the devices assembled with PP and PP:GNP counter-electrodes showed similar series resistances (R_s): 1.9 and 1.7 $\Omega \cdot \text{cm}^2$. DSSCs with PP:GNP electrode displayed lower R_{CE} of 11.3 $\Omega \cdot \text{cm}^2$ compared to 14.2 $\Omega \cdot \text{cm}^2$ for the devices with PP electrode; this agreed with slightly higher values of J_0 obtained with PP:GNP electrode films in the dummy cells (**Figure 3.4**). The most important and surprising feature in the EIS spectra was that devices with PP:GNP counter-electrode displayed lower R_K of 76.2 $\Omega \cdot \text{cm}^2$ than with PP counter-electrode – 99.6 $\Omega \cdot \text{cm}^2$. However, the photoanode in both cells has the same configuration and, logically, should display similar recombination resistances, R_K . Lower R_K for the PP:GNP devices was likely due to the protrusion of the GNP (**Figure 3.1c**), which could reach the photoanode side. This proximity benefits the diffusion of cobalt ions from counter-electrode to photoanode, shortening the effective diffusion length and reducing polarization resistance (**Figure 3.5**); however, increasing the charge transfer at the photoanode/electrolyte interface, leads to recombination losses and lowers the open-circuit potential, V_{OC} . Nevertheless, due to high electrochemical activity

(**Figure 3.4**) and significantly reduced resistance at small currents (**Figure 3.5**), PP:GNP counter-electrode made the DSSC device display a good PCE of 10.4 % under 1-Sun and amazingly high PCE of 29.7 % with a maximum output power of $82 \text{ mW}\cdot\text{cm}^{-2}$ under 1000 lx light (**Table 3.1**). The output power under the artificial light was similar to the best performing cobalt- and copper-mediated DSSCs [4,5,7,10]. This made PP:GNP cathodes attractive in DSSCs for indoor use.

The small irradiance of the indoor illumination, ca. 100-1000× less than 1-Sun, translates to a maximum power output of tenths of a milliwatt per cm^2 . For this reason, bifacial devices are desirable since they can receive light from both sides, generating up to 40 % more electrical output [17–19]. The developed PP:GNP composite had ca. 60-70 % of transparency in the wavelength region 350-800 nm (**Figure 3.8**) and can be used as cathode in bifacial devices.

Additionally, good conductivity of the PP:GNP films ($65 \text{ W}\cdot\text{Sq}^{-1}$) allowed using ordinary glass as a substrate for counter-electrode, critical for producing FTO-less DSSCs to reduce the overall cost of the device.

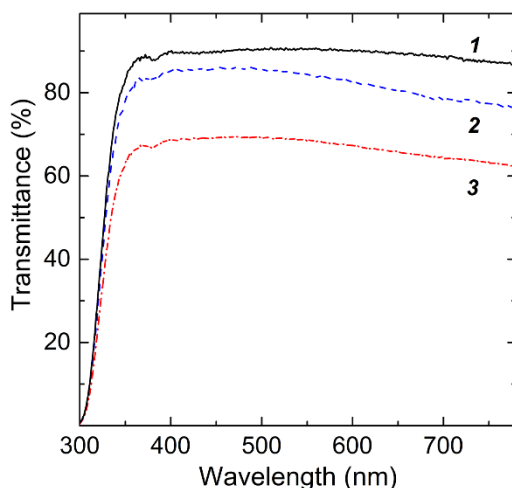


Figure 3.8. Transmittance spectra of the bare soda-lime glass substrate (**1**) and with deposited PP (**2**) and PP:GNP (**3**) films.

3.3.4 PP AND PP:GNP FILMS AS COUNTER-ELECTRODES IN FTO-LESS AND BIFACIAL DSSCs

Similar to the cells with two FTO-glasses, under 1-Sun the layers of PP and PP:GNP deposited on bare glass produced mostly the same J_{SC} , ca. 15 and 13 $\text{mA}\cdot\text{cm}^{-2}$ when illuminated from front and rear side, respectively (**Figure 3.9a**).

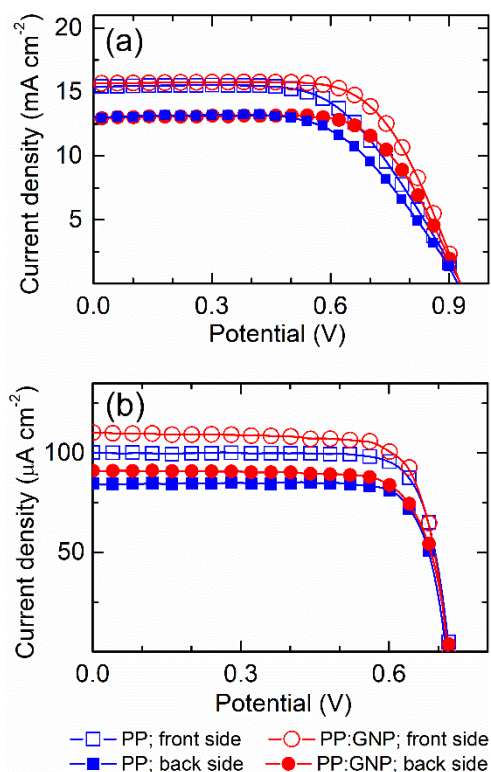


Figure 3.9. Photocurrent vs. applied potential under AM1.5G (**a**) and 1000 lx artificial light (**b**) for DSSCs fabricated using counter-electrodes made of PP (**squares**) and PP:GNP (**circles**) films on bare soda-lime glass. Empty and solid symbols stand for illumination from the front and rear sides of the device, respectively.

In both cases, PP:GNP counter electrode allowed higher fill factor (η_{FF}) (**Table 3.2**), which was related to the lower sheet resistance of the PP:GNP films, $65\ \Omega\cdot\text{Sq}^{-1}$ vs. $75\ \Omega\cdot\text{Sq}^{-1}$ for undoped PP. Under front illumination, the

DSSCs with PP:GNP cathodes assembled on bare glass rendered a PCE of 9.8 %, which was only slightly smaller when using FTO-coated glass – 10.4 % (**Table 3.1**).

Under artificial 1000 lx light, the FTO-less devices rendered a PCE of ca. 21 % and 22 % with PP and PP:GNP cathodes, respectively, when front-illuminated, and slightly smaller PCE of 18 % when illuminated from the rear side (**Table 3.2**).

As expected, when the cells were illuminated from the rear side, the PCE was lower in both cases; less current was produced because of light absorption at the counter-electrode layer (**Figure 3.8**) and cobalt electrolyte. Interestingly, the current drop was mainly due to lower quantum yield at wavelengths below ca. 520 nm (**Figure 3.10**), which coincided with the absorption spectrum of the cobalt electrolyte.

Table 3.2. Photovoltaic metrics of the DSSCs obtained at the front and rear illumination under AM1.5G and artificial 1000 lx light (average of 5 identical DSSCs).

Light	Side	Counter-electrode	η_{PCE} (%)	V_{oc} (mV)	J_{sc} (mA·cm ⁻²)	η_{FF}
AM1.5G	front	PP	8.5 ± 0.3	929 ± 4	15.4 ± 0.2	0.59 ± 0.005
		PP:GNP	9.8 ± 0.2	927 ± 8	15.7 ± 0.3	0.67 ± 0.003
	rear	PP	7.2 ± 0.2	920 ± 6	13.0 ± 0.2	0.60 ± 0.004
		PP:GNP	8.2 ± 0.2	928 ± 9	12.9 ± 0.2	0.68 ± 0.003
1000 lx	front	PP	20.8 ± 0.3	722 ± 3	0.100 ± 0.010	0.76 ± 0.001
		PP:GNP	21.9 ± 0.1	719 ± 7	0.110 ± 0.015	0.77 ± 0.002
	rear	PP	17.7 ± 0.2	716 ± 4	0.085 ± 0.007	0.80 ± 0.002
		PP:GNP	18.2 ± 0.1	721 ± 9	0.091 ± 0.010	0.81 ± 0.002

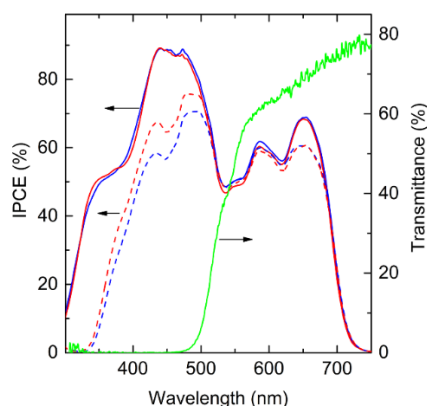


Figure 3.10. IPCE spectra of the DSSCs with PP (**blue lines**) and PP:GNP (**red lines**) counter-electrodes on bare soda-lime glass and transmittance of cobalt electrolyte (**green line**). Solid and dashed lines stand for front and rear side illumination, respectively.

The photogeneration at 520-750 nm region remained mostly the same; only a slight drop was observed at ca. 650 nm related to the light absorption by the PP and PP:GNP films. The IPCE spectra indicated that the rear side PCE was mainly affected by irradiance losses at the electrolyte rather than at PP or PP:GNP films. It made the developed PP:GNP composites very attractive for use in bifacial and FTO-less DSSCs.

3.4 CONCLUSIONS

Composite PEDOT:PSS (PP) with graphene nanoplatelets (GNP) films were produced by simple spin-coating deposition over FTO and bare soda-lime glass substrates. Electrodes of PP:GNP showed high electrocatalytic activity, displaying an apparent activation energy, E_a , for the charge transfer with $[\text{Co}(\text{bpy})]^{3+/2+}$ electrolyte of $6.2 \text{ kJ} \cdot \text{mol}^{-1}$, much lower than the apparent activation energy for PP – $17.5 \text{ kJ} \cdot \text{mol}^{-1}$. Improved electrocatalytic activity of the composite was assigned to the introduction of GNPs into the PP film, the increase of the fraction of the oxidized EDOT units in the polymer, and better match between the catalyst work function and the electrolyte redox potential. DSSCs exposed to 1-Sun illumination, both PP and PP:GNP films performed

almost equally displaying PCE of 10.8 % and 10.4 %, respectively. This behavior was due to the high exchange current densities, J_0 , for these two cathodes at room temperature (20 °C): 24.2 and 26.3 mA·cm⁻² for PP and PP:GNP electrodes, respectively; these exchange currents are high enough to support even theoretically possible photocurrent (ca. 23 mA·cm⁻²) in the device at 1-Sun.

Under indoor illumination, devices with PP:GNP counter-electrode significantly outperform counterparts assembled with PP films, generating more ca. 13 % of photocurrent. In the PP:GNP cathode, graphene nanoplatelets largely protrude from the PP matrix film and shorten the effective distance between photoanode and cathode, leading to lower cell resistance at small currents and higher photocurrent density. Under artificial 1000 lx illumination, DSSCs with PP:GNP cathodes displayed a PCE of 29.7 %, surpassing the counterpart with PP counter-electrode, which displayed a PCE of 26.8 %. Improved electric conductivity of the PP:GNP films and high transparency of ca. 65 % on bare glass substrate allowed preparing FTO-less bifacial DSSCs that for the first time ever rendered at 1000 lx a PCE of ca. 22 % when front-illuminated, and ca. of 18 % when illuminated from the rear side. DSSC devices with a PP:GNP counter-electrode are better than other devices with PP alone, making these even more efficient for indoor applications.

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CHAPTER 4

CONVENTIONAL AND BACK-ILLUMINATED
COBALT- AND IODINE-MEDIATED DYE-
SENSITIZED SOLAR CELLS FOR ARTIFICIAL
AND SOLAR LIGHT CONVERSION

Adapted from the peer-reviewed article

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CONVENTIONAL AND BACK-ILLUMINATED COBALT- AND IODINE-MEDIATED DYE-SENSITIZED SOLAR CELLS FOR ARTIFICIAL AND SOLAR LIGHT CONVERSION

ABSTRACT

Dye-sensitized solar cells (DSSCs) are among the leading PV technologies for indoor applications. These devices need to be optimized for these illumination conditions since, as it will be demonstrated, the best devices under solar conditions do not originate the best devices under artificial illumination. This work studies the impact of the photoanode thickness, its light-scattering properties, dye loading, distance from the photoelectrode to the counter-electrode on the charge transfer, recombination, and photovoltaic response of cobalt (III/II) bipyridine ($[\text{Co}(\text{bpy})_3]^{3+/2+}$) and iodide/triiodide (I^-/I_3^-) DSSCs under 1-Sun and artificial 1000 lx light illumination. The champion $[\text{Co}(\text{bpy})_3]^{3+/2+}$ device displayed a power conversion efficiency (PCE) of 11.0 % and 32.0 % under AM1.5G and 1000 lx, respectively. The best I^-/I_3^- cells yielded 9.0 % 1-Sun PCE and 23.1 % of PCE under 1000 lx. Optimized $[\text{Co}(\text{bpy})_3]^{3+/2+}$ and I^-/I_3^- DSSCs demonstrated huge potential as efficient indoor-photovoltaic (IPV) and can straightforwardly be used as back-illuminated devices to improve the output power under low illumination. Under 1000 lx room light, the champion cobalt DSSCs displayed a record PCE of 27.3 % from the rear-side with 85.3 % of retention ratio.

4.1 INTRODUCTION

In 1991, Michael Grätzel [1] introduced the dye-sensitized solar cells (DSSCs). For decades DSSCs were envisioned as a major asset for outdoor building- and agriculture-integrated photovoltaics, also very appealing for urban design solutions [2–5]. Nowadays, the growth of consumer and wearable electronics, and wireless sensor nodes for the Internet of things (IoT) have determined the need for PV technology that efficiently converts weak, diffused, and artificial indoor light to electricity [6–8]. It pushed the indoor photovoltaics (IPV) market to grow intensively [9–11]. DSSC is one of the most promising IPV technology since it displays very high-power conversion efficiency (PCE) under diffused indoor illumination with a 34.5 % record to date [12]. Moreover, this technology is easy to produce, pleasant to the eyes and suitable for interior integration, safe and sustainable as it is free of toxic compounds and display a quite small energy return on investment (EROI) [13]. Thus, DSSCs are entering the IPV market swiftly [14–16].

Several studies have shown good performances of DSSCs under artificial light, utilizing iodide/triiodide [17–23] and cobalt redox mediators [24–27], as well as copper-based systems [6,8,12,28,29], displaying respectively PCEs of 28.7 % [21], 29.7 % [21], and champion 34.5 % [21] under artificial illumination.

One of the shortcomings of IPV is related to the low irradiance of typical artificial illumination, which is ca. 10^2 – 10^4 times lower than standard AM1.5G; additionally, conventional one-side devices deliver maximum power values of only tens of milliwatts per cm^2 [10,30,31]. DSSCs can be easily fabricated bifacial [32–34], which allows to gain up to 50 % more power by collecting surrounding radiation [35–37]. For bifacial DSSCs, highly transparent and catalytically active counter-electrodes [34,36,38–41] are needed, as well as a thin electrolyte layer [37] and good light scattering in the photoanode [32,42]. Venkatesan *et al.* optimized all DSSC components of a cobalt solar cell, which led to a PCE of 20.7 % and 17.3 % for the front- and rear-side illumination (200 lx CFL light), respectively [25]. When the same authors optimized the light-scattering layers of the photoelectrode, it was possible to fabricate cobalt

devices with PCEs of 25 % and 23.1 % for the front- and rear-side illumination (1000 lx LED), respectively [26]. Although there is increasing interest in the IPV technology from the industry as well as from the research community, there is still no standard for characterizing the power conversion efficiency with accuracy [43,44]. Therefore, comparisons between results from different laboratories may be inaccurate.

It could seem logical to assume that the best performing devices under standard AM1.5G illumination would be the best under other illuminating conditions. However, this is not the case [27]. Usually, the limiting factor of the PCE is the charge recombination at the photoanode that occurs at higher power illumination, which strongly increases with the irradiance [45]. However, at low-light conditions, the photovoltage has a superior influence in the overall PCE, confirmed by the higher efficiencies displayed by copper-mediated DSSCs under artificial illumination [6,12].

This article focuses on the impact of photoanode architecture, light-scattering properties, dye loading, and device thickness on photogeneration and recombination for solar and artificial illumination. This study considered the most common and versatile types of devices: iodide/triiodide (I^-/I_3^-) and cobalt (III/II) bipyridine ($[Co(bpy)_3]^{3+/2+}$), mediated with N719 and YD2-*o*-C8 dyes, respectively. The cells were made using commercially available materials. The rear-side performance was evaluated for both electrolytes, and the $[Co(bpy)_3]^{3+/2+}$ champion cell displayed a PCE of 32.0 % when front-illuminated and 27.3 % for back illumination, under 1000 lx (LED lamp).

4.2 EXPERIMENTAL SECTION

4.2.1 MATERIALS AND REAGENTS

Fluorine-doped tin oxide (FTO)-coated glasses (TEC-7; 2.2 mm thick, 7 Ω /sq), EL-HPE electrolyte and screen-printable TiO_2 pastes (30D, 18NR-T, 18NR-AO, and WER2-O) were acquired from GreatCell Solar®. Absolute ethanol, titanium diisopropoxide bis(acetylacetonate), anhydrous isopropyl

alcohol, acetylacetone and dimethyl sulfoxide (DMSO) were purchased from Sigma Aldrich®; thermoplastic sealants (Meltonix 1170-25, 25 μm Surlyn® and Meltonix 1170-60, 60 μm Surlyn®), Platisol T/SP and Ruthenizer 535-bisTBA (N719) were ordered from Solaronix®. TiCl_4 (99.90 %) from Acros Organics was used. Porphyrin dye [5,15-bis(2,6-dioctoxyphenyl)-10-(bis(4-hexyphenyl)amino)-20-(4-carboxyphenylethynyl)porphyrinato] zinc(II) (also known as YD2-o-C8) was purchased from Everlight Chemical. Cobalt complexes tris-(2,2'-bipyridine)cobalt(II) di(tetracyanoborate) and tris-(2,2'-bipyridine)cobalt(III) tri(tetracyanoborate) DN-C03 and DN-C04, respectively, were acquired from Dyenamo. CLEVIOS™ PH 1000 (PEDOT:PSS solution) was purchased from Heraeus Epurio.

4.2.2 DSSC PREPARATION

The photoelectrodes were screen printed using TiO_2 pastes and sintered at 500 °C for 1 h. To produce titania scaffolds of various thicknesses and architectures, TiO_2 layers were deposited by screen-printing sequentially several times. Depending on the type of titania paste used for printing, each printing step leads to TiO_2 layers of different thicknesses (see **Table 4.1**) in the range of 3-8 μm . As determined by a cross-sectional SEM study, deviations in the thickness of a single printed TiO_2 layer were ca. 10 %; typical of the screen-printing technique. Layers of deposited TiO_2 were treated with a 40 mM TiCl_4 aqueous solution at 70 °C for 30 min and sintered at 500 °C for 1 h. The samples were dipped in dye solutions: 5 mM of N179 in ethanol (for 24 h); 2 mM of YD2-o-C8 in ethanol:toluene (3:1) for 16 h. The FTO glasses for counter-electrodes were drilled with two holes. Catalytic layers of the counter-electrodes were Pt nanoparticles and PEDOT:PSS films for I^-/I_3^- and $[\text{Co}(\text{bpy})_3]^{3+/2+}$ devices, respectively. The Pt nanoparticles were applied by doctor blading a platinum paste (Platisol T/SP) and sintering it at 460 °C for 30 min. A 1.3 wt.% suspension of PEDOT:PSS in water was mixed with 5 % (V/V) of DMSO and applied on the pre-drilled back substrate by spin coating at 3000 rpm for 45 s. This process was repeated three times and between each

deposition, the polymer layer was dried at 120 °C for 15 min. The photoanode and counter-electrode were sealed with Surlyn® films in a hot press at 160 °C for 15 s. The gap between the two substrates was determined by SEM from the cross-section of the devices; the gaps between two sealed glasses were 20±1.5 and 50±2 µm when using Surlyn® films with a nominal thickness of 25 and 60 µm, respectively. Cobalt electrolyte was composed of 0.165 M Co(bpy)₃(B(CN)₄)₂, 0.045 M Co(bpy)₃(B(CN)₄)₃, 1.0 M tert-butyl pyridine (TBP) and 0.1 M of LiClO₄ in acetonitrile [46]. I⁻/I₃⁻ electrolyte used was the commercial EL-HPE, based on acetonitrile:valeronitrile solvent mixture [47]. After filling the cells with electrolytes, the injection holes were sealed with Surlyn® and a round coverglass. A light reflector made from self-adhesive polyvinyl chloride white tape was attached to the backside of the cells [18]. A reflector made of white self-adhesive polyvinyl chloride tape was attached to the side of the cells opposite the incident light; light harvesting is improved by reflector [10]. Reflector was attached to the counter-electrode (when illuminated from the photoanode side) or to the photoanode glass (when illuminated from the counter-electrode side). The reflector was used in each characterization of photocurrent-potential response.

Table 4.1. Thickness of each TiO₂ paste used in this work

TiO ₂ Paste	Thickness (µm)
Mesoporous, 30 nm (ML30)	3.3 ± 0.3
Mesoporous, 20 nm (ML20)	2.9 ± 0.3
Scattering (SL)	8.0 ± 0.8
Reflective (RL)	6.0 ± 0.6

4.2.3 CHARACTERIZATION

Current vs. applied potential (*I*-*V*) response was obtained with Zennium (Zahner) electrochemical station at a potential scan rate of 50 mV·s⁻¹. *I*-*V* measurements were performed right after assembly, no later than one week after. Simulated solar light (AM1.5G, 100 mW·cm⁻²) was driven from a Solar Simulator MiniSol (LSH-7320, Newport). The electrochemical impedance spectra (EIS) were collected in dark conditions at -850 mV (for [Co(bpy)₃]^{3+/2+} cells) and -650 mV (for I⁻/I₃⁻ cells), using an Autolab (PGSTAT 302 N, Metrohm); a sinusoidal perturbation with an amplitude of 10 mV and a frequency range of 100 kHz-0.1 Hz was applied, with a time range of 7 min for each measurement. The impedance spectra were analyzed using ZView[®] software. As the source of artificial light, a LED lamp was used (Osram, Class A+, 60 W, 2700 K). The emission spectrum of the lamp is illustrated in **Figure B4**. The light flux intensity of the lamp was appraised in W·m⁻², and the luminance was measured in lx using a radiometer (Delta Ohm, HD 2102.2). *I*-*V* characterization for each testing condition was performed over 5 similar devices; cells typically display a deviation interval of PCE metrics of less than 5 %. In rare cases, devices with deviations of more than 7% from the average value in the batch were excluded from consideration. All tables present average values in the batch of 5 devices, where 5 % of deviation interval is considered. The figures show responses of devices with metrics closest to the average value in the batch, if other is not mentioned in the caption. The incident-photon-to-electron conversion efficiency (IPCE) spectra were recorded at a light chopping frequency of 8.3 Hz, for 2 nm wavelength intervals between 280 and 800 nm. A UV-Vis-NIR Spectrophotometer from Shimadzu (UV-3600) was used to determine the transmittance spectra of the photoelectrodes and to quantify the amount of adsorbed dye by desorbing the dye molecules from the TiO₂. The dyes were desorbed from TiO₂ in solutions of 0.5 M of NaOH in H₂O:EtOH (1:1, V/V) or 0.056 M of Acetic Acid in THF: EtOH (1:1, V/V) for the N719 (**Figure C2a**) or YD2-*o*-C8 sensitized photoelectrodes, respectively

(**Figure C2c**). Photoelectrodes were immersed in the desorption solutions for 24 h. To quantify the number of detached dye molecules from the TiO_2 , the molar extinction coefficient (ε) of the desorbing solution of the dye was determined using the Beer-Lambert Law (**Eq. 4.1**):

$$A = \varepsilon \times c \times l \quad (\text{Eq.4.1})$$

where A is absorbance, ε is the molar extinction coefficient ($\text{M}^{-1}\cdot\text{cm}^{-1}$), c is the concentration (M), and l is the light path length (cm) (**Figure C2e,f**).

The transmittance of the both I^-/I_3^- and $[\text{Co}(\text{bpy})_3]^{3+/2+}$ electrolytes were also measured in the UV-Vis-NIR Spectrophotometer, using thin cuvettes with a thickness of 2 mm (**Figure 4.4a** and **Figure 4.6a**).

4.3 RESULTS AND DISCUSSION

4.3.1 MORPHOLOGY AND CHARACTERIZATION OF DIFFERENT TITANIA LAYERS

An efficient photoanode should provide a high generation of photoelectrons while suppressing their recombination [48,49]; iodine DSSCs have a slow recombination rate between I_3^- ions and TiO_2 conduction band electrons (e_{CB}^-) [50,51]. In addition, iodide and triiodide ions diffuse quickly through the mesopores of the titania layer, providing high values of diffusion-limited currents [52]. In contrast, cobalt DSSCs display fast interfacial charge recombination and slow Co(III) ions diffusion through the mesoporous TiO_2 , which leads to lower charge collection efficiency in cobalt-DSSCs compared to iodine-DSSCs [53]. Moreover, extinction coefficient of the dyes used in cobalt DSSCs are typically higher compared with Ru-dyes in iodine cells. These major differences make it imperative to tune the thickness, porosity, and light-scattering ability of the photoanode for each type of DSSCs [54–56].

