

## Effect of dye on the efficiency of Grätzel cells

## Efecto del colorante en la eficiencia de celdas Grätzel

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### Abstract

Renewable energies are playing a critical role in reducing emissions in the energy generation sector. Photovoltaic technologies have reduced their cost due to the improvements in conversion efficiency, the cost of the materials, the economies of scale, and the investments made in research and development in the private and public sectors. The Grätzel cells are part of the third generation of photovoltaics. This generation of photovoltaics looks to achieve photovoltaic devices with great efficiency while keeping low costs using thin layer processes and non-toxic materials. One of the main features of these solar cells, also known as dye-sensitized solar cells (DSSCs), is that the spectrum of absorbed light depends on the dye used and can be tuned, which have a big effect on the performance of the cell. This feature grants this device great versatility, which gives this technology a great potential to give energy to devices in indoor illumination and as Building Integrated Photovoltaics (BIPV). The relevance and working principle of the Grätzel cells are presented in this text, as well as the steps that were required to build these solar cells in a laboratory setting.

DSSC, Solar energy, Grätzel cells

### Resumen

Las energías renovables están desempeñando un papel fundamental en la reducción de emisiones en el sector de la generación de energía. Las tecnologías fotovoltaicas han reducido su coste gracias a las mejoras en la eficiencia de conversión, el coste de los materiales, las economías de escala y las inversiones realizadas en investigación y desarrollo en los sectores privado y público. Las células de Grätzel forman parte de la tercera generación fotovoltaica. Esta generación de fotovoltaica busca conseguir dispositivos fotovoltaicos de gran eficiencia manteniendo bajos costes mediante procesos de capa fina y materiales no tóxicos. Una de las principales características de estas células solares, también conocidas como células solares sensibilizadas por colorante (DSSC), es que el espectro de luz absorbida depende del colorante utilizado y puede sintonizarse, lo que tiene un gran efecto en el rendimiento de la célula. Esta característica otorga a este dispositivo una gran versatilidad, lo que confiere a esta tecnología un gran potencial para dar energía a dispositivos en iluminación interior y como Fotovoltaica Integrada en Edificios (BIPV). En este texto se presentan la relevancia y el principio de funcionamiento de las células de Grätzel, así como los pasos que fueron necesarios para construir estas células solares en un entorno de laboratorio.

DSSC, energía solar, células de Grätzel

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## Introduction

The use of renewable energy and solar cells have taken a leading role in the shift towards cleaner generation sources [1]. The manufacturing of photovoltaic solar cells has decreased significantly in cost due to the great investment of the public and private sectors in innovation. Silicon photovoltaic cells also have a series of disadvantages, such as the high price of extracting the silicon necessary for the cells or the use of a limited fraction of the electromagnetic spectrum.

One of the alternatives to this type of cells are the Grätzel cells or dye-sensitized solar cells (DSSCs), which present very interesting characteristics such as: low production cost, selection of a specific absorption range, there are light and semi-transparent [2]. Moreover, these characteristics are of interest for their application in the architecture of buildings [3], electronic devices [4], terrestrial storage [5], and portable generation devices [6].

DSSCs are a type of third-generation solar cell that differs from other types of solar cells in that the charge carrier generation and the transport mechanism occur at different sites [7]. These cells perform outstandingly in other interiors, and it could take advantage of artificial light compared to solar cell technologies. This is one of the essential advantages that DSSCs have in relation to other photovoltaic cell technologies. For example, the Internet of Things (IoT), technology that aims to connect all kinds of electronic devices, sensors, wearable devices, and smart meters through wireless connections [8].

Even though many smart devices are connected with communication networks, there are significant problems in providing electricity to such devices. For IoT devices, batteries are usually the power sources, however, the disadvantage of using batteries is that their lifetime is limited to months or years. Also, the power required for IoT devices is typically low and can be supplied under indoor lighting conditions using DSSC. Therefore, indoor DSSCs are considered as promising systems for power supply to IoT devices [9-10].

## Constitution, characteristics, and operation of a DSSC

A DSSC is represented as a tandem by superimposing nanocrystalline semiconductor films between two electrode substrates (usually both transparent, ITO for example), in the following order the intermediate layers where REDOX reactions are generated to produce electrons are represented: a) mesoporous film (photoanode) sensitized with the dye, b) electrolyte solution and c) a catalyst, which covers a conductive substrate (counter electrode) (see figure 1).