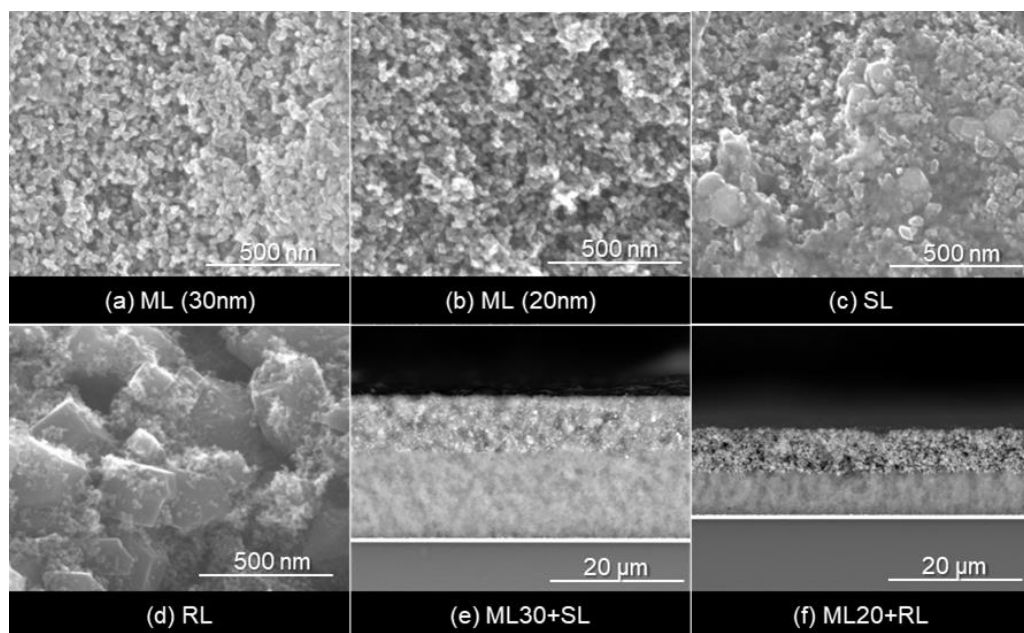


Figure 4.1. Top-view SEM images of mesoporous TiO_2 layers with an average particle size of 30 nm (a), and 20 nm (b), scattering (c), and reflective layers (d) produced from commercial 30D, 18NR-T, 18NR-AO, and WER2-O pastes respectively; cross-section of ML30 + SL (e) and ML20 + RL (f).

The most common strategy to improve light harvesting in the photoanode is to use multilayered TiO_2 films composed of transparent and light-scattering TiO_2 layers along the path of the incident light [26,57,58]. Four commercially available TiO_2 pastes were assessed for producing photoanodes in $[\text{Co}(\text{bpy})_3]^{3+/2+}$ and I^-/I_3^- devices. SEM images of the prepared TiO_2 layers are presented in **Figure 4.1**. **Figure 4.1a,b** show the top view of two mesoporous layers (ML), which differ in average particle size: 30 nm (ML30) and 20 nm (ML20) from 30D and 18NR-T pastes, respectively. **Figure 4.1c** shows the topography of the light-scattering layer (SL) produced from 18NR-AO paste and composed of monodispersed 20 nm anatase particles with the addition of larger (up to 450 nm) anatase particles. **Figure 4.1d** shows the reflective layer (RL) formed from WER2-O paste; RL is a blend of 20 nm anatase and rutile particles with sizes up to 450 nm. Our previous studies revealed that I^-/I_3^- DSSCs benefit from using ML30 and SL pastes (**Figure 4.1e**), while

$[\text{Co}(\text{bpy})_3]^{3+/2+}$ cells work best with the pastes ML20 and RL (**Figure 4.1f**) (see **Chapters 2** and **3**). When other conditions are the same (oxide layer thickness, photoanode architecture), cobalt cells with TiO_2 layers composed of 20 nm particles underperform counterparts with mesoporous coating of 30 nm titania; the opposite is true for I^-/I_3^- devices (see **Figure C1**). The exact reason for this could be addressed in future studies. Best performing TiO_2 layers were selected in $[\text{Co}(\text{bpy})_3]^{3+/2+}$ and I^-/I_3^- cells aiming ultimately to produce the best performing devices.

The thickness and structure of the photoanode define the amount of adsorbed dye, light-harvesting, and photocurrent generation [59]. The absorbed concentration of each dye vs. photoanode thickness and combination of transparent and scattering layers was studied, following similar works previously reported [60–62].

The typical absorbance spectrum of N719 shows two peaks above 350 nm (**Figure C2b**), at 376 nm and 511 nm, both assigned to the metal-to-ligand charge-transfer transition; in the UV-region the band at 308 nm is specific to the intraligand ($\pi\text{-}\pi^*$) charge-transfer transition [63]. At the 511 nm band, the N719 ϵ was $12.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The absorbance spectrum of the YD2-o-C8 (**Figure C2d**) shows a central band at 447 nm, assigned to the Soret band, and a less intense band at 644 nm, ascribed to the Q band [46]; at 447 nm the ϵ was $258 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Due to the ϵ high value for YD2-o-C8 dye, the TiO_2 layer for cobalt DSSCs should be thin [54]; a thinner TiO_2 layer originates fewer recombination losses and a lower charge transport resistance in the electrolyte [46]. Interestingly, the amount of YD2-o-C8 dye adsorbed onto the TiO_2 was lower than N719 (**Figure 4.2**), which might be due to the larger molecular size of the porphyrin sensitizer [64]. The carboxylates of N719 facilitate the dye adsorption [65]; the amount of the adsorbed dye increases linearly with the TiO_2 layer thickness (**Figure 4.2a**). Adsorption of dye in ML30 and in ML30+SL films of compatible thickness is practically the same. This could be related to the similar structure of ML30 and SL layers (**Figure 4.1a,c**), since the fraction of particles above 30 nm in SL films is small. Slightly higher dye uptake

observed in ML30+SL layer is more likely due to regular scatter of values; variation of the thickness of the printed layers can reach ca. 10 % (**Table 4.1**), wherein the detected difference in the dye uptake in ML30 and in ML30+SL is only ca. 4 %. In contrast to N719, the adsorption of the YD2-*o*-C8 dye tapered off at a titania layer thickness of ca. 15 μm (**Figure 4.2b**). This could be caused by dye aggregation at the outer TiO_2 layer; the pores clog, preventing further dye adsorption [66].

Titania layers ML30, ML20, and SL are solely composed of anatase, while RL layer is mostly rutile. The dye loading depends on the surface area, density, and crystal phase of titania [67]. Rutile has a relatively smaller specific area and thus provides less dye adsorption than anatase [68], as **Figure 4.2b** shows.

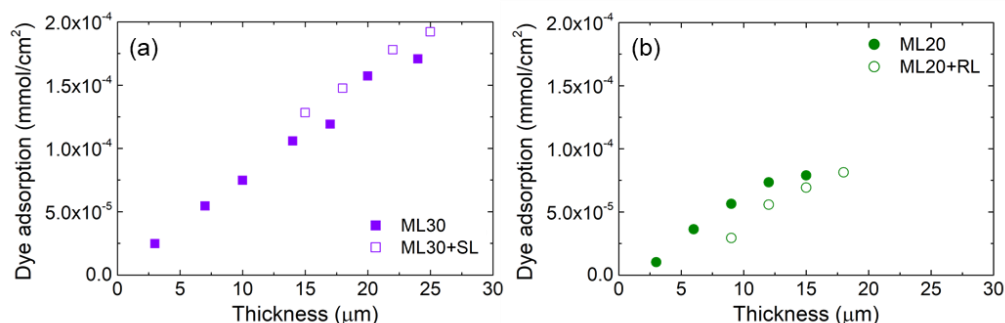


Figure 4.2. (a) Adsorbed N719 dye vs. thickness of the TiO_2 layer; ML30 represented by full symbols and ML30+SL represented by empty symbols; (b) Adsorbed YD2-*o*-C8 dye vs. TiO_2 layer thickness, ML20 in full symbols and ML20+RL in empty symbols.

Theoretical studies on photocurrent yield in DSSCs point out that optimal thickness and composition of the photoanode layer is a complex trade-off between i) light collection; ii) photogeneration; iii) recombination rate, and iv) diffusion-limiting currents in the electrolyte. The latter is determined by the ionic mobility of the redox shuttle and the thickness of the bulk electrolyte layer [69,70]. The impact of the photoanode architecture at several thicknesses of electrolyte layer on the DSSCs performance under 1-Sun and artificial light is

further considered. The thickness of the electrolyte layer in the devices was controlled by sealing the edges of the cell with Surlyn® films of 25 and 60 μm thick, which resulted in a gap between the two electrodes of 20 ± 1.5 and 50 ± 2 μm , respectively.

4.3.2 IODIDE/TRIIODIDE DSSCs

4.3.2.1 PHOTOANODE THICKNESS AND ARCHITECTURE

The impact of the photoanode thickness and of using a combination of transparent and scattering TiO_2 layers were first assessed in the devices with an inner gap of 20 μm .

In iodine DSSCs, Ru-dye regeneration kinetics is typically fast [66]. For high-performing DSSCs, the thickness of the titania layer plays a paramount role since it determines the light harvesting and photogeneration. The titania layer should be thick enough to ensure a high surface area for adsorbing the dye; however, thicker titania layers increase recombination [71]. Therefore, to obtain a device with optimal efficiency, the dye uptake and recombination must be balanced by adjusting the TiO_2 thickness. Moreover, a light-scattering layer is also beneficial for the overall performance as it bounces back the lost photons, enhancing the optical absorption. Using the light-scattering layer in combination with the transparent TiO_2 layer improves light absorption and allows thinner photoanodes, minimizing back-electron recombination [72].

The thickness of ML30 was optimized based on the J - V and EIS characterization of the DSSCs; the thickness of the ML30 layer was gradually increased from 3 to 17 μm (**Figure 4.3– full symbols**). On the top of the ML30 layer, a layer of SL with 8 μm was applied (**Figure 4.3– empty symbols**). The photovoltaic parameters of the devices were determined from I - V curves and summarized in **Table 4.2**.

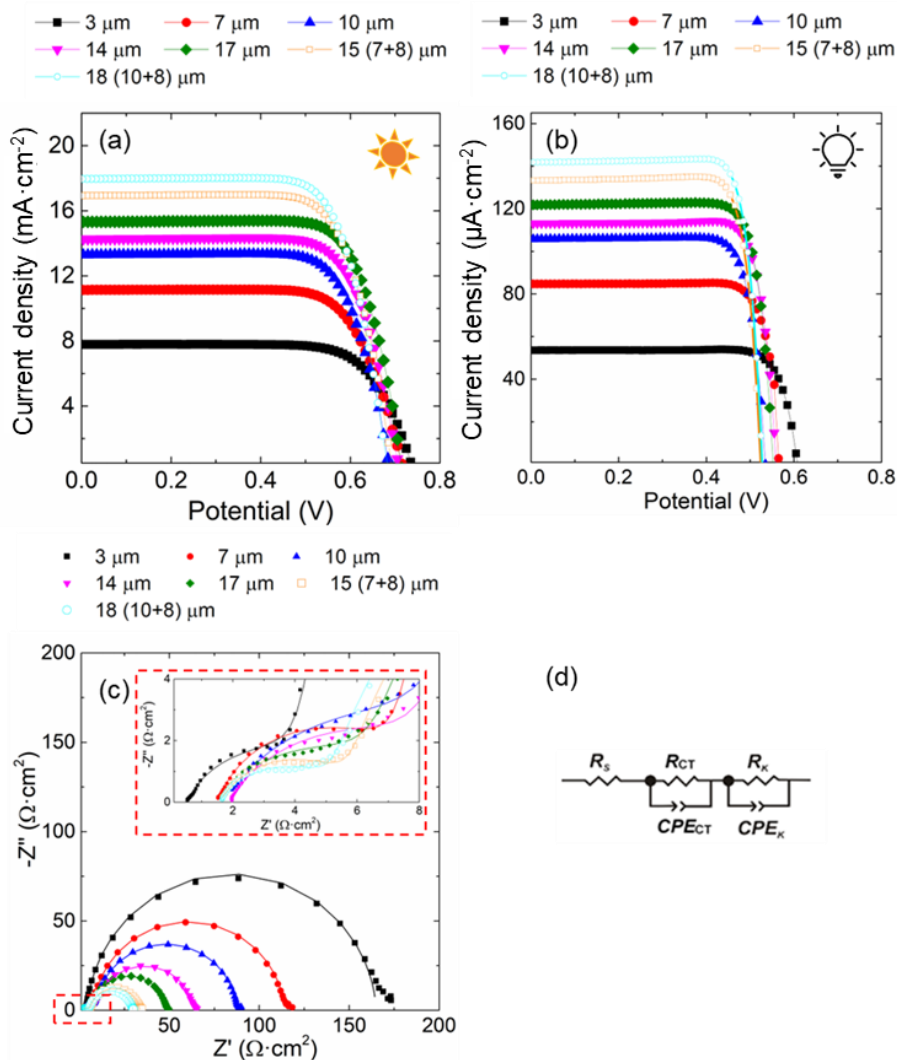


Figure 4.3. J - V response of I^-/I_3^- DSSCs under AM1.5G (a) and 1000 lx LED (b). Nyquist plots of the devices, including zoom-in section for the high frequencies data (c); solid lines show the fittings of the impedance spectra to the equivalent circuit model in chart (d). Full and empty symbols stand for ML30 and ML30+SL layers, respectively. The device gap of the cells is 20 μm .

Regardless of the source of illumination, J_{SC} steadily rises with the thickness of the ML30 (Figure 4.3a,b; Table 4.2), taking advantage of the larger number of electrons injected into the conduction band of the semiconductor, due to an increase of dye adsorption, as shown in Figure 4.1a. At a fixed thickness of the photoanode of ca. 15-18 μm , the use of the SL layer

in the photoanode leads to a noticeable photocurrent increase, which is caused by improved light collection and promotion of quantum yield above 600 nm [18,58]. The η_{FF} remained almost the same, at ca. 0.73 for solar and 0.82 for artificial illumination, regardless of the thickness of the ML30.

EIS was used to assess the internal resistances of the devices, electron transport, and recombination. The equivalent electrical circuit used for fitting the EIS response is presented in **Figure 4.3d**. In the Nyquist plot, the first Z' -axis value corresponds to the series resistance (R_s); the first semi-circle in the high frequency range is due to the charge-transfer at the interface counter-electrode/electrolyte (R_{CT}); the second semi-circle reflects electron recombination at the interface photoanode/electrolyte (R_k). Constant phase elements CPE_{CT} and CPE_k simulate the interfaces counter-electrode/electrolyte and photoanode/electrolyte, respectively. [73]. The internal resistances of the devices are summarized in **Table 4.3**. Regardless of the thickness and structure of the TiO_2 layer, R_s is mostly constant; R_{CT} fluctuates in the range of several ohms, but these small differences are negligible when compared to the variations in R_k . The values of CPE_{CT} of platinum counter-electrodes in the series are statistically the same, ca. $0.05 \cdot 10^{-3} \text{ S} \cdot \text{s}^n$. The ideality factor n of the CPE_{CT} was approximately 0.68, far from ideal capacitive behavior due to the contribution of the Faradaic process, *i.e.*, oxidation of iodide ions (dark condition, forward bias). The element CPE_k displays close to capacitive response for thin titania films (n is above 0.95-0.97). However, an apparent decrease of ideality factor n is observed with increasing the layer thickness (**Table 4.3**), which could be due to the diffusion obstacles in a thicker mesoporous layer, and faster depletion of oxidized species. Pseudo-capacitive values of CPE_k element naturally increase with TiO_2 film thickness due to increasing TiO_2 surface area. A noticeable drop of R_k for higher photoanode thicknesses is observed due to the larger surface of TiO_2 for dye adsorption. Thicker mesoporous layer originates lower photovoltages, from 728 mV at 1-Sun (606 mV under 1000 lx) to 717 mV (552 mV under 1000 lx); this reduction is due to a higher recombination, which is confirmed by lower R_k (**Table 4.2**).

The addition of a scattering layer leads to a noticeable drop in the V_{OC} . The SL promotes the recombination to a greater extent than the ML of the same thickness (**Table 4.3**); however, the use of SL leads to a higher overall PCE owing to gains in photocurrent.

Table 4.2 suggests that the optimum photoanode structure for best converting solar and artificial light in I^-/I_3^- DSSCs is the same: 10 μm of ML30 with 8 μm of SL atop (overall thickness of 18 μm). Other studies report an optimum photoanode thickness for I^-/I_3^- DSSCs under 1-Sun in the range of 18-22 μm [18,74,75]. The 20 μm gap device displayed a J_{SC} of $18 \text{ mA}\cdot\text{cm}^{-2}$ (1-Sun) and $142 \text{ }\mu\text{A}\cdot\text{cm}^{-2}$ (1000 lx), rendering a PCE of 9.0 % and 22.4 % at AM1.5G and 1000 lx illumination, respectively.

Figure C3 helps readers follow the differences in the photovoltaic metrics of the devices under solar and artificial illumination. Only the V_{OC} showed a slightly different trend under both illumination conditions, but it was not large enough to affect the overall PCE.

Table 4.2. Photovoltaic parameters of I^-/I_3^- DSSCs with different photoanode architectures for device gap of 20 and 50 μm^* .

		AM 1.5 G, 100 mW·cm ⁻²				LED, 1000 lx, 275 μW·cm ⁻²					
Photoanode Thickness (μm)	Device Gap (μm)	η _{PCE} (%)	V _{OC} (mV)	J _{SC} (mA·cm ⁻²)	η _{FF}	η _{PCE} (%)	V _{OC} (mV)	J _{SC} (μA·cm ⁻²)	η _{FF}	MPP (μW·cm ⁻²)	
ML30	3	20	4.04	728	7.6	0.73	9.6	606	53.6	0.82	26.6
		50	2.96	741	5.3	0.76	6.6	622	35.2	0.83	18.2
	7	20	5.67	718	11.0	0.72	14.0	565	84.7	0.81	38.8
		50	4.60	722	8.7	0.73	12.6	585	71.4	0.82	34.4
	10	20	6.57	716	12.4	0.74	16.6	534	105.7	0.81	46.0
		50	5.61	714	10.7	0.74	14.3	560	86.5	0.81	39.3
	14	20	7.20	711	14.0	0.73	18.8	558	113.1	0.82	51.9
		50	6.03	713	11.1	0.76	15.0	554	89.8	0.83	41.5
	17	20	8.06	717	15.1	0.74	20.1	552	121.8	0.82	55.0
		50	6.74	711	12.9	0.74	16.5	547	101.4	0.82	45.4
	20	20	-	-	-	-	-	-	-	-	-
		50	6.46	719	11.8	0.76	13.1	539	80.2	0.83	36.1
	24	20	-	-	-	-	-	-	-	-	-

Overall = ML30+SL	15 (7+8)	50	6.09	706	11.2	0.77	12.7	537	77.5	0.84	35.1
		20	8.52	695	16.9	0.72	21.3	529	133.5	0.83	58.9
	18 (10+8)	50 (I ₂ -50)	7.82	703	16.0	0.70	22.9	551	133.8	0.86	63.3
		20 (I ₂ -20)	8.95	683	18.0	0.69	22.4	527	141.8	0.83	61.8
	22 (14+8)	50	8.17	703	16.7	0.70	22.1	551	131.2	0.85	61.1
		20	-	-	-	-	-	-	-	-	-
	25 (17+8)	50	7.78	693	15.9	0.71	21.5	538	130.7	0.85	59.5
		20	-	-	-	-	-	-	-	-	-
		50	7.12	702	13.6	0.74	15.8	536	97.0	0.83	43.5

*Light gray color marks the metrics for the best-performing devices. Dark gray identifies the cells for rear-side illumination assessment, with the designation of the cells in parentheses.

Table 4.3. Internal resistances of the I^-/I_3^- DSSCs extracted from fitting EIS response to model in **Figure 4.3d**.

	Photoanode Thickness (μm)	Device Gap (μm)	R_s	R_{CT}	R_k	CPE_k	n	τ_n (ms)
			(Ω·cm ²)	(Ω·cm ²)	(Ω·cm ²)			
ML	3	20	1.6	11.6	481.7	0.041	0.97	49.1
		50	1.7	22.2	1027.8	0.020	0.96	50.1
	7	20	1.5	6.0	106.6	0.109	0.95	27.4
		50	2.0	11.2	175.5	0.071	0.96	29.7
	10	20	1.7	7.9	77.9	0.108	0.97	20.4
		50	1.7	8.9	82.9	0.103	0.95	19.7

Overall = ML30+SL	14	20	1.9	6.8	55.1	0.180	0.93	20.8
		50	1.8	8.8	73.5	0.179	0.93	28.6
	17	20	1.4	5.7	41.3	0.215	0.95	19.9
		50	1.6	9.4	54.5	0.319	0.90	34.1
	20	20	-	-	-			-
		50	1.5	8.2	48.2	0.193	0.94	20.5
	24	20	-	-	-			-
		50	1.6	13.4	43.3	0.364	0.87	27.8
	15 (7+8)	20	1.6	4.4	27.8	0.410	0.92	23.5
		50	1.8	5.8	47.9	0.384	0.91	38.8
	18 (10+8)	20	1.6	3.9	24.3	0.465	0.92	23.6
		50	1.8	5.8	45.8	0.406	0.91	39.2
	22 (14+8)	20	-	-	-			-
		50	1.7	6.1	35.3	0.533	0.89	36.3
	25 (17+8)	20	-	-	-			-
		50	1.7	6.1	33.1	0.520	0.84	27.0

4.3.2.2 DEVICE GAP

The I^-/I_3^- DSSCs, with a device gap of 50 μm , displayed J - V and EIS responses similar to the counterparts with a gap of 20 μm (**Figure C4**). As expected, under 1-Sun illumination, the devices with larger gap displayed a lower PCE for all photoanode architectures (**Table 4.2**). This loss of efficiency was assigned to the increase of ohmic resistance related to the ionic transport [69]. It is noteworthy that the V_{OC} , both under AM1.5G and artificial light, increased for the thicker devices. EIS identified the origin of this higher V_{OC} : resistance R_k was the most sensitive parameter to the device thickness (**Table 4.3**), displaying higher values in cells with a gap of 50 μm . The back-electron recombination in the photoanode is ultimately due to electron capture by the oxidized redox shuttle, in this case by the triiodide [76]. The increase in the device gap leads to a slight increase of R_s and then to a decrease in the current density, and these two phenomena lower the concentration of I_3^- ions in the mesoporous layer of the photoanode; moreover, it should be noted that the mass transport of the iodide is much faster than triiodide. When the device gap increases, the R_k rises which should be assigned to lower $[\text{I}_3^-]$ species in the mesoporous layer and as consequence a slightly higher V_{OC} should be observed.

Similarly to the 20 μm device gap, 10 μm of ML30 with 8 μm of SL (18 μm total thickness) was the best photoanode architecture for solar light conversion, with a PCE of 8.2 %. However, for this thicker device, the conversion of artificial light benefited from implementing a thinner photoanode: 7 μm of ML with 8 μm of SL (15 μm total thickness), resulting in a PCE of 22.9 % at 1000 lx (7.8 % 1-Sun PCE - **Table 4.2**). Due to higher R_k (**Table 4.3**), recombination losses were lower, leading to a higher V_{OC} and η_{FF} under artificial illumination.

Figure 4.4a shows the IPCE spectra of I^-/I_3^- devices with optimized photoanode configurations for 20 μm and 50 μm device gaps. Both cells displayed a similar spectral distribution of quantum yield. The electrolyte layer absorbs light below ca. 600 nm; the thinner electrolyte layer allows more

irradiance to reflect back and be absorbed at the photoelectrode, mostly in the region below 700 nm (**Figure 4.4a**). The higher irradiance originates a higher photocurrent for all artificial irradiances, but this advantage decreases for the lower irradiances (**Figure 4.4b**). For 400 lx, the photocurrent is almost the same for both devices, and this should be related to the ability of the device to absorb the whole irradiance. At low irradiances, the PCE of the thicker devices becomes higher because the V_{OC} and FF is higher, while the J_{SC} is almost the same for both type of devices (**Table C1**, devices I_2 -20 and I_2 -50).

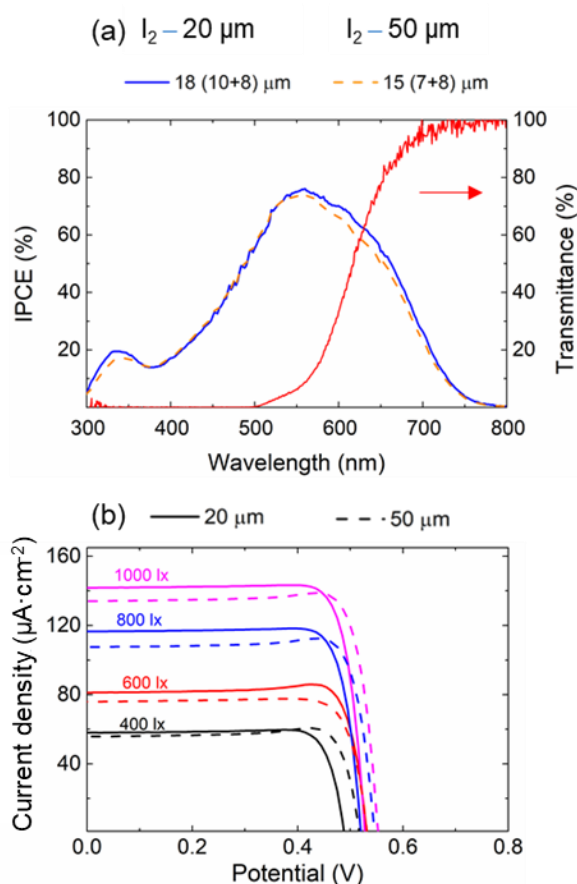


Figure 4.4. (a) IPCE spectra of the best performing I^-/I_3^- DSSCs with photoanode thickness of 15 (7+8) μm and 50 μm gap (**dashed line**), 18 (10+8) μm and 20 μm gap (**solid line**); transmittance of I^-/I_3^- electrolyte (**solid red line**). (b) Photocurrent vs. applied potential under 400, 600, 800 and

1000 lx for the device gaps of 20 μm and 50 μm - ***solid and dashed lines***, respectively.

4.3.3 COBALT (III/II) BIPYRIDINE DSSCs

4.3.3.1 PHOTOANODE THICKNESS AND ARCHITECTURE

Cobalt redox mediators in DSSCs display fast recombination kinetics, thus slowing the dye regeneration. As previously mentioned, for high performing devices, the thickness of the photoanode should be optimized for the best compromise between light absorption, photogeneration and recombination [53].

Figure 4.5 presents J - V and EIS curves of the $[\text{Co}(\text{bpy})_3]^{3+/2+}$ DSSCs obtained with mesoporous layers of different thicknesses, from 3 μm to 15 μm (full symbols); a reflective layer, RL, with a fixed thickness of 6 μm was deposited atop the mesoporous layer of some of the devices to improve the light harvesting (empty symbols) (see **Chapter 3**). **Table 4.4** summarizes the photovoltaic parameters of the cells, and **Table 4.5** displays the internal resistances of the devices.

Figure 4.5a and **5b** clearly show that 9 μm of ML20 cell produces the highest photocurrent and V_{OC} , leading to an average η_{PCE} of 10.6 % and 31.9 % under 1-Sun and 1000 lx, respectively (**Table 4.4**). This concurs with the known literature data, which present optimum thicknesses for $[\text{Co}(\text{bpy})_3]^{3+/2+}$ DSSCs at 8-10 μm [77–79]. The remarkable PCE of 31.9 % under 1000 lx was mainly due to high J_{SC} of 140 $\mu\text{A}\cdot\text{cm}^{-2}$, comparable to the photocurrent of I^-/I_3^- DSSCs under artificial illumination. The mass transport limitations intensify with the increase of incident power, as a higher photocurrent requires enhanced mass transport in the electrolyte [66]. Under lower light irradiance, the diffusion restrictions of the cobalt shuttles do not limit the generation of photocurrent, hence the high PCE under artificial light [27,45]. Increasing the thickness of the mesoporous layer above 9 μm leads to a drastic drop in photocurrent (**Figure C5a**); a behavior which is the opposite of

the I^-/I_3^- cells (**Figure C3a**). This drop in photocurrent is assigned to dye aggregation (**Figure 4.2b**), which increases the charge recombination in the TiO_2 /electrolyte interface and limits the access of the reduced cobalt species to the oxidized dye. The device with smallest TiO_2 particles for the mesoporous layer, ML20, displays an increased charge recombination (lower R_K) due to a larger surface area of the mesoporous layer (**Table 4.5**) and a lower photovoltage (**Table 4.4**); this trend was also observed by other authors [66,80].

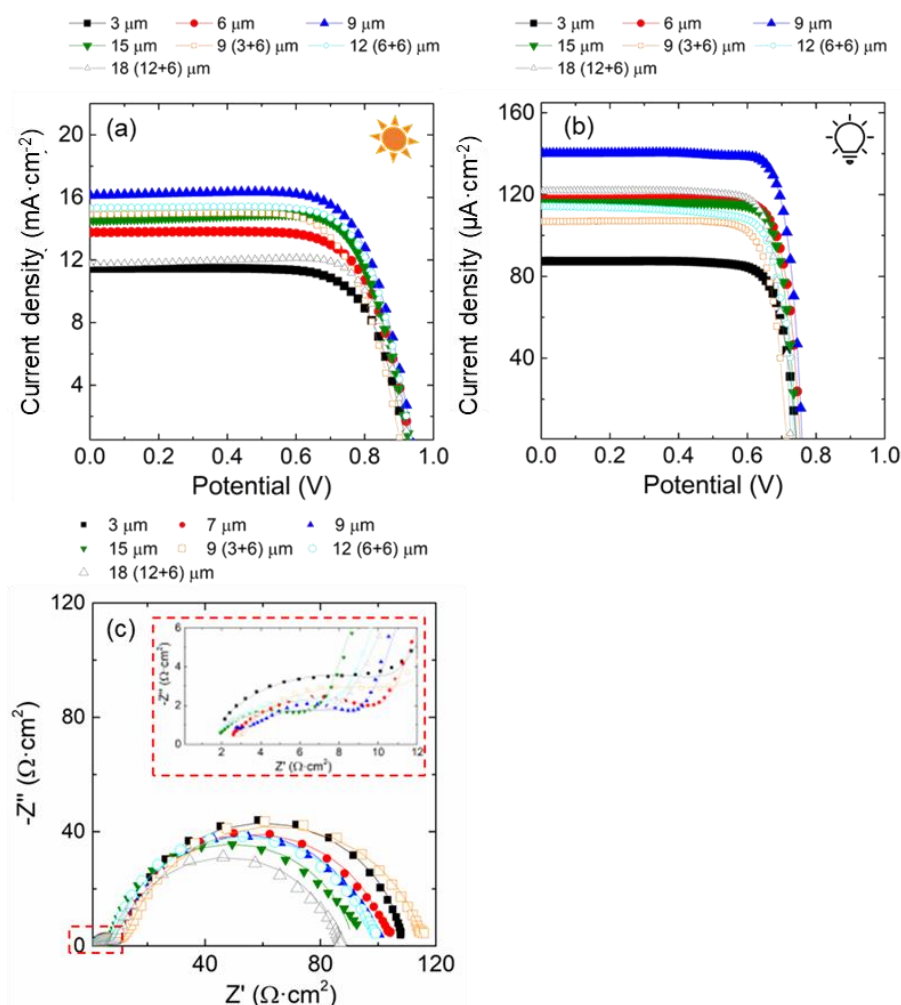


Figure 4.5. J - V response of $[Co(bpy)_3]^{3+/2+}$ DSSCs under AM1.5G (**a**) and 1000 lx LED light (**b**). Nyquist plots of the impedance spectra, including zoom-in section for the high frequencies data (**c**); **solid lines** are the fittings to the

equivalent circuit (**Figure 4.3d**). *Full* and *empty symbols* stand for ML20 and ML20+RL layers, respectively. The internal gap of the device is 20 μm .

The values of CPE_{CT} element of PEDOT:PSS counter-electrodes is ca. $0.04 \cdot 10^{-3} \text{ S} \cdot \text{s}^n$, with an ideality factor of ca. 0.64, slightly less compared to Pt activated counterpart in iodine devices. The values of CPE_k in cobalt cells gradually increase with the thickness of TiO_2 layer (**Table 4.5**), wherein descending factor n may point to the appearance of diffusion obstacles in thicker titania films.

The RL layer, a mixture of anatase and rutile particles, has superior light-reflecting properties, benefiting the effective light harvesting [81], but smaller specific surface area [68]. Unexpectedly, the addition of a RL atop of the transparent mesoporous TiO_2 layer decreases the photovoltaic performance of the cobalt cells. While under AM1.5G, the 12 μm (6 μm of ML20 and 6 μm of RL) device produce a similar PCE as the best ML20 device (9 μm of ML20) at 10.5 %, under 1000 lx the best device had an 18 μm photoanode (12 μm ML20 + 6 μm RL) and attained a PCE of 26.3 %, lower than the 31.9 % PCE of the ML20 device. This difference was mainly due to higher recombination, as shown **Table 4.5**, which in turn lowered the V_{OC} and the photon collection, as is apparent from the smaller J_{SC} . The lower photon collection could be ascribed to the poorer dye adsorption by the ML20+RL titania film.

Table 4.4. Photovoltaic parameters of $[\text{Co}(\text{bpy})_3]^{3+/2+}$ DSSCs with different photoanode architectures for devices with 20 and 50 μm of gap*.

		AM 1.5 G, 100 mW·cm ⁻²				LED, 1000 lx, 275 μW·cm ⁻²					
Photoanode Thickness (μm)	Device Gap (μm)	η _{PCE} (%)	V _{OC} (mV)	J _{SC} (mA·cm ⁻²)	η _{FF}	η _{PCE} (%)	V _{OC} (mV)	J _{SC} (μA·cm ⁻²)	η _{FF}	MPP (μW·cm ⁻²)	
ML20	3	20	7.63	924	11.47	0.72	18.8	742	87.4	0.80	51.7
		50	6.50	916	10.44	0.68	17.5	728	82.6	0.80	48.3
	6	20	8.78	922	13.69	0.70	26.2	753	117.5	0.82	72.1
		50	7.84	927	11.60	0.73	24.1	734	111.1	0.81	66.2
	9	20 (Co-20)	10.61	941	15.60	0.72	31.9	758	139.9	0.83	87.1
		50	8.90	931	13.08	0.73	27.0	739	122.5	0.82	74.3
	12	20	10.18	937	14.42	0.75	25.9	751	114.3	0.83	71.4
		50	8.58	926	12.14	0.76	23.8	738	107.9	0.82	65.5
	15	20	10.11	932	14.56	0.75	25.7	743	115.9	0.82	70.7
		50	8.41	926	11.88	0.76	26.6	736	119.7	0.83	73.1
Overall = ML20+RL	9 (3+6)	20	9.30	907	14.96	0.69	22.2	715	107.0	0.80	61.4
		50	7.79	931	11.42	0.73	15.8	721	76.2	0.79	43.5
	12 (6+6)	20	10.49	938	15.36	0.73	23.8	734	114.1	0.78	65.6

15 (9+6)	50	8.35	932	12.24	0.73	21.5	715	104.0	0.80	59.3
	20	9.98	907	15.07	0.73	25.7	716	123.5	0.80	71.0
	50	8.27	925	11.75	0.76	19.0	711	92.7	0.80	52.5
	20	9.60	921	13.00	0.76	26.3	726	121.8	0.82	72.4
18 (12+6)	50	7.41	925	10.18	0.79	16.5	703	81.1	0.80	45.5

*Light gray color marks the metrics for the best-performing devices. Dark gray identifies the cells for rear-side illumination assessment, with designation of the cells in parentheses.

Table 4.5. Internal resistances of $[\text{Co}(\text{bpy})_3]^{3+/2+}$ DSSCs extracted from fitting EIS response.

	Photoanode	Device	R_s	R_{CT}	R_k	CPE_k	n	τ_n (ms)
	Thickness (μm)	Gap (μm)	($\Omega \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)			
ML20	3	20	1.1	11.2	96.4	0.062	0.93	12.0
		50	2.3	12.0	87.5	0.058	0.92	9.5
	6	20	2.2	8.9	92.1	0.180	0.90	32.3
		50	1.7	9.6	77.4	0.151	0.92	24.5
	9	20	2.0	8.6	86.9	0.189	0.93	36.0
		50	1.5	19.5	75.0	0.172	0.92	26.8
	12	20	1.6	10.5	88.6	0.283	0.89	50.9
		50	1.6	15.9	75.6	0.269	0.89	39.6
	15	20	1.5	6.1	84.0	0.352	0.90	61.5

		50	1.5	10.7	69.4	0.326	0.91	47.3
Overall = ML20+RL	9 (3+6)	20	2.6	10.2	103.1	0.121	0.87	20.7
		50	3.0	10.2	76.2	0.113	0.85	12.5
	12 (6+6)	20	1.3	7.6	89.4	0.184	0.90	32.4
		50	2.3	11.0	75.7	0.195	0.91	29.6
	15 (9+6)	20	1.6	14.3	76.3	0.228	0.92	36.6
		50	2.4	13.8	71.2	0.217	0.88	28.2
	18 (12+6)	20	0.6	8.6	77.2	0.467	0.86	68.9
		50	2.6	13.9	68.2	0.298	0.89	38.9

4.3.3.2 DEVICE GAP

Typical J-V response and EIS spectra of $[\text{Co}(\text{bpy})_3]^{3+/2+}$ DSSCs with a gap of 50 μm are presented in **Figure C6**, and their photovoltaic parameters are summarized in **Table 4.4**. **Figure C5** compares primary photovoltaic metrics of 20 and 50 μm sealed $[\text{Co}(\text{bpy})_3]^{3+/2+}$ DSSCs. The photovoltaic performance was substantially affected by the increase in thickness of the TiO_2 layer and of the device gap. This indicates that both the diffusion through the mesoporous titania layer and the electrolyte limits the performance of the cobalt shuttle, both under solar and artificial illumination. Like I^-/I_3^- devices, an increase in the distance between the two electrodes reduces the photocurrent density. On the other hand and opposite to I^-/I_3^- , the V_{OC} lowers for the cobalt cells with 50 μm of gap. The V_{OC} decrease is normally related to the increase of recombination, which is the present case, since R_{K} (**Table 4.5**) actually decreases with the gap of the device. The recombination is related to the concentration of the oxidized species (Co^{3+}) in the TiO_2 layer; thus, the increase of recombination should be ascribed to the slower mass transport of the Co species, leading to an accumulation of Co^{3+} complex ions in the mesopores of TiO_2 [82].

The most efficient $[\text{Co}(\text{bpy})_3]^{3+/2+}$ DSSCs with a 50 μm device gap have a 9 μm thick photoanode made of ML20 TiO_2 particles; displaying a PCE of 8.90 % and 27.0 % under 1-Sun and 1000 lx, respectively (**Table 4.4**). **Figure 4.6a** presents the IPCE spectra of the cells with 9 μm ML20 photoanode with 20 μm and 50 μm device gaps. The difference in the spectral distribution of quantum yield between the 20 μm and 50 μm gap devices should also be assigned to the back irradiance – reflected at the counter-electrode side. The back irradiance is higher for the 20 μm gap, since the electrolyte thickness is smaller and this minimizes the light absorbance at the electrolyte. Because the electrolyte transmittance is lower for wavelengths below 550 nm, the larger current densities differences should be observed in this spectrum range. The lower photon collection efficiency demonstrated by the 50 μm device is mainly due to the lower photocurrents exhibited on **Table 4.4**. **Figure 4.6b** shows J-V

curves of the cells at several artificial light irradiances. Both devices show a monotonic photocurrent increase with light intensity, delivering the highest PCE of 31.9 % and output power of $87.1 \text{ mW} \cdot \text{cm}^{-2}$ at 1000 lx for $20 \mu\text{m}$ gap devices (**Table C2**).

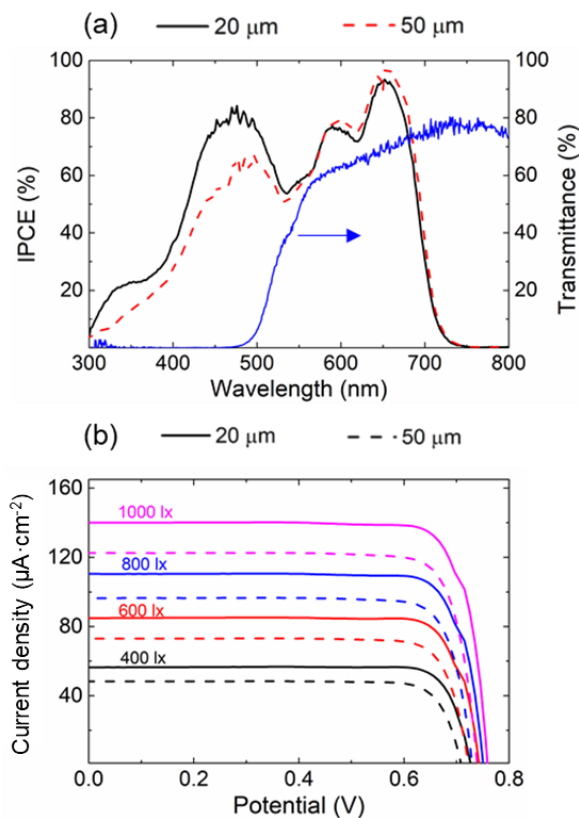


Figure 4.6. (a) IPCE spectra of the $[\text{Co}(\text{bpy})_3]^{3+/2+}$ DSSCs with the photoanode thickness of $9 \mu\text{m}$, $50 \mu\text{m}$ and $20 \mu\text{m}$ internal gaps - *dashed* and *solid lines*, respectively; transmittance spectrum of cobalt electrolyte (*solid blue line*). (b) Photocurrent vs. applied potential under 400, 600, 800 and 1000 lx LED light.

4.3.4 BACK ILLUMINATION

Most effective configurations of I^-/I_3^- and $[\text{Co}(\text{bpy})_3]^{3+/2+}$ DSSCs were evaluated with back illumination (from the counter-electrode side, **Figure 4.7**). Selected architectures of the cells are marked with dark grey color in **Table 4.2**

and **Table 4.4**; corresponding devices are denoted as I₂-20, I₂-50, and Co-20, respectively I⁻/I₃⁻ DSSCs with 20 μm of gap, I⁻/I₃⁻ DSSCs with 50 μm of gap and [Co(bpy)₃]^{3+/2} DSSCs with 20 μm of gap. Since the cobalt devices with 20 μm gap display a similar behavior to the 50 μm gap, only the devices with 20 μm gap were characterized.

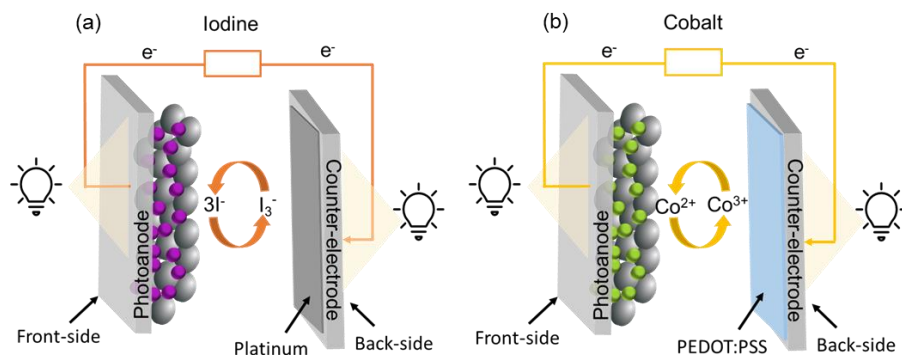


Figure 4.7. Schematic illustration of design structure of back-illuminated (a) iodide/triiodide and (b) cobalt (III/II) bipyridine DSSCs.

Counter-electrodes made of PEDOT:PSS ([Co(bpy)₃]^{3+/2} cells) and Pt nanoparticles I⁻/I₃⁻ (cells) displayed transmittance of ca. 70 % and ca. 80 %, respectively (**Figure 4.8**); the cells with these counter-electrodes may straightforwardly be used for back illumination.

The on-set of the transmittance curves for the I⁻/I₃⁻ and [Co(bpy)₃]^{3+/2} electrolytes are ca. 580 and 470 nm, respectively; when illuminated from the counter-electrode side, *i.e.*, back-illuminated, the irradiance reaching the photoelectrode is much higher for the cobalt devices. **Figure 4.9** presents *J-V* curves of the I⁻/I₃⁻ and [Co(bpy)₃]^{3+/2} DSSCs under 1-Sun and artificial back and front illuminations.

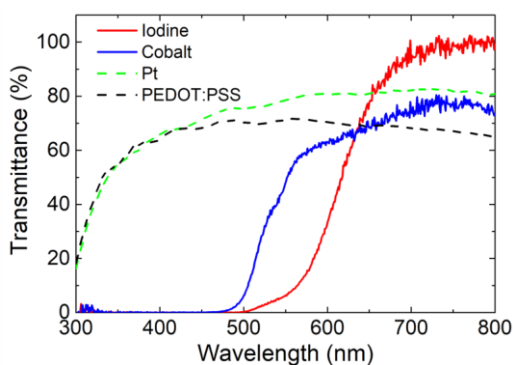


Figure 4.8. Transmittance spectra of Pt (**green dashed line**) and PEDOT:PSS (**black dashed line**) counter-electrodes; I^-/I_3^- (**red solid line**) and $[Co(bpy)_3]^{3+/2}$ (**blue solid line**) electrolytes.

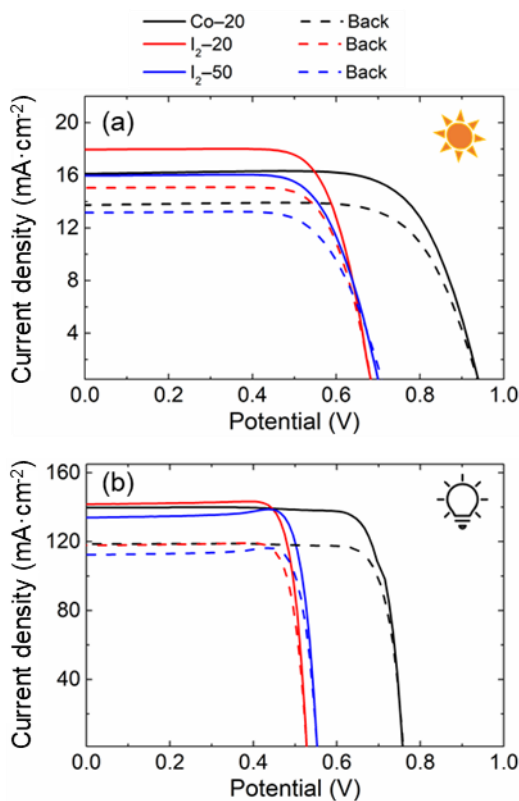


Figure 4.9. J-V curves of bifacial DSSCs under AM1.5G (**a**) and 1000 lx LED light (**b**).

The I_2-20 DSSC display a J_{SC} of $18 \text{ mA} \cdot \text{cm}^{-2}$, more than the Co-20 device with J_{SC} of $16.1 \text{ mA} \cdot \text{cm}^{-2}$ (**Table 4.6**). The higher photocurrents displayed by

the I^-/I_3^- devices were assigned to the higher thickness of the photoabsorber layer, which display $9.1 \times 10^{-5} \text{ mmol}\cdot\text{cm}^{-2}$ more adsorbed dye than the Co-20 device (**Figure 4.2**). While there was almost a 10.6 % difference in J_{SC} under 1-Sun between the I_2 -20 and Co-20, under 1000 lx the difference in J_{SC} practically vanishes to a mere 1.3 %. One of the critical observations in this study is that the device with the highest photocurrent under 1-Sun (I_2 -20) yields almost the same photocurrent as other devices (I_2 -50 and Co-20) under artificial light. This is related to the lower recombination under low irradiance [45], while under high irradiance back-electron recombination becomes one of the PCE limiting factors (see **Chapter 3**). At weak illumination conditions, the ability of the device to generate high photovoltage becomes decisive for overall device performance, as observed by the PCE under 1-Sun and 1000 lx of back illumination for I_2 -20 and I_2 -50 devices.

Table 4.6. Photovoltaic metrics of the champion bifacial DSSCs

DSSC	Illum. side	AM 1.5 G, 100 mW·cm ⁻²				1000 lx, 275 μW·cm ⁻²				
		η_{PCE} (%)	V_{OC} (mV)	J_{SC} (mA·cm ⁻²)	η_{FF}	η_{PCE} (%)	V_{OC} (mV)	J_{SC} (μA·cm ⁻²)	η_{FF}	MPP (μW·cm ⁻²)
Co-20	Front	11.0	942	16.1	0.72	32.0	759	140.0	0.83	88.1
	Rear	9.37	942	13.4	0.72	27.3	759	119.0	0.83	75.0
I ₂ -20	Front	9.01	685	18.0	0.73	22.4	528	141.8	0.83	62.0
	Rear	7.55	685	15.1	0.73	18.7	528	117.9	0.83	51.6
I ₂ -50	Front	7.88	703	16.0	0.70	23.1	552	134.1	0.86	63.7
	Rear	6.26	703	12.5	0.71	19.3	553	112.4	0.86	53.4

Both I^-/I_3^- and $[\text{Co}(\text{bpy})_3]^{3+/2}$ DSSCs demonstrated good performance under indoor light (**Figure 4.9b**) due to the absorption spectra of N719 and YD2-o-C8 dyes (**Figure C2b,d**) matching the emission of the LED lamp (**Figure B4**). IPCE spectra (**Figure 4.10**) show a drastic difference in spectral distribution of quantum yield in $[\text{Co}(\text{bpy})_3]^{3+/2}$ and I^-/I_3^- DSSCs in the region from 340 to 520 nm. I^-/I_3^- cells hardly convert any photons to power in the 340-450 nm range; from 450-520 nm and 620-750 nm the IPCE is still much lower when compared with the Co-20 device. The IPCE from back illumination was expected to be lower compared with the front illumination; the decrease in the IPCE for front and back illumination is in good agreement with the electrolyte cut-off wavelength (**Figure 4.8**).

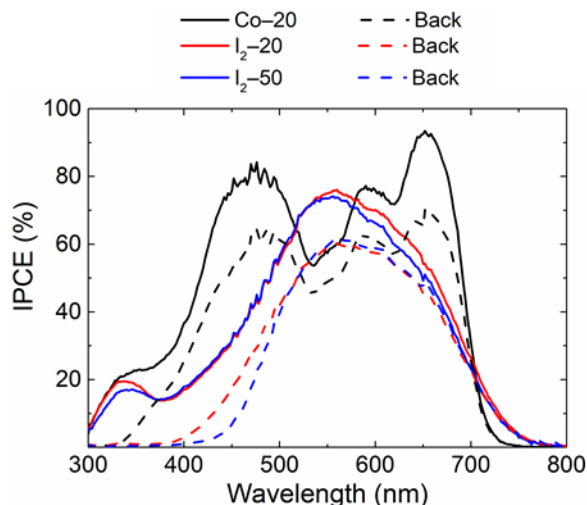


Figure 4.10. IPCE spectra collected from the front (***solid lines***) and from the rear (***dashed lines***) sides of the bifacial DSSCs.

The efficiency of a back-illuminated photovoltaic device is typically assessed by the retention ratio, which is the quotient between the photovoltaic metrics of back to front illumination [38]. From back illumination of 1000 lx, the device $\text{I}_2\text{-50}$ displayed a PCE of 19.3 % with a retention value of 81.4 %; the device $\text{I}_2\text{-20}$ showed a PCE of 18.7 % with a retention of 83.4 %, and the device Co-20 displayed a PCE of 27.3 % with 85.3 % of retention ratio (**Table 4.6**).

Even for back illumination, the optimized Co-20 device displayed a power density of $75.0 \mu\text{W}\cdot\text{cm}^{-2}$ at 1000 lx ($88.1 \mu\text{W}\cdot\text{cm}^{-2}$ for the front illumination), rivalling the best results for cobalt- and copper-mediated DSSCs [6,25–28]. The results are attractive for constructing bifacial devices, *i.e.*, operating in conditions where both sides are illuminated simultaneously. This will be a critical advancement to increasing overall output power under weak illumination, especially under indoor light.

4.4 CONCLUSIONS

The impact of the photoanode architecture, thickness, light-scattering properties, dye loading, and device thickness on the photogeneration, recombination, and performance of I^-/I_3^- and $[\text{Co}(\text{bpy})_3]^{3+/2}$ DSSCs, under standard AM1.5G and artificial illumination was studied. The architecture displaying the best performance under artificial illumination conditions cannot be anticipated based only on the results from 1-Sun illumination. This article successfully demonstrated that, to obtain the best photovoltaic performing DSSCs, every system should be tuned separately for each specific illumination conditions. I^-/I_3^- devices with 18 μm thick photoanode and 20 μm of device gap (I_2 -20) achieved a PCE of 9.0 % and 22.4 % under 1-Sun and 1000 lx, respectively; when using a 15 μm thick photoanode with a 50 μm device gap (I_2 -50) the PCE was 7.8 % and 23.1 % under AM1.5G and artificial illumination, respectively. The ability of the I_2 -50 device to generate high photovoltage was one of the most decisive factors for the overall PCE under artificial light, which explained the discrepancies between PCEs under 1-Sun and artificial light. I^-/I_3^- and $[\text{Co}(\text{bpy})_3]^{3+/2}$ devices produced almost the same photocurrent density under weak light conditions; however, due to higher photovoltage, $[\text{Co}(\text{bpy})_3]^{3+/2}$ cells are better for indoor light conversion. Thoroughly optimized, cobalt DSSCs (Co-20: 9 μm ML20 and 20 μm gap) rendered a PCE of 11.0 % and 32 % under 1-Sun and artificial illumination (1000 lx), respectively. Both I^-/I_3^- and $[\text{Co}(\text{bpy})_3]^{3+/2}$ devices proved to be

efficient indoor photovoltaics; when assessing the back-illuminated devices, the optimized $[\text{Co}(\text{bpy})_3]^{3+/2}$ DSSCs displayed a record PCE of 27.3 % and a retention ratio of 85.3 %.

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CHAPTER 5

COUPLING DYE-SENSITIZED SOLAR CELLS
WITH BIOSENSORS: A NEW AUTONOMOUS
AND SELF-SIGNALING BIOSENSING DEVICE
FOR SARCOSINE DETECTION

Under peer-review in Talanta

COUPLING DYE-SENSITIZED SOLAR CELLS WITH BIOSENSORS: A NEW AUTONOMOUS AND SELF-SIGNALING BIOSENSING DEVICE FOR SARCOSINE DETECTION

ABSTRACT

An early diagnosis is the gold standard for cancer survival. Biosensors have proven their effectiveness in monitoring cancer biomarkers but are still limited to a series of requirements. This work proposes an integrated power solution, with an autonomous and self-signaling biosensing device. The biorecognition element is produced *in situ* by molecular imprinting to detect sarcosine, a known biomarker for prostate cancer. The biosensor was assembled on the counter-electrode of a dye-sensitized solar cell (DSSC), simultaneously using EDOT and Pyrrole as monomers for the biomimetic process and the catalytic reduction of triiodide in the DSSC.

After the rebinding assays, the hybrid DSSC/biosensor displayed a linear behavior when plotting the power conversion efficiency (PCE) and the charge transfer resistance (R_{CT}) against the logarithm of the concentration of sarcosine. The latter obtained a sensitivity of 0.468 Ω /decade of sarcosine concentration, with a linear range between 1 ng/mL and 10 μ g/mL, and a LOD of 0.33 ng/mL. When interfacing an electrochromic cell, consisting of a PEDOT-based material, with the hybrid device, a color gradient between 1 ng/mL and 10 μ g/mL of sarcosine was observed. Thus, the device can be used anywhere with access to a light source, completely equipment-free, suitable for point-of-care analysis and capable of detecting sarcosine within a range of clinical interests.

5.1 INTRODUCTION

Prostate cancer is the second most commonly occurring cancer in men and the fourth most common cancer worldwide [1]. The early detection of prostate cancer is usually made based on rectum digital examination, endorectal ultrasonography, prostatic puncture biopsy, computed tomography and magnetic resonance imaging [2]. These standard examination tests are invasive, expensive and do not meet current point-of-care needs, thus stimulating the development of biosensors. Lately, biosensing devices have become ubiquitous in the point-of-care detection of any target analyte [3,4]; the most common and widely available are the glucose meters, pregnancy tests and now, the COVID antigen tests [5–7]. Biosensors can also be used for cancer biomarkers monitoring [8–10], and sarcosine is a known biomarker for prostate cancer [11,12]. Healthy patients have normal sarcosine levels of ca. $(1.4 \pm 0.6) \mu\text{M}$, and these levels are significantly increased during the progression and the metastatic process of prostate cancer [13,14]. High values of sarcosine are also known indicators of Alzheimer, sarcosinemia, dementia, colorectal and stomach cancer, among others [15].

A biosensor is mainly composed of two elements: a bioreceptor or biorecognition element and a transducer. The biorecognition element determines the selectivity of the biosensor towards the target analyte. The bioreceptors can either be biological or synthetic. Although biological bioreceptors ensure simplicity and high selectivity of the device, they are very expensive, require special storage conditions and have limited shelf-life [16]. A different pathway considers the use of plastic antibodies [17], which simulate the recognition properties of biological materials. Plastic antibodies are usually prepared using molecularly imprinted polymers (MIPs). This technique involves imprinting a specific molecule, also known as template, in a 3D structure [18], so that a polymeric network is grown around the template. When the template is removed from the polymeric matrix, it reveals the binding positions displaying analogous behavior to natural antibodies. These binding positions should match the size and shape of the target. This technique can be

challenging, but research on MIPs for protein recognition has been already addressed successfully [19,20].

Some biomimetic sensor approaches for sarcosine detection have been described in the literature. For example, Nguy et al. [21] reported a biomimetic sensor for sarcosine detection using the molecularly imprinting technique with aminothiophenol monomer electropolymerized onto carbon electrodes with gold-nanoparticles interlayer. The biosensor was assessed by Electrochemical impedance spectroscopy (EIS) and the authors reported a sensitivity of 1.44 k Ω / decade of $C_{\text{sarcosine}}$, over a linear range between 1 ng/mL to 1.6 μ g/mL. Another example of a biosensor developed using the MIP technique was proposed by Sheydaei et al. [22], using methacrylic acid as a functional monomer to imprint sarcosine onto a carbon paste electrode. This time the device was evaluated through differential pulse voltammetry, and the sensitivity reported was 0.0438 μ A/ μ M, over a concentration range of 5 μ M – 1.1 mM (0.44 – 98 μ g/mL). In contrast to these previous potentiometric examples of sensors, Kumar et al. [14] suggested an amperometric sarcosine biosensor based on covalent immobilization of sarcosine oxidase onto gold electrodes. The linear range extended from 0.1 – 100 μ M (8.9 ng/mL – 8.9 μ g/mL.) Additionally, Narwal et al. [23] and Deswal et al. [24] used similar approaches to also develop amperometric sarcosine biosensors, immobilizing sarcosine oxidase onto carbon/chitosan composites, electrodeposited onto gold electrodes. Both biosensors showed high sensitivity of 277.5 μ A/ μ M, with a linear range between 0.1 – 100 μ M and 0.001 – 100 μ M, respectively.

Electrochemical biosensors, such as described previously, are known to be small, fast, cheap and, most importantly, they may replace the time-consuming laboratory analyses [15]. Yet, they remain electrically dependent, since they need batteries to operate. Photovoltaic cells, such as dye-sensitized solar cells (DSSCs), convert photons into electrical energy and they can be used as electrochemical transducers, while providing electrical power to biosensing devices. Merging biosensors with DSSCs has already been reported [25–27]; the simplest approach is to replace the counter-electrode material with the biosensing film. Moreover, aiming at developing a fully autonomous and self-signaling device, an electrochromic cell will be interfaced in the external

circuit of the hybrid DSSC/biosensor [28,29]. This work proposes an integrated power solution for a device that will be able to detect sarcosine in urine samples within a range of clinical interest, which, to the best of our knowledge, has not been reported yet.

5.2 EXPERIMENTAL SECTION

5.2.1 REAGENTS AND SOLUTIONS

The chemicals used throughout this work were of analytical grade and the water was ultrapure Milli-Q laboratory grade. Screen-printable TiO_2 pastes (30NR-D and 18NR-AO) and EL-HPE iodine electrolyte were acquired from Greatcell Solar Materials®. Dye N719 (ruthenizer 525-bisTBA), and chenodeoxycholic acid (CDA) were ordered from Solaronix®. TiCl_4 (99.9 %) and Sarcosine were from Acros Organics. Absolute ethanol, titanium diisopropoxide bis(acetylacetonate), anhydrous isopropyl alcohol and dimethyl sulfoxide (DMSO), potassium hydroxide (KOH), lithium perchlorate (LiClO_4 , 98 %) and sodium perchlorate hydrate (NaClO_4 , 99.99 %) were purchased from Sigma Aldrich®. Potassium Chloride (KCl) was acquired from Merck; acetonitrile from Carlo Erba; 3,4-Ethylenedioxythiophene (EDOT, 98 %) from TCI; pyrrole (Py, 98 %) from Alfa Aesar, phosphate buffered saline (PBS) tablets from Fisher BioReagents; potassium di-hydrogen phosphate (KH_2PO_4) and Dipotassium hydrogen phosphate (K_2HPO_4) were purchased from Panreac; creatinine was from Fluka; urea was from Fagron; and Nafion™ in alcoholic solution (20 wt.%) was ordered from QuinTech.

5.2.2 APPARATUS AND MATERIALS

Electrochemical measurements were performed with an Autolab (PGSTAT302N, Metrohm) electrochemical station, equipped with a frequency response analysis (FRA) module controlled by the NOVA 2.1 Software. Current vs. applied potential (I-V) response of the DSSCs was obtained under simulated solar light (AM1.5G, 100 mW cm^{-2}) using a Solar Simulator MiniSol (LSH-7320, Newport). The electrochemical impedance spectroscopy (EIS) was

performed in dark conditions at -0.65 V; a sinusoidal perturbation with an amplitude of 10 mV and a frequency range of 100 kHz- 0.1 Hz was applied.

Throughout the work, fluorine-doped tin oxide (FTO)-coated glasses (TEC-7; $7 \Omega/\text{sq}$) acquired from Greatcell Solar Materials® were used as conductive substrates for the construction of the biosensor, DSSCs and electrochromic device. The digital images of the electrochromic devices were obtained with a 17 Mp smartphone camera (Xiaomi), with the aid of tripod to always use the same lighting conditions, and the color coordinates of these images were collected using ImageJ in three different points. The color coordinates were analyzed according to the Hue, Saturation and Luminousness – HSL – color system. The quantitative color calibration was achieved by plotting the Saturation vs. the logarithm of the analyte concentration, where the Saturation represents the intensity of the color of the image.

5.2.3 PREPARATION OF THE PHOTOANODE

The photoanode was prepared following the optimizations accomplished on **Chapter 2**: first a blocking layer was deposited; then, two TiO_2 mesoporous layers (30NR-D) and one TiO_2 scattering layer (18NR-AO) were deposited by screen printing technique, resulting in a thickness of $21 \pm 1.0 \mu\text{m}$. The thickness was assessed by analyzing the cross-section image with Scanning Electron Microscopy (SEM, FEI Quanta 400 FEG ESEM). The photoelectrodes had an active area of 0.196 cm^2 . After the first sintering stage at 500°C , the photoanodes were treated in a 40 mM TiCl_4 aqueous solution to improve the adhesion of the titania layer and suppress recombination losses. Finally, after the second sintering step at 500°C , the photoanodes were dipped in a fresh solution of 0.5 mM N719 dye and 5 mM CDA in absolute ethanol for 20 ± 1 hours. Finally, the identical photoanodes were washed with absolute ethanol, dried in N_2 flow, and immediately used.

5.2.4 PREPARATION OF THE BIOSENSOR

The glass substrates were cleaned in an ethanol solution of KOH (2.67 M in EtOH $70 \text{ wt.}\%$) in an ultrasonic bath, washed with distilled water, and dried.

The steps involved in the construction of the sarcosine biosensor through molecular imprinting technique are illustrated in **Figure 5.1**.

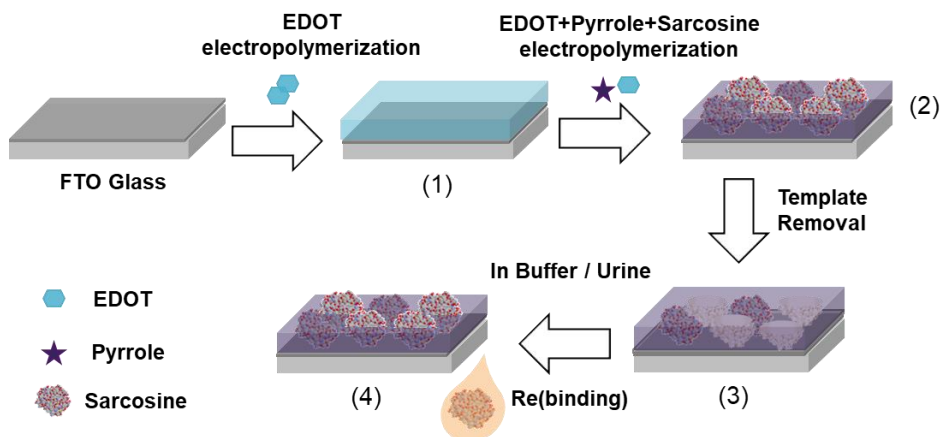


Figure 5.1. Schematic illustration of the several steps for the sarcosine biosensor construction through molecular imprinting polymer technique.

The construction of the biosensor was made in a three-electrode configuration, with the FTO glass acting as the working electrode, Ag/AgCl (0.1 M KCl) acting as the reference electrode and a platinum wire acting as a counter-electrode. To build the biosensor, two conductive polymers were electropolymerized: EDOT and Py. Both have been reported earlier as effective catalysts in DSSCs [30–35], albeit PEDOT presents a much higher conductivity ($300\text{--}750\text{ S cm}^{-1}$) than PPy ($2\text{--}100\text{ S cm}^{-1}$) [36–38]. After cleaning the FTO glasses, a solution of EDOT (10 mM in KCl) was electropolymerized at a constant potential of 1.2 V for 15 s, and the FTO glass turned to a bright blue (step A in **Figure 5.1**). Then, the PEDOT-coated glasses were immersed into a solution of EDOT (10 mM), Py (2 mM) and sarcosine (0.1 mM) in PBS buffer (pH 7.4) and subjected to further electropolymerization by applying 10 cycles of electrode potential sweep (50 mV/s) from -0.3 V to 1.0 V and back to -0.3 V. The resulting MIP sensor was visible to the naked eye because the glass substrate changed from bright blue to dark purple (step B in **Figure 5.1**).

After imprinting sarcosine, the amino acid template was removed from the polymeric matrix by incubating the biosensing film with an EtOH:H₂O solution (7:3, V/V) for 90 min and a pure H₂O solution overnight (step C in **Figure 5.1**).

To check non-specific interactions between the polymeric matrix and sarcosine, a non-imprinted polymer (NIP) was prepared in parallel following the same protocol without the sarcosine template. The rebinding of the target template was performed on both MIP and NIP sensors and accomplished by incubating either blank buffer or standard solutions prepared in the buffer in the modified area of the electrode for 30 min (step D in **Figure 5.1**). The sarcosine standard solutions were prepared either in phosphate buffer or urine (diluted 10 times). The sarcosine standard solutions were incubated, starting from the lowest (1 ng/mL) to the highest concentration (10 µg/mL), with a washing step between each standard.

5.2.5 ASSEMBLY OF HYBRID DEVICE, SARCOSINE REBINDING AND ELECTROCHEMICAL CHARACTERIZATION

The set-up of the hybrid DSSC/biosensor is represented in **Figure 5.2**. In a conventional DSSC the photoanode and the counter-electrode are sandwiched together with a thermoplastic sealant in the middle for a permanent sealing of the solar cell. The DSSC used herein had a more temporary option as sealant – scotch magic tape, so that the biosensor could be easily accessible to the rebinding assays. This unorthodox sealant worked due to the presence of acetonitrile in the commercial iodine electrolyte (EL-HPE) used herein, which slightly melted the scotch tape and created a temporary seal, lasting ca. 1 h, time enough to conclude the necessary characterizations. After each rebinding stage, where the standard solution of sarcosine prepared either in buffer or in urine (diluted 10 times) was incubated on the counter-electrode, the DSSC was assembled with one of the identical photoanodes produced as described in **Section 5.2.3**. The hybrid device was evaluated by recording *I-V* curves in linear sweep voltammetry from -0.8 V to 0.1 V as well as EIS in dark conditions at -0.65 V from a frequency range of 100 kHz-0.1 Hz. All assays were conducted in triplicate.

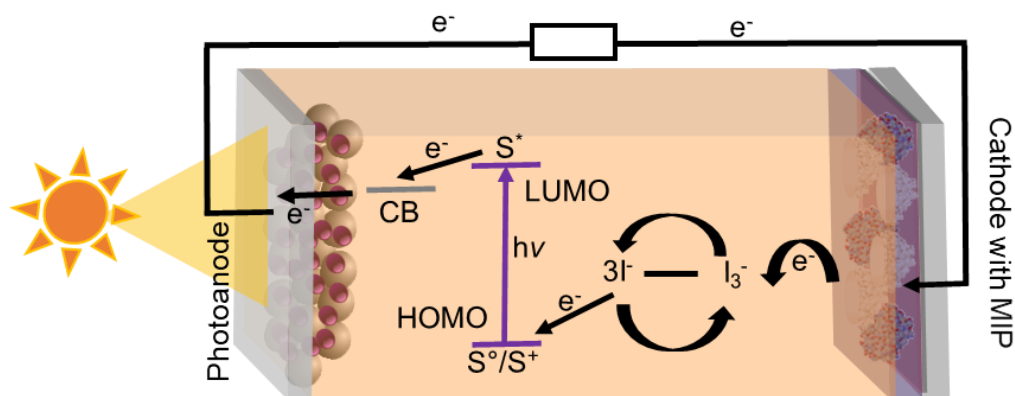


Figure 5.2. Schematic illustration of the operation of a DSSC coupled with the sarcosine biosensor.

5.2.6 ASSEMBLY AND PERFORMANCE OF ELECTROCHROMIC CELL

5.2.6.1 PREPARATION OF ELECTROCHROMIC MATERIAL

The electrochemical component was developed according to previous works [28,29,40]. By itself, EDOT has electrochromic properties but the 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)aniline (SNS-NH₂) was added to the mixture to enhance the color features of the final electrochromic device. The synthesis and chemical structure of SNS-NH₂ is described in the **Appendix E (Scheme E1)**. To prepare the electrochromic cell, first, a solution of 0.25 mM of SNS-NH₂, 100 mM of EDOT, 100 mM of NaClO₄ and 100 mM of LiClO₄ were prepared in acetonitrile. Then, the electrochromic electrode was obtained by *in situ* electropolymerization of the solution previously described, in a three-electrode configuration, with a single sweep of electrode potential from 0 V to 1.3 V at a scan-rate of 50 mV/s; the FTO substrate turned blue. To ensure that the electrochromic electrode was ready to use and in its neutral state, a constant potential of 0 V was applied for 20 s with 0.1 M KCl as electrolyte, after which the glass electrode changed color from blue to purple.

5.2.6.2 ASSEMBLY OF THE ELECTROCHROMIC DEVICE AND INTERFACE WITH HYBRID DSSC/BIOSENSOR

The electrochromic device was assembled by sandwiching two FTO glass substrates, one with the electrochromic material and one with bare FTO, with a NafionTM electrolyte connecting both electrodes (**Figure 5.3B**). Then, the electrochromic device was interfaced with the hybrid DSSC/biosensor by connecting the photoanode of the DSSC to the bare FTO electrode of the electrochromic device (black pathway in **Figure 5.3**) and the counter-electrode with the biosensing film to the electrochromic electrode (red pathway in **Figure 5.3**). Under working operation, the hybrid DSSC/biosensor is illuminated by the solar simulator (or another light source available) and the current produced flows through the electrochromic device and causes a color change, which will be dependent of sarcosine concentration in the sample analyzed (**Figure 5.3C**). When sarcosine is not present in the sample, *i.e.*, blank sample, the catalytic film won't have any obstacles for the charge transport, so the hybrid device will produce the maximum power/photovoltage and the electrochromic cell will turn blue. When the sample has a high concentration of sarcosine, the analyte will attach itself to the specific bindings and obstruct the charge transport, so the hybrid device will generate much less power/photovoltage and the electrochromic cell will turn purple.

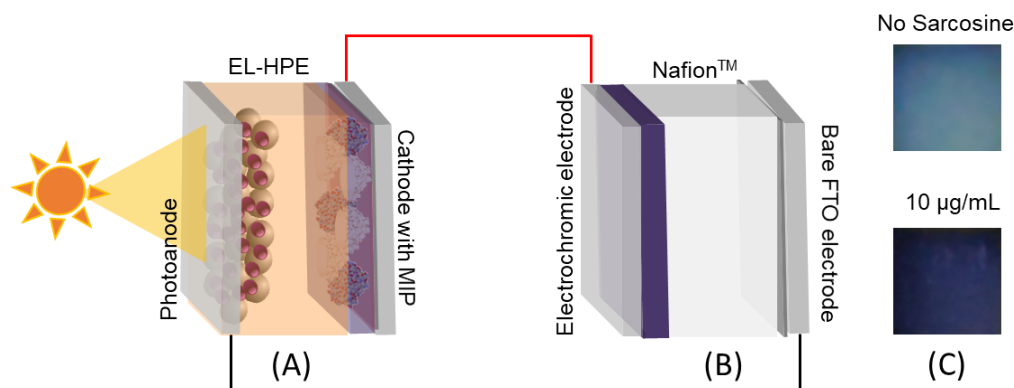


Figure 5.3. Schematic representation of the interface between hybrid DSSC/biosensor (**A**) the electrochromic device (**B**) and two examples of

electrochromic response depending on the concentration of sarcosine present in the sample tested (C).

5.3 RESULTS AND DISCUSSION

The sarcosine concentration in the formation of the MIP layer was varied between 1 mM, 0.1 mM, and 0.01 mM, aiming at optimizing the number of cavities within the polymeric network and, thereby, enhancing the rebinding of the target template in the detection stage. These preliminary studies are discussed in **Appendix D**, where the biosensor was evaluated in a three-electrode configuration, using an iron electrolyte. The MIP sensor with a sarcosine concentration of 0.1 mM displayed the best sensitivity ($0.20 \Omega/\text{decade } C_{\text{sarcosine}}$) and the lowest LOD (0.30 ng/mL) when calibrated in urine samples. So, the hybrid DSSC/biosensor device was assembled applying the optimized biosensing film onto the counter-electrode of the DSSC (**Figure 5.2**). The biosensing film on the counter-electrode was incubated with the standard solutions containing the target analyte, separately from the photoanode. Afterwards, the counter-electrode was washed and assembled with the photoanode to assess the photovoltaic performance.

5.3.1 PHOTOELECTROCHEMICAL PERFORMANCE OF THE DSSC/BIOSENSOR DEVICE

The performance of the hybrid DSSC/biosensor was electrochemically characterized after the deposition of each component layer, similarly to what was done for the MIP sensor. The characterization methods employed include: i) standard J - V curves, to determine the open-circuit potential (V_{OC}), the short-circuit current density (J_{SC}), the fill factor (η_{FF}), the maximum power point (MPP) and the power conversion efficiency (η_{PCE}); and ii) the EIS under dark conditions, to quantify the series resistance (R_s), the charge transfer resistance at the interface counter-electrode/electrolyte (R_{CT}) and the resistance to the recombination in the interface photoanode/electrolyte (R_k). These results are

displayed in **Figure 5.4**; the impedance spectra were fitted with the equivalent electrical circuit in **Figure 5.4c**.

When the counter-electrode consists solely of PEDOT, a PCE of 7.3 % was achieved under 1-Sun illumination (**Table 5.1**). When the MIP layer was applied, the photovoltaic performance significantly dropped, mainly because the η_{FF} was more than 50 % lower and the V_{OC} decreased 26 mV, resulting in a PCE of 2.7 %. This decrease in η_{FF} and the shape of the J - V curve are most likely related to a substantial decrease of the shunt resistance of the whole device. The copolymerized EDOT/Py film loaded with sarcosine (MIP) displays an interface with the electrolyte which exhibits a substantially higher R_{CT} ; the R_k is quite low, and this leads to higher recombination in the photoanode. After both sarcosine removal steps – 1.5 h and overnight, the overall PCE of the device recovered slightly, mostly because the R_{CT} at the counter-electrode interface decreased. The non-imprinted electrode (NIP) displayed a higher PCE than the imprinted material (MIP) because displays a lower R_{CT} .

— (1) PEDOT — (2) After MIP — (3) After NIP — (4) After removal — (5) After overnight removal

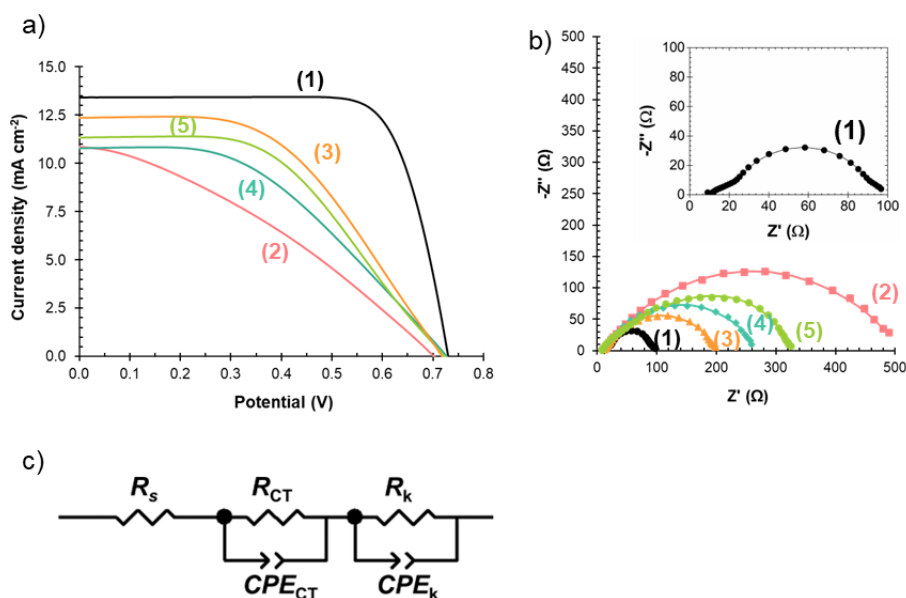


Figure 5.4. J - V curve (a) and (b) EIS data, measured for the hybrid DSSC/biosensing device after EDOT electropolymerization (1), after MIP (2),

after NIP (**3**), after template removal (**4**) and overnight removal (**5**) in the MIP electrode. (**c**) Equivalent electrical circuit used for fitting the spectra.

Table 5.1. Photovoltaic performance and electrochemical data obtained for the hybrid DSSC/biosensor at the various steps of biosensing film construction. Resistances ($\Omega\cdot\text{cm}^2$) of the device were obtained by fitting the model (**Figure 5.4c**) to the impedance spectra in **Figure 5.4b**).

	η_{PCE} (%)	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	V_{oc} (mV)	η_{FF}	MPP ($\text{mW}\cdot\text{cm}^{-2}$)	R_{s} ($\Omega\cdot\text{cm}^2$)	R_{CT} ($\Omega\cdot\text{cm}^2$)	R_{k} ($\Omega\cdot\text{cm}^2$)
PEDOT	7.27	13.09	731	0.76	7.19	3.42	15.2	28.7
After MIP	2.72	10.30	705	0.37	2.69	4.44	167.0	12.7
After NIP	4.45	12.10	723	0.51	4.41	3.31	63.2	20.2
After Removal	3.54	10.79	728	0.44	3.50	4.15	109.9	15.4
After Overnight Removal	4.09	11.34	725	0.49	4.05	3.17	84.7	17.0

5.3.2 REBINDING ASSAYS OF THE HYBRID DSSC/BIOSENSOR DEVICE

The analytical performance of the hybrid DSSC/biosensor was assessed by rebinding assays, as described in **Section 5.2.5**. The calibration of the device was performed using standard solutions that were first prepared in a phosphate buffer (**Figure 5.5**) and then in human urine from healthy male volunteers, diluted 10 $\times$ in phosphate buffer (**Figure 5.6**). The concentration of sarcosine spiked buffer solution ranged from 1 ng/mL to 10 $\mu\text{g/mL}$ and the electrochemical behavior was assessed based on the J - V curves and the EIS plots, using a commercial iodine electrolyte in a DSSC configuration. From

these two techniques, the $\Delta\eta_{PCE}$ and the ΔR_{CT} are determined, according to **Eq. 5.1** and **Eq. 5.2**, respectively.

$$\Delta\eta_{PCE} = \frac{\eta_{PCE_{sarcosine\_sample}} - \eta_{PCE_{blank}}}{\eta_{PCE_{blank}}} \quad \text{Eq. 5.1}$$

$$\Delta R_{CT} = \frac{R_{CT_{sarcosine\_sample}} - R_{CT_{blank}}}{R_{CT_{blank}}} \quad \text{Eq. 5.2}$$

When plotting the logarithm of $C_{sarcosine}$ against either $\Delta\eta_{PCE}$ and the ΔR_{CT} , the slope of the linear regression will determine the sensitivity of the device.

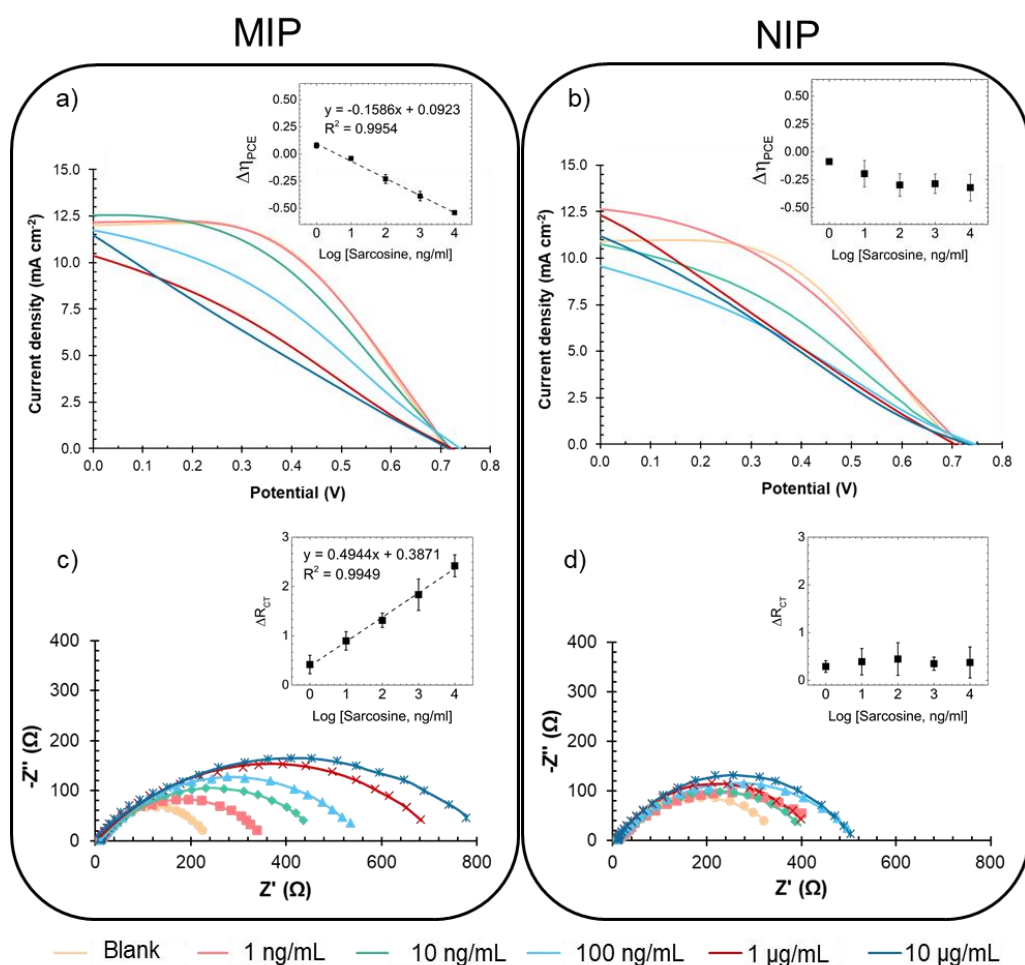


Figure 5.5. *J*-*V* characterization (a), (b), and Nyquist plots (c), (d), for the rebinding assays in phosphate buffer for the MIP (a), (c), and NIP electrodes

(b), (d), performed in a DSSC configuration. Inset: typical regression lines plotting the $\Delta\eta_{\text{PCE}} / \Delta R_{\text{CT}}$ against the logarithm of sarcosine concentration.

After successive incubations, the sarcosine present in the spiked solutions adsorbed on the imprinted cavities, making the electrochemically active surface area substantially smaller; and consequently the R_{CT} increased as shown in **Figure 5.5c** and **Figure 5.6c**. The increase in the overall resistance of the device has a very negative effect on the FF, affecting the shape of the J - V curves for both calibration mediums as it can be observed on **Figure 5.5a** (buffer) and **Figure 5.6a** (urine). Overall, when the concentration of sarcosine increases in the spiked solutions (both in buffer or in urine) the PCE decreases, and the $\Delta\eta_{\text{PCE}}$ displays a linear response vs. the logarithm of sarcosine concentration (**Figure 5.5a** and **Figure 5.6a**). The anionic slope of the $\Delta\eta_{\text{PCE}}$ regression is very similar between buffer and urine calibration medium; the obtained sensitivities were respectively -0.159 % (**Figure 5.5a**) and -0.154 % (**Figure 5.6a**) per decade of sarcosine concentration, with a determination coefficient of $R^2 = 0.99$. Comparably, the cationic slope of the ΔR_{CT} regression vs. the log of $C_{\text{sarcosine}}$ also shows similar values for the calibrations performed with the buffer and with the urine, the obtained sensitivities were respectively 0.494 Ω (**Figure 5.5c**) and 0.468 Ω (**Figure 5.6c**) per decade of sarcosine concentration, with a determination coefficient of $R^2 = 0.99$. Moreover, the LOD of the hybrid DSSC/biosensor calibrated in urine was 0.32 ng/mL. Repeated calibrations ($n = 3$), with standard deviations < 12 % for all concentrations, were obtained indicating a good-precision and stable device. The control electrode (NIP) showed random responses with the target template concentration, validating the performance of the electrode to determine sarcosine in complex samples (**Figure 5.6b** and **d**).

In general, the device shows that efficiency and charge transfer resistance are concentration dependent. Moreover, the system responds to sarcosine concentration ranges that are clinically relevant. The MIP and NIP show different electrochemical behaviors that demonstrate the ability of the MIP electrode to interact with sarcosine, mostly through its imprinted sites,

displaying a small non-specific interaction with non-imprinted sites at the polymer surface.

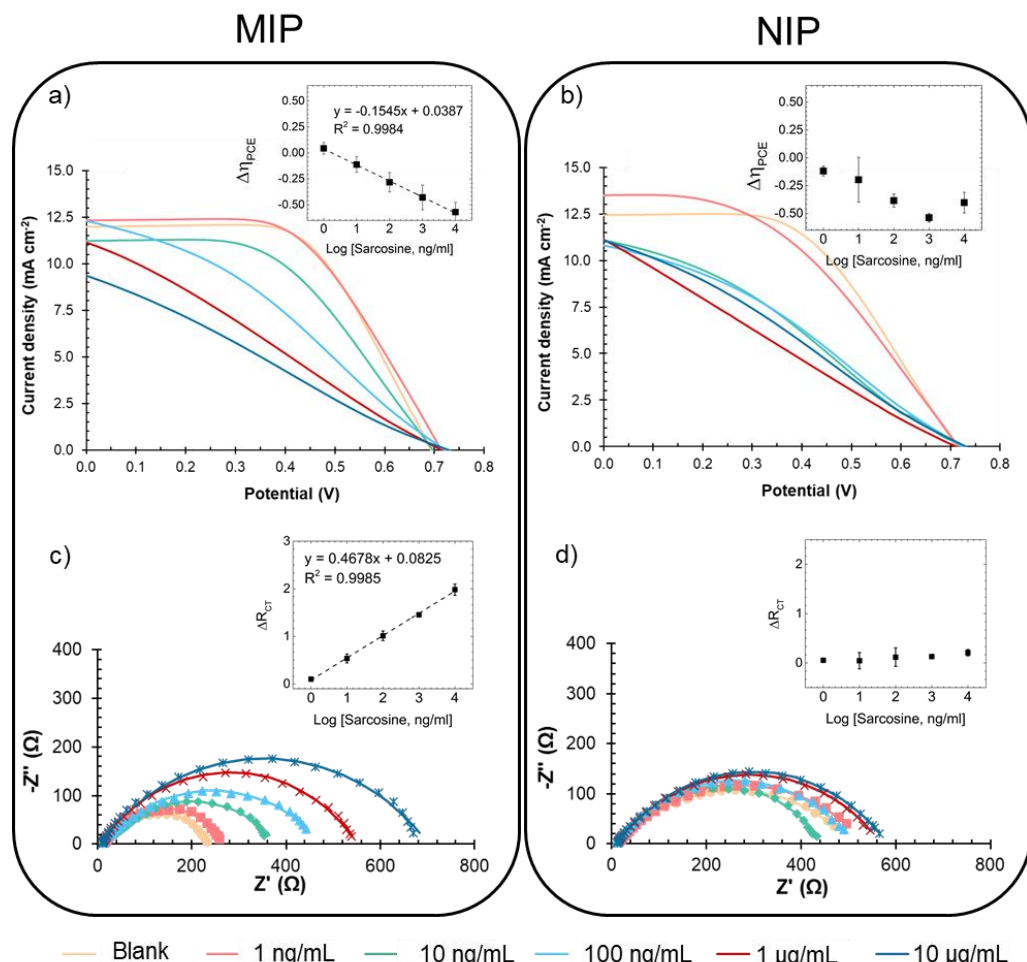


Figure 5.6. J-V characterization (a), (b), and Nyquist plots (c), (d), for the rebinding assays in human urine diluted in phosphate buffer for the MIP (a), (c), and NIP electrodes (b), (d), performed in a DSSC configuration. Inset: typical regression lines plotting the $\Delta\eta_{PCE}/\Delta R_{CT}$ against the logarithm of sarcosine concentration.

5.3.3 SELECTIVITY OF THE HYBRID DEVICE

The selectivity of the hybrid DSSC/biosensor was assessed when chemical compounds that could potentially interfere with the sarcosine

detection are present. Creatinine and urea were the selected interferents since they are among the most abundant compounds in urine. Considering the reference values for these two compounds [41] and the dilution of urine (10×), the concentrations used for creatinine and urea were 0.1 mg/mL and 1 mg/mL, respectively. The sarcosine spiked solution used in the selectivity test had a concentration of 100 ng/mL.

The selectivity was obtained using a single component solution, with the interfering species. Each compound was incubated separately, for 30 min, and afterwards the *J-V* curves and EIS data were collected. The results are displayed on **Figure 5.7**, and they indicate no significant interference with sarcosine detection. The single component approach used to evaluate the selectivity of the device demonstrated low rebinding properties for creatinine (7.5 ± 2.8) % and for urea (9.7 ± 1.7) %. In general, the device showed great selectivity of the biosensing film, confirming that the biosensor has a high affinity for the target analyte.

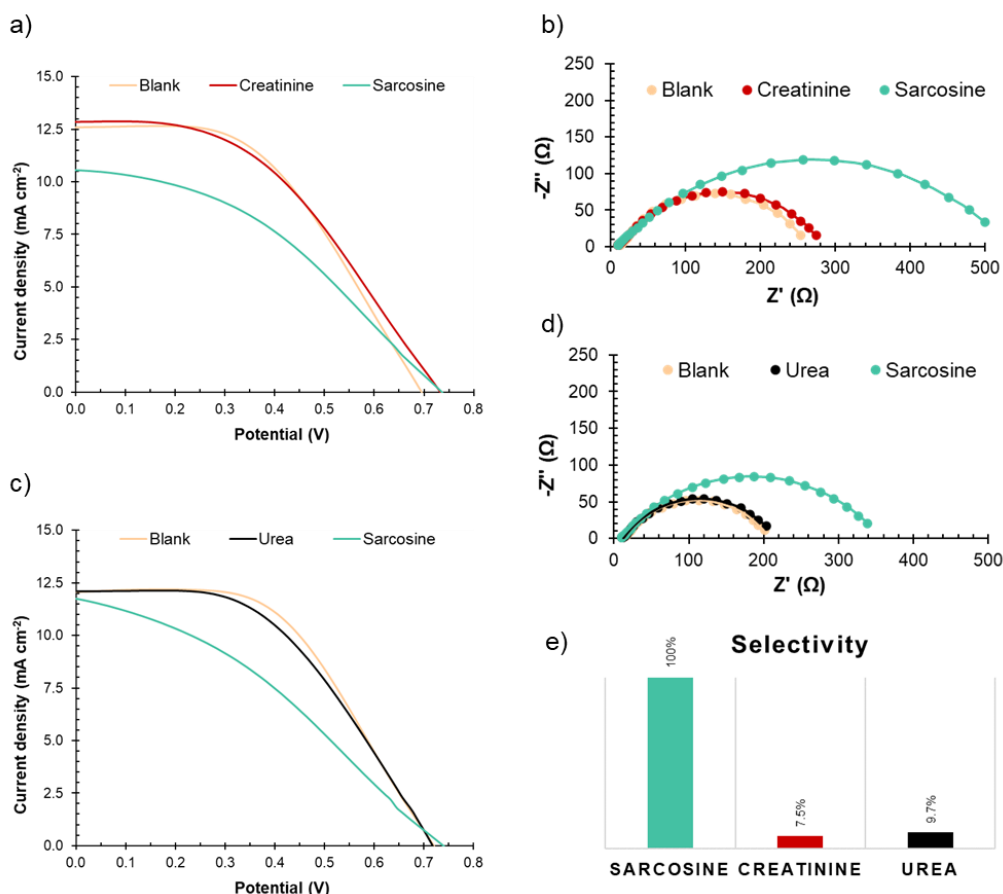


Figure 5.7. J-V characterization **(a)** and **(c)** and Nyquist plots **(b)** and **(d)** regarding the selectivity of the hybrid DSSC/biosensor device when incubated with a single interfering compound, Creatinine **(a)** and **(b)**, and Urea **(c)** and **(d)**. The concentrations used upon the incubation of the biosensing film were 0.1 mg/mL, 1 mg/mL and 100 ng/mL for creatinine, urea, and sarcosine respectively. Selectivity study with single solution of sarcosine and interfering species (creatinine and urea) **(e)**.

5.3.4 ADDITION OF THE SELF-SIGNALING DEVICE

The hybrid DSSC/biosensor device showed a clear dependence of performance vs. concentration, but to operate this device in an equipment-free environment it is necessary to establish a self-signaling approach. Since

electrochromic cells change color intensity depending on the power input and the power produced by the DSSC/biosensor device decreases with the sarcosine concentration, combining the two devices allows to visually assess the sarcosine concentration in a biological sample using a fully autonomous device, *cf.* **Figure 5.3**. The developed electrochromic cell varied its color from blue to purple for sarcosine concentrations of 1 ng/mL to 10 μ g/mL; the preparation of the electrochromic material is described in the supplementary information.

The rebinding assays of the new self-signaling device set-up were made for sarcosine concentrations between 1 ng/mL to 10 μ g/mL. The standard solutions used to calibrate the device were prepared using human urine diluted in a phosphate buffer, incubated for 30 min. The time established for the electrochromic cell to reach a stable color was set to 2 min.

The colors obtained for each standard in urine are displayed on **Figure 5.8a**. The blank assay corresponds to the incubation of urine solution without the target analyte, which achieved the highest power output by the hybrid device; when connected to the electrochromic cell, the resulting color was a light blue. When the sarcosine concentration in the standard solutions increases, the power generated by the hybrid DSSC/biosensor slowly decreases and the electrochromic cell goes from light blue to darker blue, and for the final standard, at 10 μ g/mL, it turns purple. Thus, there is a noticeable color gradient which allows visual detection of pathogenic concentration of sarcosine, > 1 ng/mL. The developed sensor displays a working concentration range similar to other published works [21,23,24]. However, the present work reports a fully autonomous device with self-signaling ability.

Quantitative data was extracted from the color calibration, following the approach reported first by Silva *et al.* [42]. The color coordinates of the HSL color space (Hue, Saturation and Luminance) were determined using the image J software for each digital picture, taken in three different spots. When plotting the Saturation against the logarithm of the sarcosine concentration, a

linear trend was achieved: $y = 9.4 \log(C_{\text{sarcosine}}) + 92.8$, with a corresponding determination coefficient of ca. $R^2 = 0.99$ (**Figure 5.8b**).

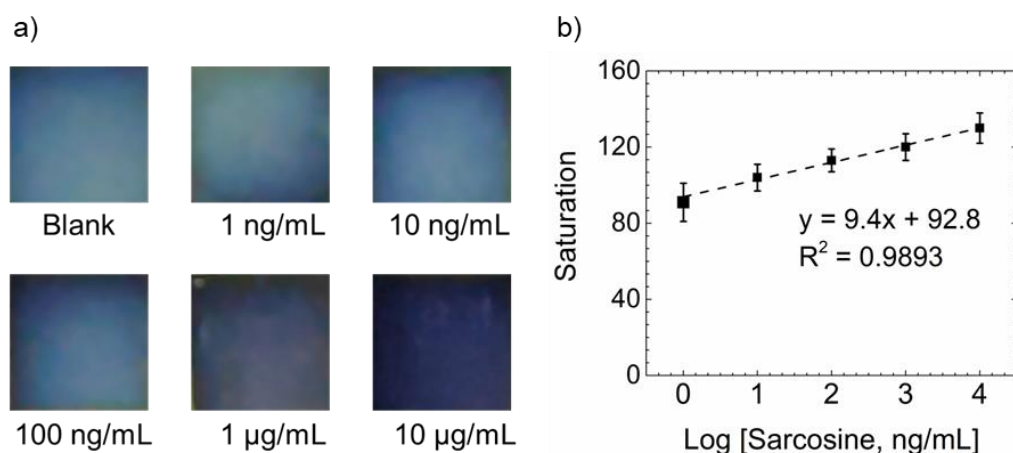


Figure 5.8. Color behavior of the self-signaling device (**a**), composed of the electrochromic cell interfaced in the external circuit of the hybrid DSSC/biosensor device, and the respective calibration (**b**), determined by the saturation coordinate of the HSL color system vs. $\log(C_{\text{sarcosine}})$.

5.4 CONCLUSIONS

A self-signaling and electrically autonomous biosensor was successfully assembled on the counter-electrode of a DSSC, interfaced with an electrochromic cell. The biosensor was first assessed in a three-electrode configuration, targeting the quantification of sarcosine in human urine samples from healthy male volunteers. The biosensing film was produced *in situ* molecularly imprinting it on a polymerized EDOT and Py film. The concentration of the target molecule was optimized, and the highest sensitivity and lowest LOD was achieved for a sarcosine concentration of 0.1 mM in the MIP material. So, the optimized biosensing film was evaluated by assembling it in the counter-electrode of the DSSC. It was found that the $\Delta\eta_{\text{PCE}}$ and the ΔR_{CT} of the DSSC were linearly dependent with the logarithm of sarcosine concentration, with a sensitivity in urine of -0.154 %/decade of $C_{\text{sarcosine}}$ and 0.468 Ω /decade of $C_{\text{sarcosine}}$, respectively. The linear range was also between

1 ng/mL and 10 µg/mL, and the LOD 0.32 ng/mL. The biosensor was selective towards sarcosine, as it is apparent from the selectivity study performed with two of the most abundant compounds in urine: creatinine and urea.

Finally, an electrochromic cell was interfaced with the hybrid DSSC/biosensor and there was a clear color gradient permitting visual detection of pathogenic concentration of sarcosine present in an actual biological sample. The saturation vs. the logarithm of sarcosine concentration displayed a linear trend in the same concentration range tested herein and $R^2 = 0.99$. Overall, the device reported herein is equipment-free, fit for point-of-care analysis and able to screen sarcosine in real samples. This device only requires a light source to power the DSSC, to provide clinically relevant information anywhere. Furthermore, this simple integration of a biorecognition element with the DSSC can be applied to almost any cancer biomarker.

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CHAPTER 6

GENERAL CONCLUSIONS AND OUTLOOK

GENERAL CONCLUSIONS AND OUTLOOK

6.1 GENERAL CONCLUSIONS

Among the solar research community, it is consensual that the biggest opportunities for dye-sensitized solar cells (DSSCs) lie in indoor applications. They are perfectly suited for this type of illumination; besides, they are easy to produce, aesthetically pleasing, safe and sustainable, as they are free of toxic compounds. Moreover, they display a quite small energy return on investment (EROI), which is an amazing asset for successful market integration. The boom of small electronic devices of the Internet of Things (IoT) and the growing need of effective point-of-care biosensing devices will certainly increase the number of battery-operated devices. DSSCs can easily power small IoT devices or biosensors, and this thesis discloses the development of the most efficient DSSC systems for both solar and artificial illumination. Currently, most of the research reported focus on elaborate protocols to reach high-performing solar cells. However, this thesis seeks to find simple and cheap solutions, with great performance results.

Conventional DSSCs have been developed since 1991 and record-breaking power conversion efficiencies are nowadays rare, so the reported devices are typically quite sophisticate. **Chapter 2** reports on conventional DSSCs sensitized with N719 dye and assembled using just commercial materials, which were tuned for efficient electricity production under solar and indoor light. The balance between photocurrent generation, electron

recombination and titania layer thickness were optimized based on the *J-V* and electrochemical impedance spectroscopy (EIS) responses. The optimal thickness is ca. 21 μm , using both mesoporous TiO_2 (ca. 14 μm) and active scattering TiO_2 (ca. 7 μm) layers. When increasing the thickness of the mesoporous layer alone, the photocurrent remained the same, but the recombination losses increase tremendously. With the addition of the active scattering layer, the light harvesting was enhanced, and it resulted in an improvement on the IPCE at wavelengths above 580 nm. The inclusion of a TiO_2 blocking layer at the FTO-glass/mesoporous TiO_2 interface and a chemical bath of TiCl_4 of the titania layer successfully suppressed most of back electron recombination at the photoanode/electrolyte interface. Approximately 90 % of the theoretically current density in N719-sensitized cells was reached, thus rendering devices routinely displaying a power conversion efficiency (PCE) of 9.84 % under simulated solar light. Perfect match of the spectral response from N719-sensitized cells with the emission spectra of typical daylight sources translate in a high PCE of 28.7 % under artificial room-light, demonstrating the great potential of conventional DSSCs for the indoor light harvesting.

DSSCs are perfectly fitted for indoor use, showing incredibly high and stable PCE, surpassing the 34 % landmark. The best performing DSSCs to the date use Co(III)/Co(II) and Cu(II)/Cu(I) redox shuttles to yield an output potential difference above 1.0 V. However, with the arrival of Co(III/II) shuttles, it soon became apparent that conventional platinum (Pt) counter-electrodes, typically used for iodine-based DSSCs, display poor charge transfer with cobalt complexes. **Chapter 3** reports composite PEDOT:PSS (PP) with graphene nanoplatelets (GNPs) films, which were produced by spin-coating deposition over fluorine-doped tin oxide (FTO) and bare soda-lime glass substrates. Electrodes of PP:GNP showed high electrocatalytic activity, displaying an apparent activation energy, E_a , for the charge transfer with $[\text{Co}(\text{bpy})]^{3+/2+}$ electrolyte of $6.2 \text{ kJ}\cdot\text{mol}^{-1}$, much lower than the E_a for PP ($17.5 \text{ kJ}\cdot\text{mol}^{-1}$). By introducing the GNPs into the PP film, the fractions of the oxidized EDOT units

in the polymer increased, thus improving the electrocatalytic activity of the composite. When DSSCs with PP and PP:GNP films were both assessed under 1-Sun illumination, their performance was similar, displaying a PCE of 10.8 % and 10.4 %, respectively. This behavior was assigned to the high exchange current densities, J_0 , for these two catalytic materials at 20 °C: 24.2 and 26.3 mA·cm⁻² for PP and PP:GNP electrodes, respectively, which were high enough to support the theoretically maximum photocurrent (ca. 23 mA·cm⁻²) in the device at 1-Sun. However, under indoor illumination, PP:GNP counter-electrode outperformed PP electrodes, because the former generates 13 % more photocurrent, resulting in a PCE of 29.7 % under 1000 lx illumination. In the PP:GNP electrodes, the graphene nanoplatelets largely protrude from the PP matrix film and shorten the effective distance between photoanode and counter-electrode, thus reducing the resistance of the cells for small currents and increase the photocurrent density. FTO-less bifacial DSSCs were prepared using PP:GNP film, only possible because of the enhanced electric conductivity and high transparency of ca. 65 % of the catalytic layer. These devices displayed a PCE of ca. 22 % when front-illuminated, and ca. of 18 % when illuminated from the rear side at 1000 lx, the highest reported up until now. The FTO-less bifacial devices are especially suitable for indoor applications as they allow to obtain ca. 30 % more power than one-side illuminated counterparts.

Since DSSCs are among the leading PV technologies for indoor applications, it seems logical that they should be optimized for these illumination conditions. Typically, the limiting factor on the performance of DSSCs is the charge recombination at the photoanode that occurs at high power illumination, *i.e.*, higher irradiance. However, at low-light conditions, the photopotential has a greater impact in the overall performance, which has been confirmed by the higher PCEs of Cu-mediated DSSCs under indoor illumination. **Chapter 4** studied the impact of the photoanode architecture, thickness, light-scattering properties, dye loading, and device thickness on the photogeneration, recombination and performance of iodine- and cobalt-

mediated DSSCs, under standard AM1.5G and artificial illumination. Iodine-based devices with 18 μm thick photoanode and 20 μm of device gap (acronym $\text{I}_2\text{--}20$) achieved a PCE of 9.0 % and 22.4 % under 1-Sun and 1000 lx, respectively. However, when using a 15 μm thick photoanode with a 50 μm device gap (acronym $\text{I}_2\text{--}50$), with iodine electrolyte, the PCEs achieved were 7.8 % and 23.1 % under AM1.5G and artificial illumination, respectively. The differences between the PCEs under 1-Sun and artificial light were assigned to the ability of the $\text{I}_2\text{--}50$ device to generate higher photovoltage under artificial light, which explains the large differences between PCEs under 1-Sun and artificial light. Moreover, both iodine and cobalt devices produce very similar photocurrent densities under weak light conditions. Since cobalt cells produce higher photovoltage, their indoor light conversion was much higher. Thoroughly optimized, cobalt DSSCs (acronym $\text{Co--}20$: 9 μm of ML20, 20 μm gap) rendered a PCE of 11.0 % and 32 % under 1-Sun and artificial illumination (1000 lx), respectively. Both cobalt and iodine devices proved to be efficient indoor photovoltaics; when assessing the back-illuminated devices, the optimized cobalt DSSCs displayed a record PCE of 27.3 % and a retention ratio of 85.3 %.

There is a growing need for rapid and trustworthy methods for point-of-care detection, which can be achieved with biosensing devices. Biosensors have already proven their effectiveness in monitoring cancer biomarkers, but they are still limited to a power source. **Chapter 5** proposes a self-signaling and electrically autonomous biosensor assembled on the counter-electrode of a DSSC, interfaced with an electrochromic cell. The biosensor was produced *in situ* through molecular imprinting of EDOT and pyrrole, with sarcosine as a molecular template. The hybrid DSSC/biosensor was assessed in human urine samples from healthy male volunteers, targeting the quantification of sarcosine. The performance of the device was evaluated based on the overall power conversion performance ($\Delta\eta_{\text{PCE}}$) and charge transfer resistance (ΔR_{CT}) of the hybrid DSSC/biosensor. The $\Delta\eta_{\text{PCE}}$ and the ΔR_{CT} of the device were linearly dependent on the logarithm of sarcosine concentration, between

1 ng/mL and 10 μ g/mL, with a sensitivity -0.15 %/decade of sarcosine concentration and 0.47 Ω /decade of sarcosine concentration, respectively. The limit of detection (LOD) of the system analyzed was 0.33 ng/mL. Furthermore, the device showed high selectivity towards sarcosine, as is apparent from the selectivity study performed with two of the most abundant compounds in urine: creatinine and urea. To achieve a self-signaling device, an electrochromic cell was interfaced with the hybrid device and the color gradient obtained with the calibration of the self-signaling device was evident. Determining the saturation of the digital image using Image J and plotting it against the logarithm of sarcosine concentration, a linear trend in the same concentration range tested herein was observed, with a determination coefficient of ca. 0.99.

Thus, a proof-of-concept was achieved because the device developed within the scope of this thesis is equipment-free, fit for point-of-care analysis and able to screen sarcosine in actual biological samples. This device only requires a light source to power the DSSC, and it will provide clinically relevant information anywhere. Furthermore, the simple integration of a biorecognition element in the DSSC is transversal to almost any cancer biomarkers.

6.2 OUTLOOK

DSSCs are already entering the future of power generation, as proved by the emergence of multiple companies with a rich portfolio of these devices. To foster the development of DSSCs it is important to understand critical fundamental aspects of this technology, where the charge recombination continues to be the major cause of efficiency loss. DSSCs are a complex system, comprising a photoanode, an electrolyte and a counter-electrode catalyst, so, when introducing a new material to one of these components, a thorough study should be performed to optimize the overall system. In this regard, computational studies such as DFT and molecular simulation is becoming an important tool to deepen the knowledge on DSSCs. New algorithms combining machine learning and artificial intelligence could be

extremely useful to shift the study from single component to multiple variables at a time, crucial for the full optimization of DSSCs.

The development of new organic and panchromatic dyes, non-toxic, cost-competitive, and sustainable, will be of greatest interest to the field of DSSCs, especially if their absorption onsets are able to extend into NIR wavelengths with high quantum yields, allowing for transparent dyes. If one could combine highly efficient NIR dyes with the right redox mediators, the PCE record for DSSCs would certainly be surpassed because it would allow for the optimal position of the LUMO and HOMO energy levels resulting in higher photopotentials. Additionally, the transparency of the full device (photoanode, counter-electrode and electrolyte) would play a major role in differentiating DSSCs from Perovskite Solar Cells (PSCs), especially in the integration of these solar cells on building facades and windows. In the development of new dyes, it will be of paramount interest to fully understand the electron injection from the dye's excited state to the semiconductor's conduction band, which in turn will minimize the potential loss at this interface.

Another possible avenue to advance on the DSSC field is to produce single substrate solar cells, using a monolithic configuration, printable dyes, and solid-state hole transport materials (HTMs), which could further increase the stability and robustness of DSSCs under extreme conditions – high moisture and temperature. These solid-state DSSCs will not display the same electrolyte leakage and instability issues, seen on unencapsulated liquid-state DSSCs.

From a realistic point of view, DSSCs will always be compared with their close competitors, the PSCs. While under solar illumination, DSSCs have long been surpassed by their counterparts, under indoor illumination DSSCs and PSCs perform equivalently. PSCs still face the undeniable backlash of using lead in their structure, while DSSCs are safer and more sustainable, being lead-free; thus, DSSCs are more widely accepted in the IPV market. Currently, DSSCs have already a wide range of applications, namely woven into textiles for wearables electronics given their flexibility; applied on windows, skylights,

and glass facades since they can be thin, colorful, or transparent depending on the materials utilized; DSSCs can also be incorporated into portable electronics and sensing devices, due to their versatility.

As for the hybrid DSSC/biosensor device, instead of being interfaced with an electrochromic cell, the autonomous device could be connected to a mobile phone which would give instantaneous data reading provided by the biosensor. This device would continue to meet point-of-care requirements, but it would be easier to be operated by non-specialized personnel.

APPENDIX

APPENDIX A. Additional characterization on DSSC system developed on Chapter 2

APPENDIX B. Morphology and optimization of counter-electrodes developed on Chapter 3

APPENDIX C. Supplementary information regarding Chapter 4

APPENDIX D. Preliminary optimization of sarcosine concentration using molecularly imprinted polymers

APPENDIX E. Synthesis of electrochromic derivative, SNS-NH₂

APPENDIX A. ADDITIONAL CHARACTERIZATION ON DSSC SYSTEM

DEVELOPED ON CHAPTER 2

Top-view SEM images showing the morphology platinum nanoparticles catalyst before and after the sintering process – activation of Pt – are presented in **Figure A1**.

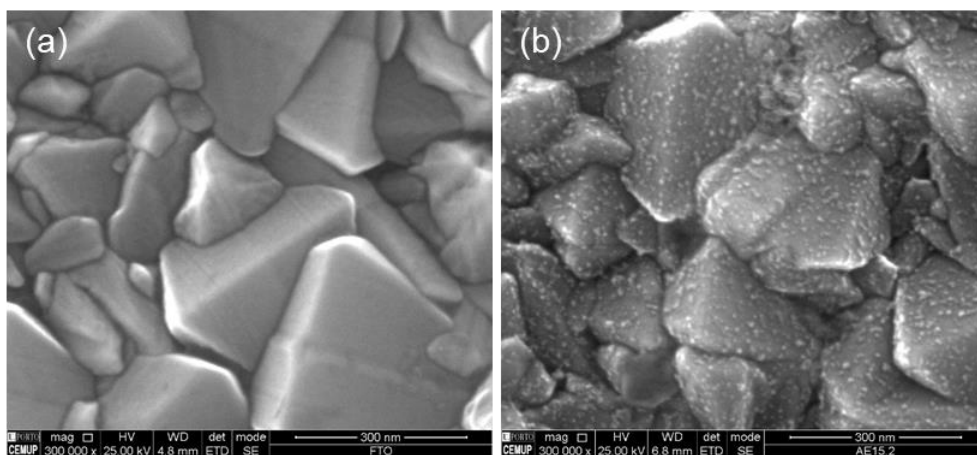


Figure A1. SEM images of the FTO-glass surface before **(a)** and after activation with Pt **(b)**.

Cross-sectional SEM images showing the morphology of the transparent mesoporous titanium dioxide layer (*Tr-TiO₂*) and the scattering opaque titanium dioxide layer (*Op-TiO₂*) are displayed in **Figure A2**.

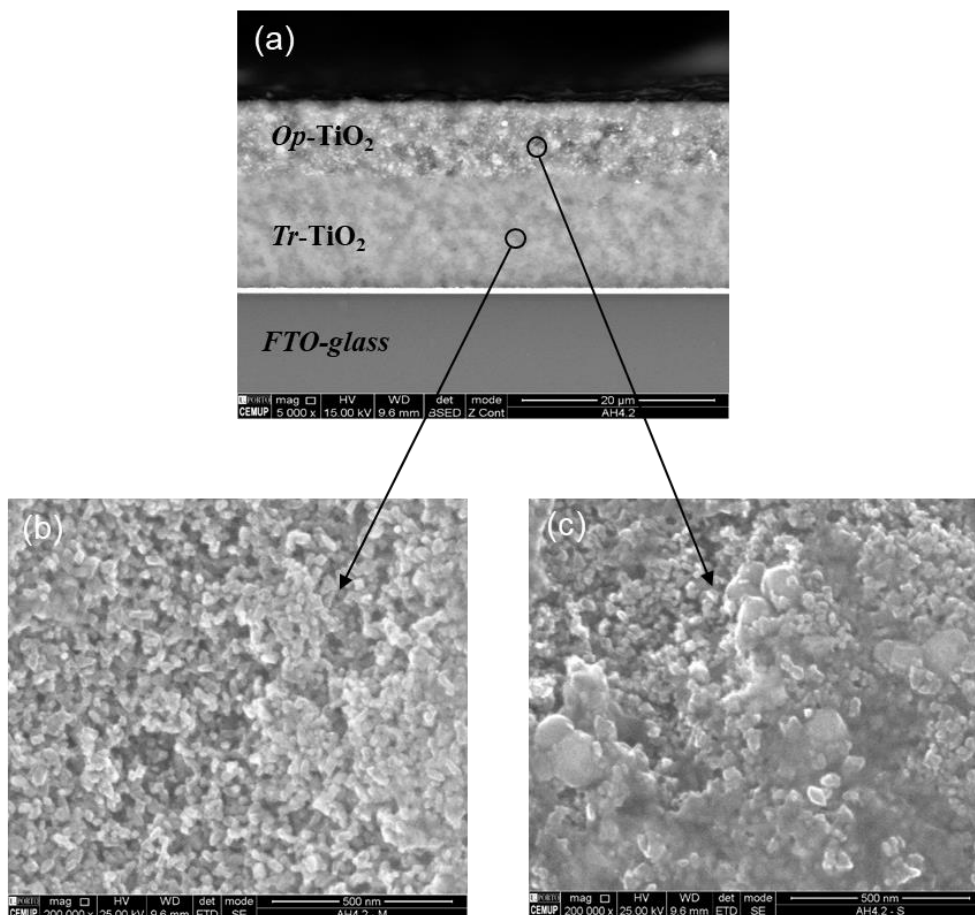


Figure A2. (a). Typical cross-sectional SEM image of TiO_2 film deposited on FTO-glass: the film comprises Tr-TiO_2 layer and Op-TiO_2 atop layer. Magnified view of image (a) for: (b) Tr-TiO_2 layer and (c) Op-TiO_2 layer.

The transmittance spectra for different thicknesses of Tr-TiO_2 are shown in **Figure A3a**, while the transmittance and reflectance spectrum of the $7\ \mu\text{m}$ Op-TiO_2 layer are exhibited in **Figure A3b**. The spectra were collected using Shimadzu UV-3600 spectrophotometer equipped with LISR-3100 integrating sphere. Reflectance from BaSO_4 powder compact was used as baseline in reflectance spectrum.

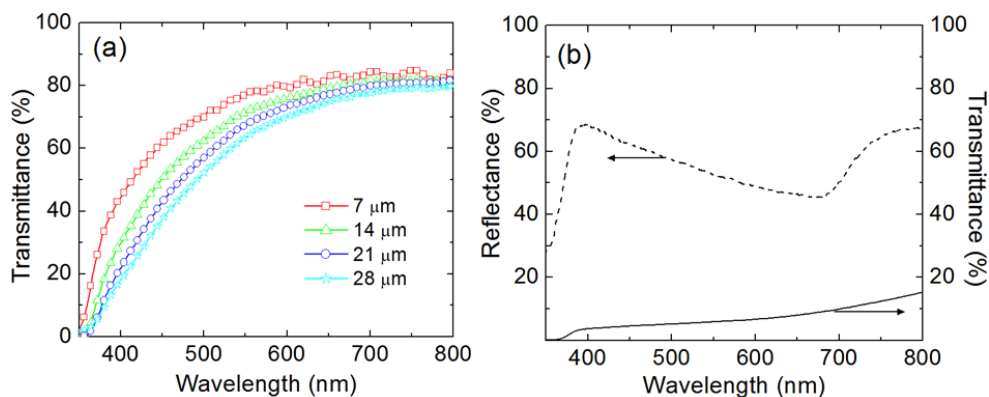


Figure A3. (a) Transmittance of Tr - TiO_2 layers of different thickness; (b) reflectance and transmittance of 7 μm Op - TiO_2 layer.

The schematic illustration an assembled DSSC is displayed on **Figure A4**.

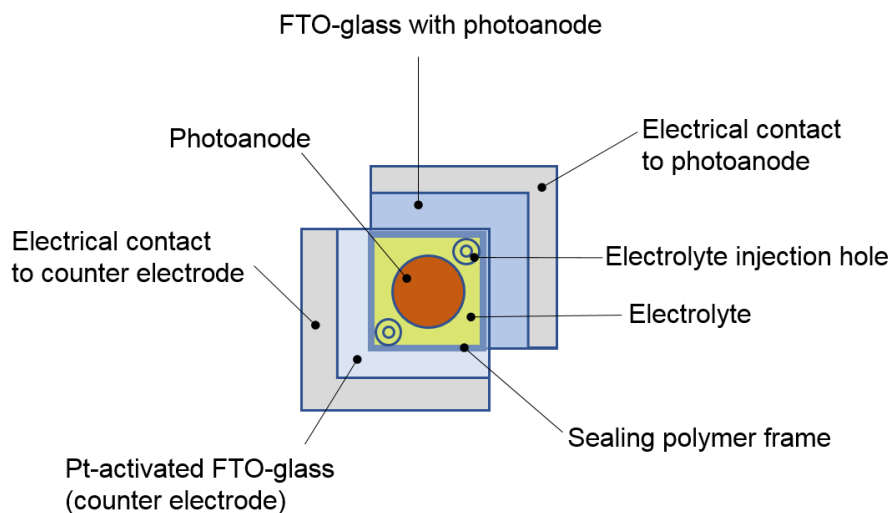


Figure A4. Schematic representation of an assembled DSSC.

The transmittance spectra of the different Tr - TiO_2 films sensitized with N719 dye are presented in **Figure A5**.

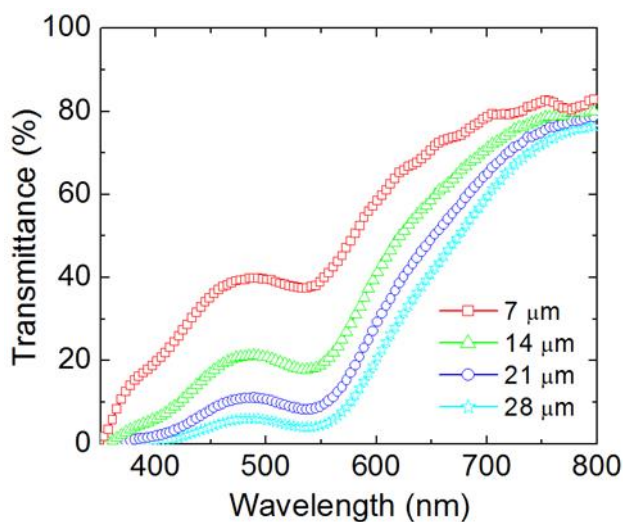


Figure A5. Transmittance spectra of Tr - TiO_2 layers of different thickness after N719 dye absorption.

The reflectance of the FTO-glass and the FTO-glass with the PVC light reflector on the backside of the conductive glass are exhibited on **Figure A6**.

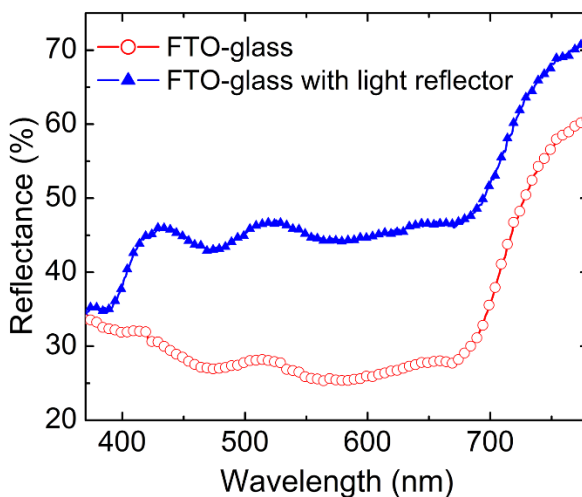


Figure A6. Reflectance spectra of FTO-glass (circles) and FTO glass with PVC light reflecting film on the backside of the glass (triangles).

The ration between the IPCE of the cell with and without the light reflector on the backside of DSSC is displayed on **Figure A7**.

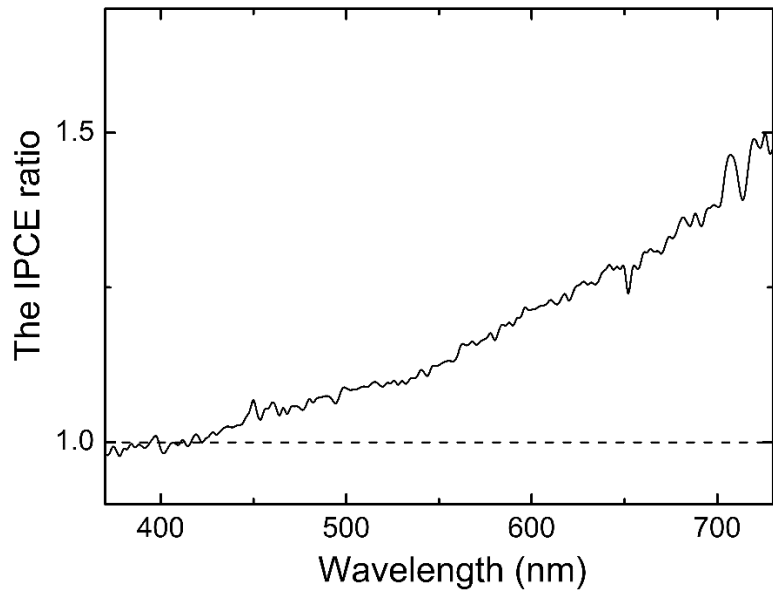


Figure A7. The ratio of IPCE from the cell with light reflector in the backside to the IPCE from the cell without light reflector.

APPENDIX B. MORPHOLOGY AND OPTIMIZATION OF COUNTER-ELECTRODES
DEVELOPED ON CHAPTER 3

Figure B1 presents the top-view SEM image showing the morphology of typical commercial graphene powder, used in **Chapter 3**, to prepare PEDOT-graphene composites.

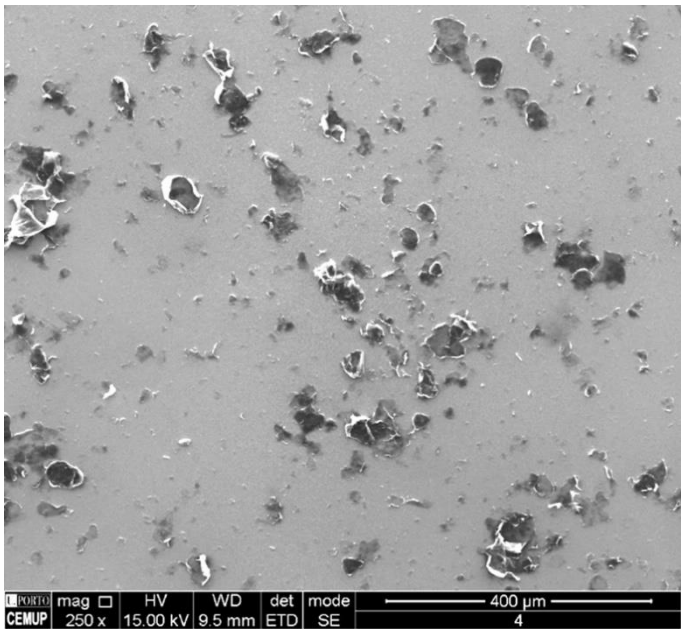


Figure B1. Typical SEM image obtained for commercial graphene powder used in this study to prepare PEDOT-graphene composites.

Figure B2 displays cross-sectional SEM images showing the morphology of the two counter-electrodes proposed on **Chapter 3**.

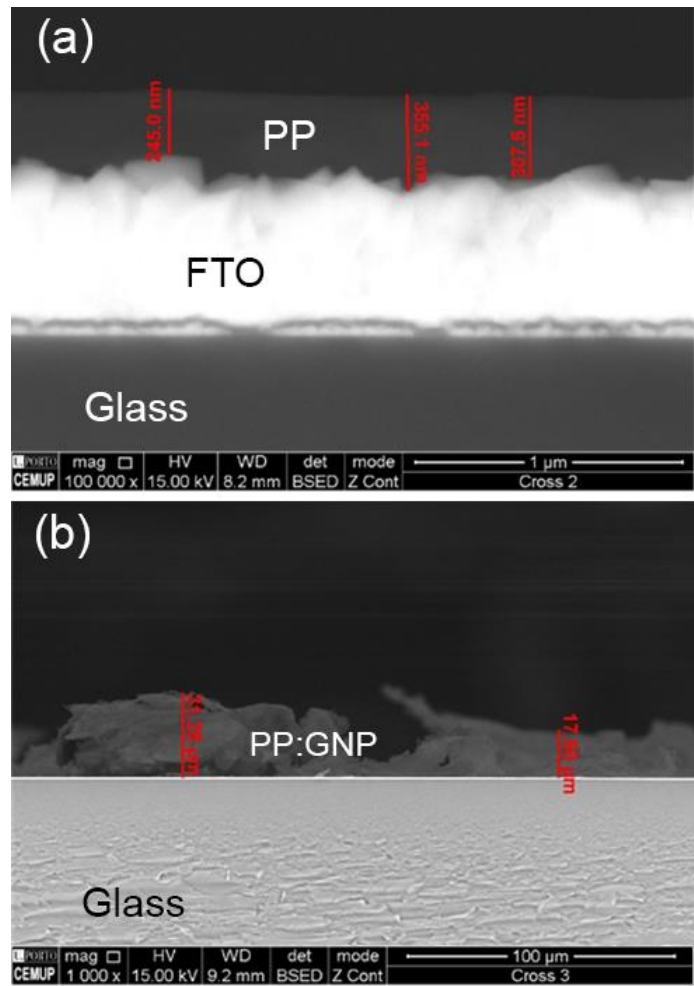


Figure B2. Cross-sectional SEM images of PP (a) and PP:GNP (b) films

The optimization of the concentration of graphene nanoplatelets used in the PEDOT:PSS solution to produce the composite materials for the counter-electrode proposed is displayed on **Figure B3**.

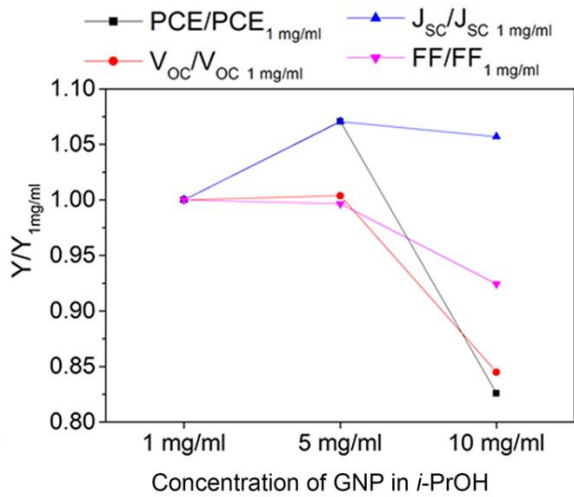


Figure B3. Normalized photovoltaic metrics of the DSSCs with PP:GNP counter-electrodes produced using different concentrations of GNPs in added isopropanol suspension.

The emission spectra of the white LED Lamp as light source for the indoor characterization of DSSCs is exhibited in **Figure B4**.

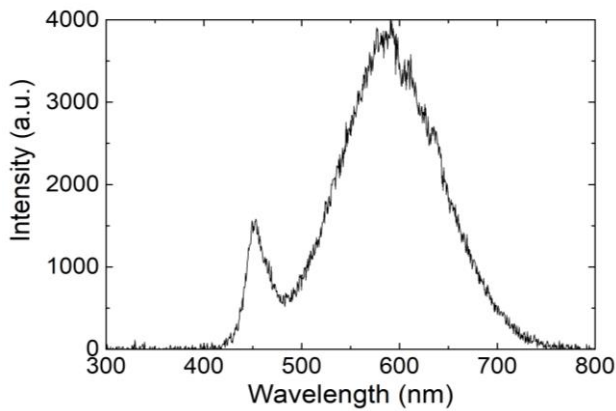


Figure B4. Emission spectra of white LED lamp (Color temperature 2700 K) used for *I*-*V* characterization of the DSSCs under artificial light.

APPENDIX C. SUPPLEMENTARY INFORMATION REGARDING CHAPTER 4

Figure C1 presents previous studies with the two mesoporous pastes (ML30 and ML20), used in **Chapter 4**.

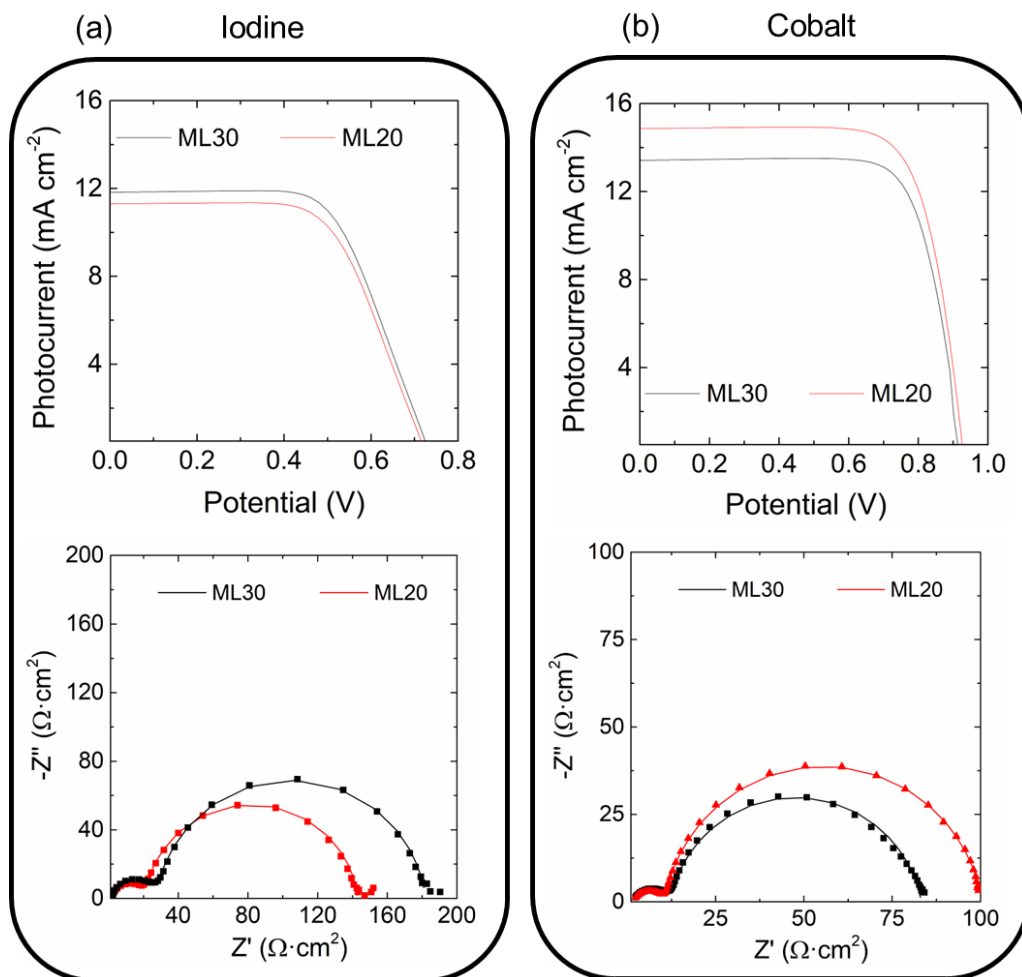


Figure C1. Preliminary studies (*J-V* and EIS data) regarding the influence of the size of the TiO₂ particles in the mesoporous paste used with **(a)** iodide/triiodide electrolyte and **(b)** cobalt (II/III) bipyridine electrolyte; mesoporous TiO₂ layer with an average particle size of 30 nm (**black**) and 20 nm (**red**).

Figure C2a,c present the experimental procedure used to desorb the dyes N719 and YD2-o-C8, respectively, from the photoanodes. The absorption spectra at different concentrations for each dye are displayed on **Figure C2b,d**, while the respective calibration curves employed to quantify the molar extinction coefficient (ϵ) are exhibited on **Figure C2e,f**, for N719 and YD2-o-C8, respectively

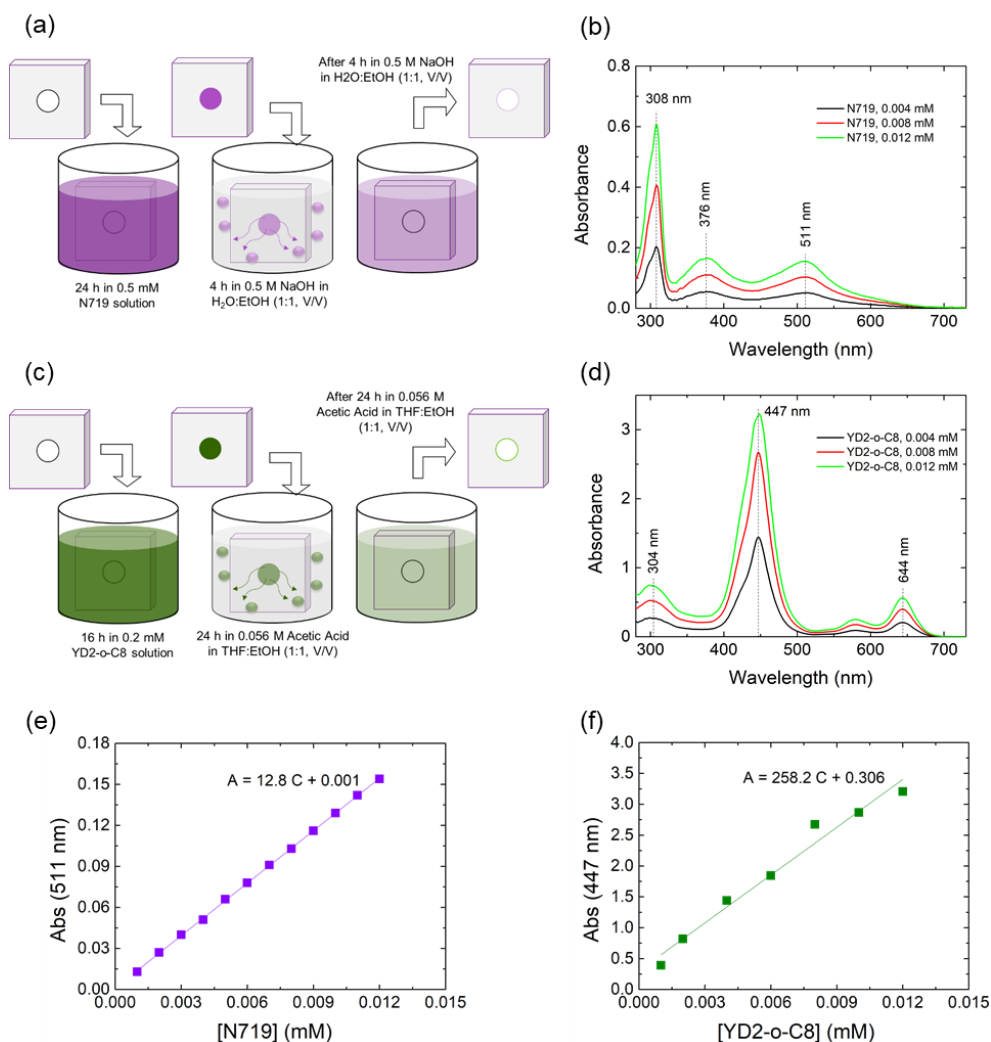


Figure C2. Experimental procedure for dye desorption from photoanodes: (a) N719 and (c) YD2-o-C8 dyes. Absorption spectra of N719 (b) and YD2-o-C8 (d) at different concentrations. Calibration curves used to determine the ϵ for N719 (e) and YD2-o-C8 (f) dyes.

Figure C3 compares the photovoltaic parameters of iodine solar cells using a mesoporous titania layer alone (ML30) and a combination of ML30 and a scattering titania layer (SL) with a device gap of 20 μm and 50 μm , under solar and artificial illumination.

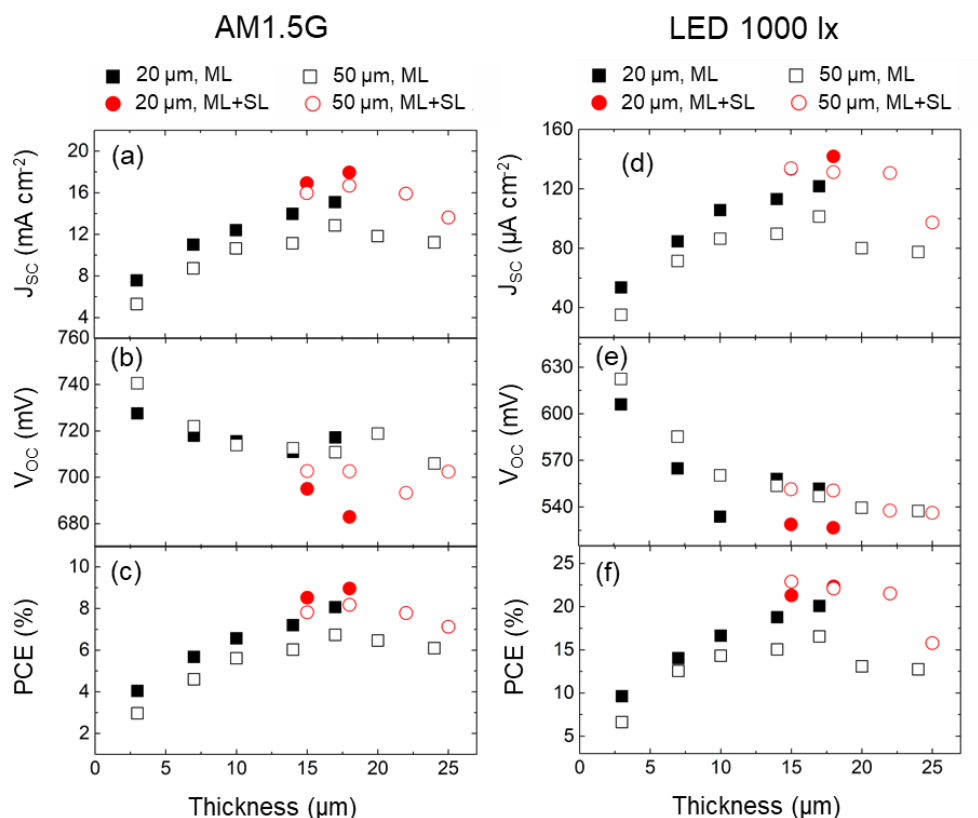


Figure C3. Comparison of the photovoltaic parameters for iodine DSSCs with 20 μm (**full symbols**) and 50 μm inner gaps (**empty symbols**) under AM1.5G (**on the left**) and 1000 lx (**on the right**). **Squares** and **circles** stand for solely ML and a combination of ML+SL TiO_2 layers respectively. J_{sc} (**a, d**), V_{oc} (**b, e**), and PCE (**c, f**).

Figure C4 shows the optimization of the thickness of the ML30 layer, which was gradually increased from 3 to 24 μm , using a device gap of 50 μm ; on the top of the ML30 layer, a layer of SL with 8 μm was applied and the overall thickness of both ML30+SL was increased from 15 to 25 μm . The

photoanode thickness was evaluated through J - V curves under solar and artificial illumination and EIS at -0.65 V.

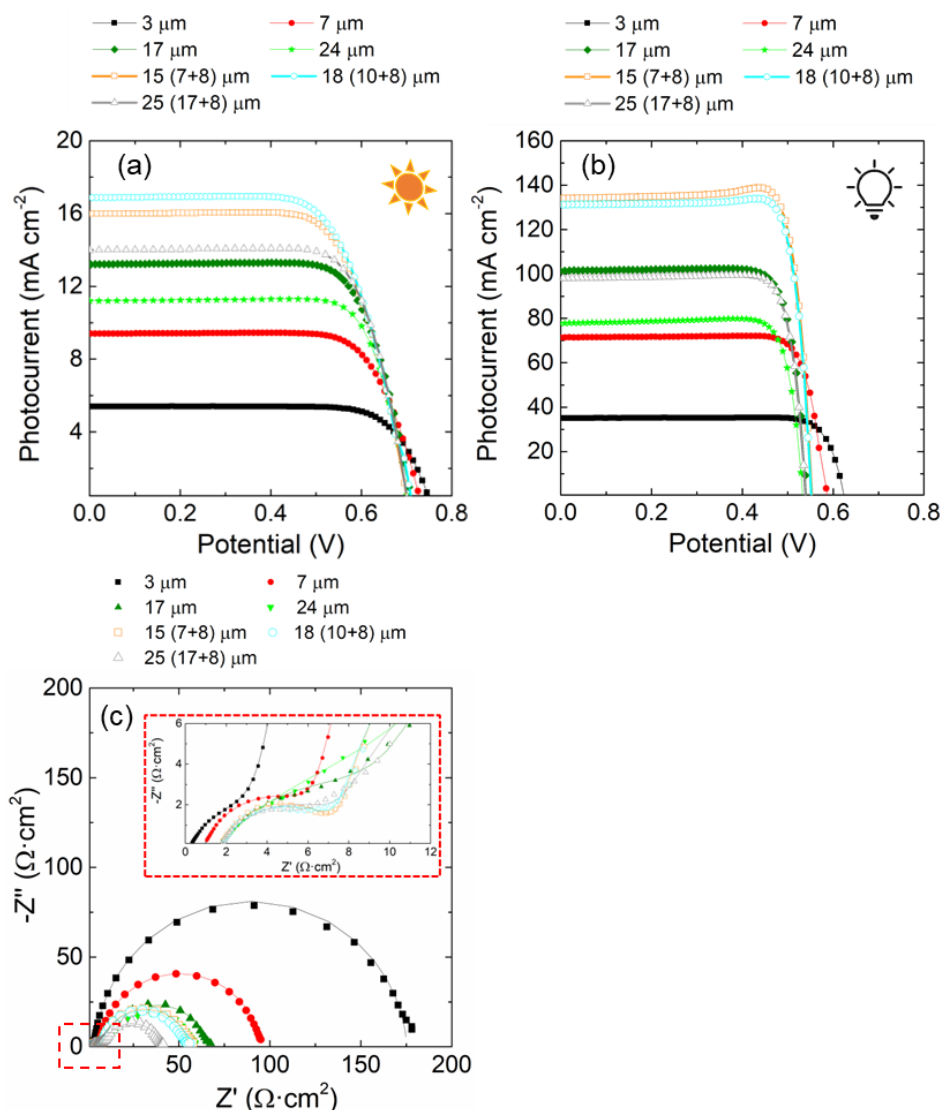


Figure C4. I - V response of iodine DSSCs under AM1.5G (a) and 1000 lx light (b). Nyquist plots of the devices obtained from EIS (c); **solid lines** show the fittings of the impedance spectra to the equivalent circuit presented in Figure 4.3d (in Chapter 4). **Full** and **empty symbols** stand for ML30 and ML30+SL layers, respectively. The inner gap of the device is 50 μm .

Figure C5 compares the photovoltaic parameters of iodine solar cells using a mesoporous titania layer alone (ML20) and a combination of ML20 and a reflecting titania layer (RL) with a device gap of 20 μm and 50 μm , under solar and artificial illumination.

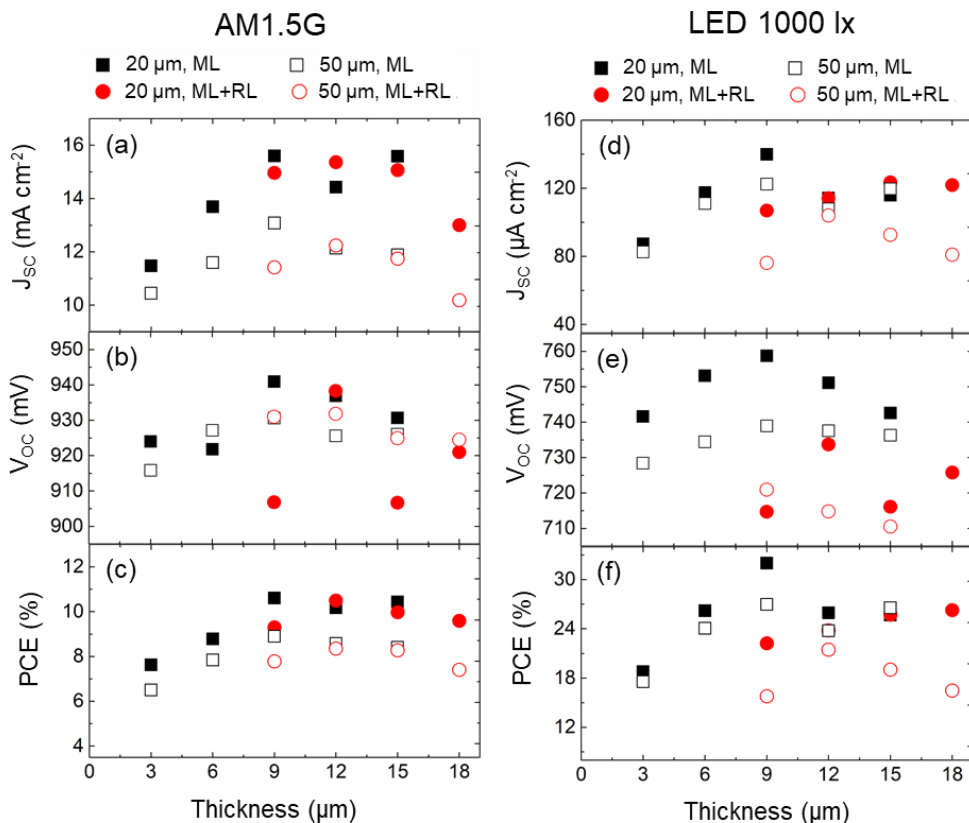


Figure C5. Comparison of the photovoltaic parameters for cobalt DSSCs with 20 μm (**full symbols**) and 50 μm inner gaps (**empty symbols**) under AM1.5G (**on the left**) and 1000 lx (**on the right**). ML20 (**squares**); ML20+RL (**circles**): (a, d) J_{sc} ; (b, e) V_{oc} ; (c, f) PCE.

Figure C6 shows the optimization of the thickness of the ML20 layer, which was gradually increased from 3 to 24 μm , using a device gap of 50 μm ; on the top of the ML30 layer, a layer of RL with 8 μm was applied and the overall thickness of both ML30+RL was increased from 15 to 25 μm . The photoanode thickness was evaluated through J - V curves under solar and artificial illumination and EIS at -0.65 V.

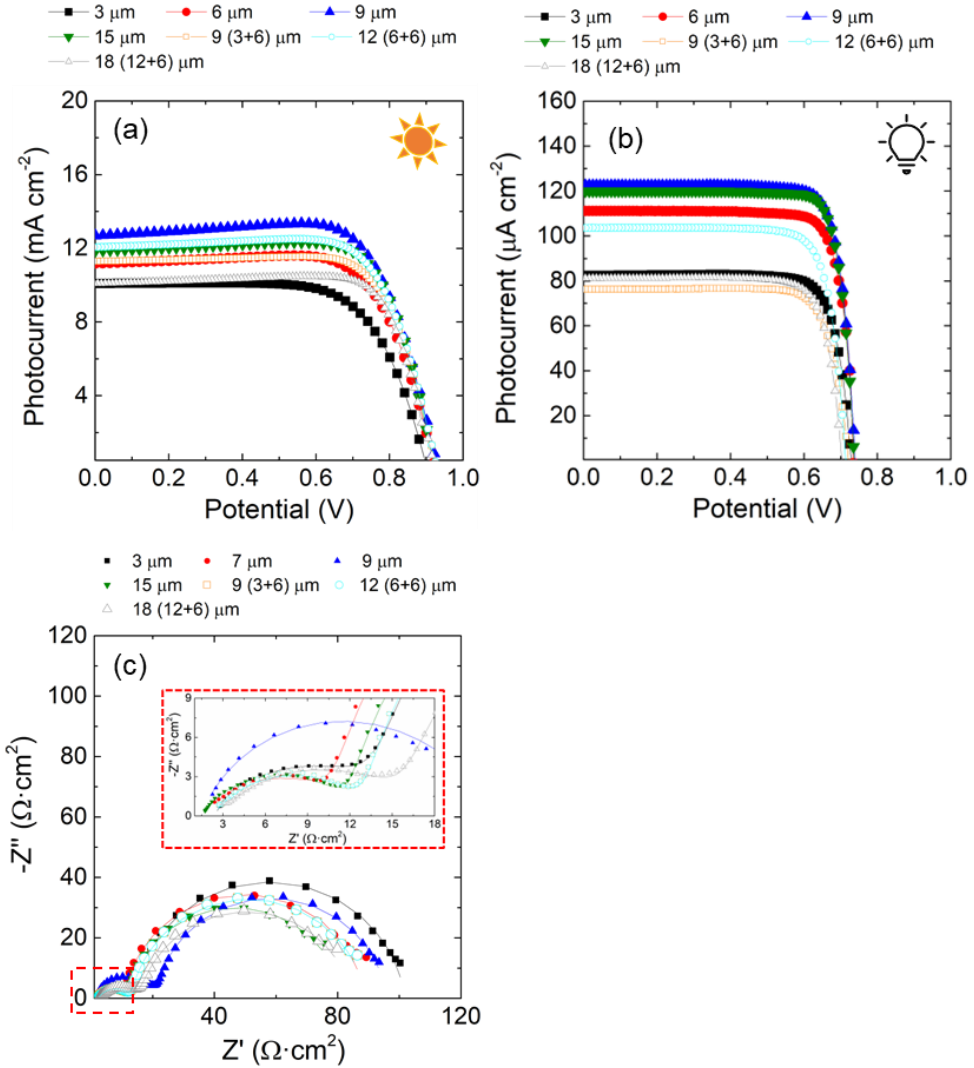


Figure C6. Cobalt mediated solar cells; device thickness: 50 μm . (a) I - V curves under 1-Sun and (b) under 1000 lx; (c) EIS spectra, **solid lines** represent the fitting by the equivalent circuit model. ML20 in **full symbols**; ML20+RL in **empty symbols**.

The photovoltaic parameters of the iodine solar cells were determined from the *I*-*V* curves under varying LED light intensities and are summarized in **Table C1**

Table C1. Photovoltaic metrics of the iodine DSSCs obtained under varying LED intensities.

Iodine DSSCs	LED	PCE (%)	V _{oc} (mV)	J _{sc} ($\mu\text{A}\cdot\text{cm}^{-2}$)	FF	P _{out} ($\mu\text{W}\cdot\text{cm}^{-2}$)
I₂-20 (10+8 μm)	400 lux, 111 $\mu\text{W}\cdot\text{cm}^{-2}$	22.0	495	56.9	0.86	25.1
	600 lux, 166 $\mu\text{W}\cdot\text{cm}^{-2}$	22.9	509	87.9	0.84	37.7
	800 lux, 216 $\mu\text{W}\cdot\text{cm}^{-2}$	22.7	519	116.5	0.84	50.5
	1000 lux, 275 $\mu\text{W}\cdot\text{cm}^{-2}$	22.4	528	141.8	0.83	62.0
I₂-50 (7+8 μm)	400 lux, 111 $\mu\text{W}\cdot\text{cm}^{-2}$	23.5	516	55.8	0.86	26.4
	600 lux, 166 $\mu\text{W}\cdot\text{cm}^{-2}$	23.2	530	81.1	0.87	38.1
	800 lux, 216 $\mu\text{W}\cdot\text{cm}^{-2}$	22.9	544	107.5	0.87	50.9
	1000 lux, 275 $\mu\text{W}\cdot\text{cm}^{-2}$	22.9	551	133.8	0.86	63.3

The photovoltaic parameters of the iodine solar cells were determined from the *I-V* curves under varying LED light intensities and are summarized in **Table C2**.

Table C2. Photovoltaic metrics of the cobalt DSSCs obtained under varying LED intensities

Cobalt DSSCs	LED	PCE (%)	V _{oc} (mV)	J _{sc} ($\mu\text{A}\cdot\text{cm}^{-2}$)	FF	P _{out} ($\mu\text{W}\cdot\text{cm}^{-2}$)
Co-20 (9 μm)	400 lux, 111 $\mu\text{W}\cdot\text{cm}^{-2}$	31.2	726	56.3	0.84	34.5
	600 lux, 166 $\mu\text{W}\cdot\text{cm}^{-2}$	32.0	743	84.9	0.84	53.0
	800 lux, 216 $\mu\text{W}\cdot\text{cm}^{-2}$	31.8	750	110.3	0.83	68.8
	1000 lux, 275 $\mu\text{W}\cdot\text{cm}^{-2}$	32.0	759	140.0	0.83	88.1
Co-50 (9 μm)	400 lux, 111 $\mu\text{W}\cdot\text{cm}^{-2}$	25.6	709	48.2	0.83	28.4
	600 lux, 166 $\mu\text{W}\cdot\text{cm}^{-2}$	26.3	723	73.0	0.82	43.5
	800 lux, 216 $\mu\text{W}\cdot\text{cm}^{-2}$	26.8	729	96.4	0.82	57.9
	1000 lux, 275 $\mu\text{W}\cdot\text{cm}^{-2}$	27.0	739	123	0.82	74.3

APPENDIX D. PRELIMINARY OPTIMIZATION OF SARCOSINE CONCENTRATION USING MOLECULARLY IMPRINTED POLYMERS

As mentioned in **Chapter 5**, the construction of the biosensor was done in a three-electrode configuration, using FTO-glass substrates as working electrode, an Ag/AgCl (0.1 M KCl) as reference electrode and a platinum wire for counter-electrode. The schematic illustration of the biosensor construction is represented in **Figure 5.1** (in **Chapter 5**). and the concentration of the sarcosine in the imprinting stage was varied between 0.01, 0.1 and 1 mM. The concentration of the sarcosine was adjusted to improve the rebinding of the template in the polymeric matrix.

As the biosensor was built, the assembled layers were examined by electrochemical impedance spectroscopy (EIS) at 0 V and the Nyquist plots were fitted to an equivalent electric model – Randles model, **Figure D1**. The charge transfer resistance (R_{CT}) of each new layer/electrolyte interface was obtained, where the used electrolyte was an iron redox aqueous solution [5 mM of potassium hexacyanoferrate(II) trihydrate and 5 mM of potassium hexacyanoferrate(III) in potassium phosphate buffer at a pH 7.0].

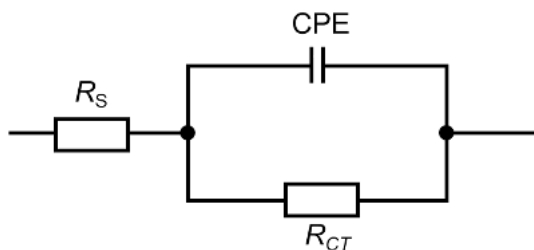


Figure D1. Randles equivalent circuit, used as an electrical analog to fit the electrochemical data gathered in a three-electrode set-up

The Randles model comprises the series resistance (R_S) between the working and reference electrode, and the R_{CT} and a constant phase element

that models the behavior of a double layer, the latter representing the standard deviation from ideal capacitance [1,2].

After the polymerization of EDOT (step A, **Figure 5.1**) to obtain PEDOT, the R_{CT} is very low and difficult to quantify, because PEDOT is highly conductive (**Figure D2**). The next preparation step (step B, **Figure 5.1**) considers the application of a layer of copolymerized EDOT with Py loaded with sarcosine, forming the MIP layer. This step increases the R_{CT} to ca. 4540 Ω , 6120 Ω , 8800 Ω and 9100 Ω for the MIP 1 mM (**Figure D2a**), 0.1 mM (**Figure D2b**), 0.01 mM (**Figure D2c**), and NIP (**Figure D2d**), respectively. From curves (1) to (2) – MIP – and from curves (1) to (3) – NIP, in **Figure D2**, the interfacial conductivity of the overall sensor decreases substantially, as evidenced by the significantly higher R_{CT} . The increase in the resistance was assigned to the presence of the encapsulated sarcosine.

The MIP layer is thin and holds pores that allows the exit of sarcosine. After removing the sarcosine template (step C, **Figure 5.1**), the R_{CT} decreases almost 60 % for all MIP sensors and only 18 % for the NIP sensor. Expectedly, this removal step should actually affect the NIP sensor much less than the MIP sensors, because it was not originally loaded (and then not unloaded) with sarcosine. After removing the sarcosine overnight, the R_{CT} value decreased 32.2 %, 22.7 % and 21.7 % for the MIP sensors originally loaded using a sarcosine solution of 1 mM, 0.1 mM, and 0.01 mM, respectively. It is noteworthy to highlight that curves (4) and (5), which refer to the NIP after being treated with the sarcosine removal solution for 1.5 h and overnight, are mostly overlapped. This indicates that the extraction process does not interfere with the resistance of the EDOT/Py layer.

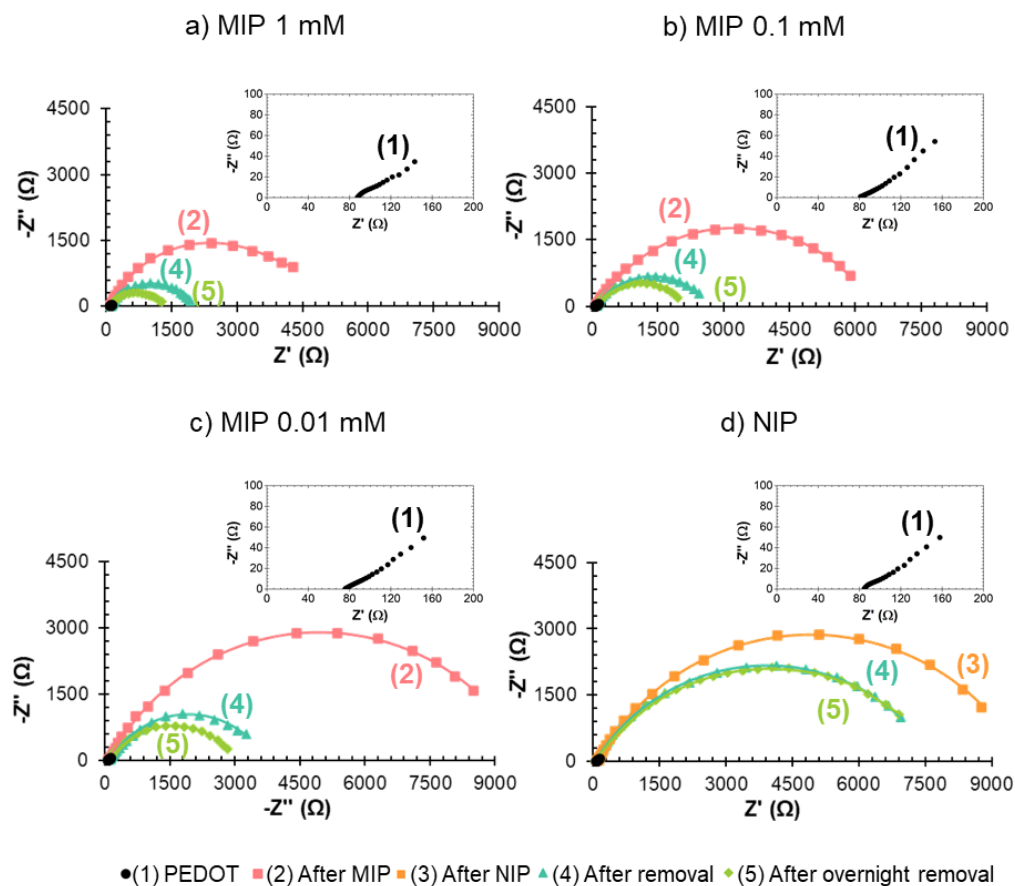


Figure D2. Electrochemical data of the different stages involved in the biosensor construction, varying the concentration of the sarcosine template, in the ranges of 1 mM (**a**), 0.1 mM (**b**) and 0.01 mM (**c**), as well as the control - NIP (**d**). The EIS spectra were obtained in a three-electrode configuration, with an iron electrolyte, after the EDOT polymerization (**1**), after copolymerization of EDOT and Py in the presence of sarcosine – MIP – (**2**) and in the absence of sarcosine – NIP – (**3**), after template removal with alcoholic solution (**4**) and finally after overnight removal with ultrapure water (**5**).

The rebinding between the biosensing film and sarcosine was appraised by performing EIS assays, as described in **Section 5.2.5**; and the results are displayed in **Figure D3**. In the EIS assays, the calibration of all biosensors was plotted for ΔR_{CT} against the logarithm of sarcosine concentration. To mitigate the background conductivity interference of the FTO-electrodes (PEDOT layer

on a FTO glass substrate) on R_{CT} of the MIP layer, the following correction was used (**Eq. D1**):

$$\Delta R_{CT} = \frac{R_{CT_{sarcosine\_sample}} - R_{CT_{blank}}}{R_{CT_{blank}}} \quad \text{Eq. D1}$$

In general, the presence of bounded sarcosine on the biosensing film yields higher R_{CT} values, which is clearly associated to the electrical properties of the interface electrode/electrolyte. The performance of the biosensor is essentially evaluated by the sensitivity and the limit of detection (LOD). The sensitivity is obtained from the slope of the linear regression ΔR_{CT} vs $\log(C_{sarcosine})$, while the LOD is the detectable lowest concentration of analyte. The LOD is calculated multiplying the ratio of the standard deviation of the response and the slope, by a factor of 3 [3]. So, these parameters were used to assess the rebinding of sarcosine in the various biosensing films, loaded using aqueous sarcosine solutions of 1 mM, 0.1 mM, and 0.01 mM.

In all MIP sensors (**Figure D3a, b and c**) the ΔR_{CT} increases systematically with the sarcosine concentration in the standard solutions (impregnation solutions). This behavior was assigned to the binding between sarcosine and imprinted cavities in the MIP layer, which decreases proportionally the electroactive area for the redox reaction with the iron electrolyte, $[\text{Fe}(\text{CN})_6]^{3-/4-}$ [4]. This behavior is also consistent with the previously reported EIS values, in **Figure D2**, where the ΔR_{CT} decreases when sarcosine is removed from the polymeric matrix.

Every MIP exhibited a clear cationic slope in the concentration range between 1 ng/mL and 10 $\mu\text{g/mL}$, with a determination coefficient (R^2) > 0.98. Additionally, the imprinted sensors displayed high reproducibility, since the calibration curves of independent MIP sensors had a low standard deviation – from three sensors for each sarcosine concentration, the obtained standard deviation was < 10 %. The sensitivity and the LOD of the MIP sensors had the following trend: MIP 0.1 mM > MIP 1 mM > MIP 0.01 mM (**Table D1**). The best results were obtained with the biosensor imprinted with a sarcosine impregnation solution of 0.1 mM, displaying a sensitivity of 0.17 Ω/decade , a

$R^2 = 1.00$, and a LOD of 0.40 ng/mL. The NIP corresponding devices showed a random trend, with much less reproducibility, showing that the non-specific interaction between the copolymer film (PEDOT+PPy) and sarcosine were not dictating the electrochemical response of the electrode and, thus, validating the biosensors herein produced.

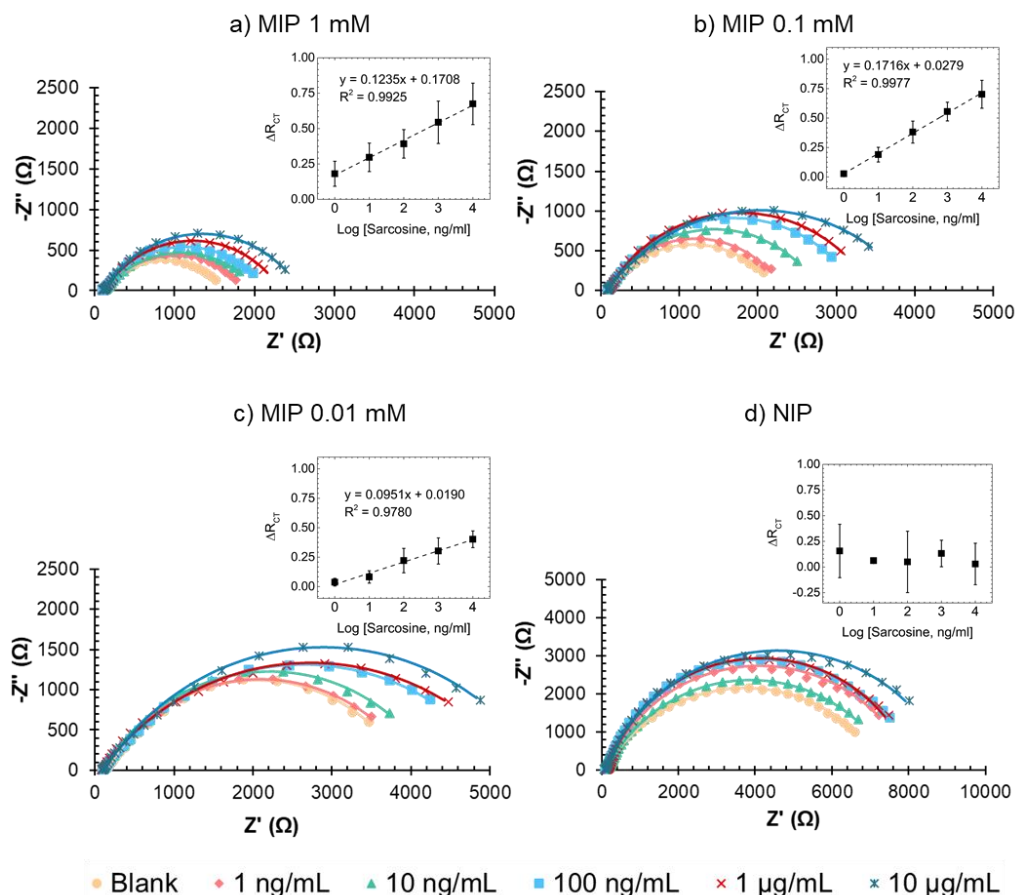


Figure D3. Nyquist plots and calibration curves of the MIP 1 mM (a), 0.1 mM (b), 0.01 mM (c) and NIP electrodes (d), obtained after incubating the electrodes in gradually higher concentrations of sarcosine prepared in phosphate buffer. The EIS assays were performed with an iron electrolyte in a three-electrode configuration.

After optimizing the imprinting sarcosine concentration in the MIP layer, the MIP 0.1 mM sensor was calibrated using urine samples, collected from

healthy male volunteers, and diluted 10 × in phosphate buffer. The biosensor tested in urine showed a linear response within the concentration range between 1 ng/mL and 10 µg/mL, with a $R^2 > 0.99$ (Figure D4). Although this behavior is very similar to the calibrations performed using a buffer, the sensitivity was slightly higher (0.20 Ω/decade $C_{\text{sarcosine}}$) and the LOD was lower (0.30 ng/mL). Once again, the NIP electrode showed even less interaction between the non-imprinted polymer and the target analyte.

Table D1. Analytical features of the biosensors tested (in phosphate buffer and urine)

Sarcosine concentration	Sensitivity	LOD (ng/mL)
	(Ω/decade $C_{\text{sarcosine}}$)	
1 mM, Buffer	0.1235	0.716
0.1 mM, Buffer	0.1716	0.395
0.01 mM, Buffer	0.0951	1.229
0.1 mM, Urine	0.2048	0.302

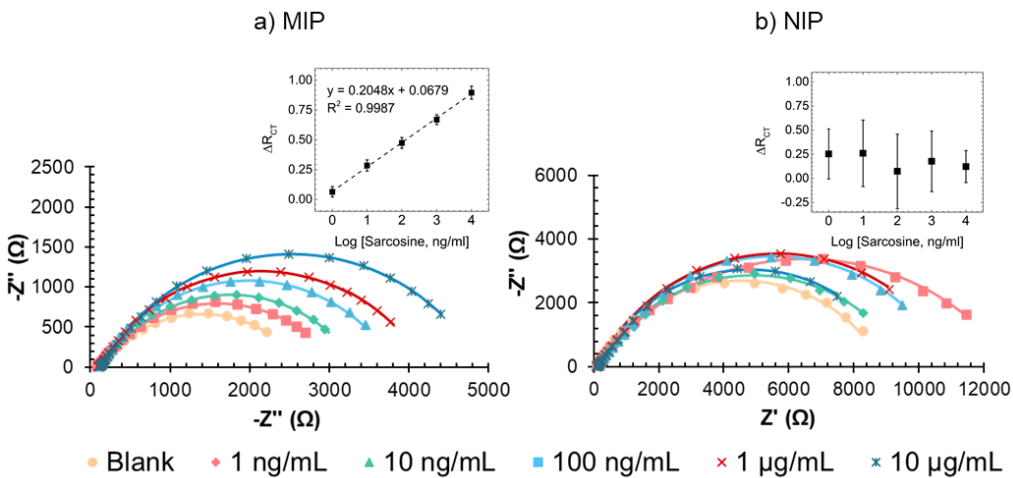


Figure D4. Nyquist plots and calibration curves of the MIP containing a sarcosine solution of 0.1 mM (a) and NIP (without sarcosine) (b) electrodes, obtained after incubating the electrodes in gradually higher concentrations of

sarcosine prepared in diluted urine. The EIS assays were performed with iron electrolyte in a three-electrode configuration.

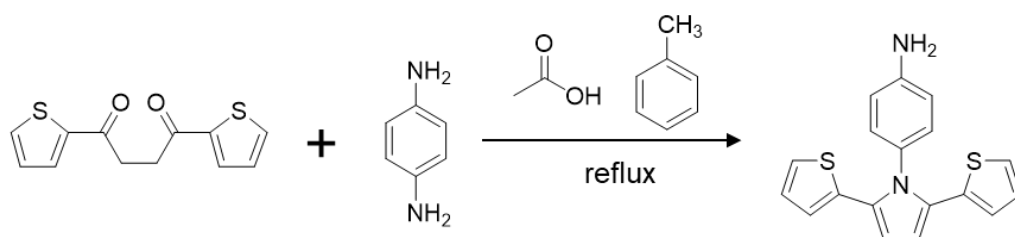
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APPENDIX E. SYNTHESIS OF ELECTROCHROMIC DERIVATIVE, SNS-NH₂

The electrochromic component was produced based on previous works [1–3]. The 4-[2,5-di(thiophen-2-yl)-1*H*-pyrrol-1-yl]aniline (SNS-NH₂) was synthesised according to **Scheme E1**: 1,4-bis-2-thienylbutane-1,4-dione (0.002 mol) and *p*-phenylenediamine (0.005 mol) were dissolved in anhydrous toluene (25 mL) and acetic acid was added until the pH was 4. This mixture was refluxed for 24 h, under N₂ flow, and the formation of the synthesised component was tracked by thin layer chromatography (TLC). The final monomer was achieved by flash chromatography with dichloromethane, in a yield of 69 %, also tracked by TLC.

Electrochromic material was a PEDOT-based film placed on an FTO-glass support. This film was obtained by electropolymerizing EDOT, but in the presence of a derivative that would improve the colour change through potential variations.



Scheme E1. Synthesis of SNS-NH₂

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