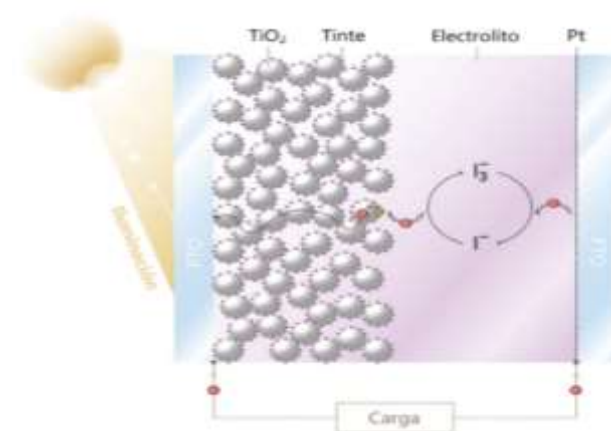


Figure 1 Operating principle of a Grätzel cell [11]

The operation of the DSSC's occurs when electrons are produced from the light that passes through the transparent conductor and interacts with a dye, which is supported on a mesoporous layer of semiconductor nanoparticles (2-15  $\mu\text{m}$  thick and 10-30 nm in diameter, usually  $\text{TiO}_2$ ). When light interacts with the dye, a portion of the light is absorbed and shifts a portion of the dye's electrons to a higher energy state (bringing the dye to its  $S^*$  excited state).

Consequently, these electrons can be used if they are injected into the mesoporous layer or they can be lost through a series of recombination pathways to the dye (10-4 s), to the electrolyte (10-2 s) or the decay of the dye to its ground state (10-9 s). The electrolyte is a layer or medium that facilitates charge transport to the anode (I-/I-3 dissolved in acetonitrile is usually used) [12].

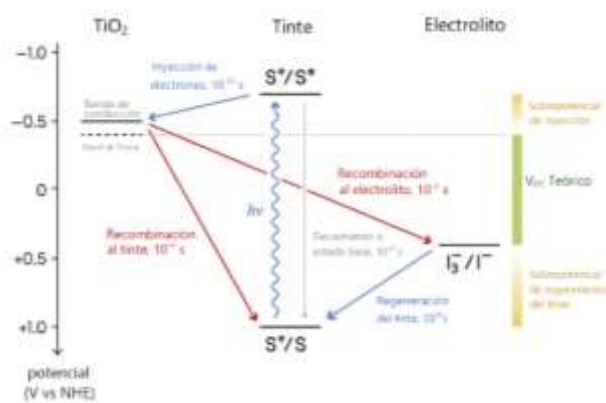


Figure 2 Energy diagram of a Grätzel cell [9].

## Methodology

For the assembly of the DSSC's, glass slides were used and a layer of ITO (250nm, 70-100  $\Omega$  /cm<sup>2</sup>) was deposited for the top electrode (cathode) and for the bottom electrode (anode) a layer of ITO (250 nm, 70-100  $\Omega$ /cm<sup>2</sup>) + Pt (50 nm) (ITO was deposited by sputtering and Pt by e-beam evaporation). Next, the assembly of the DSSC's cells is described in 4 steps:

1. A layer of TiO<sub>2</sub> NP's was deposited on the top electrode from 100  $\mu$ l of a solution of 2 g TiO<sub>2</sub> NP's + 0.05 g of PEG + 0.5 ml of Triton X-100 in 6 ml of 1M HNO<sub>3</sub>.
2. The top electrode (glass+ITO+ TiO<sub>2</sub> NP's) was heated to 80°C and immersed in the dye for 24 hours and allowed to dry at room temperature.
3. The surface of TiO<sub>2</sub> NP's + dye of the top electrode was impregnated by dripping with a solution of 0.5M Potassium Iodide + 0.05M Ethylene Glycol Iodide.
4. The previously activated bottom electrode was placed at 400°C for 15 min.

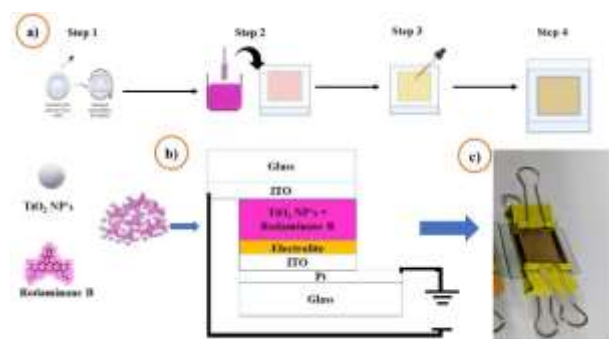


Figure 3 DSSC's assembly diagram. a) shows 4 steps to assemble the DSSC's, b) diagram of the DSSC model and c) DSSC assembled in the laboratory

## Results and Discussion

In the present work, the open circuit voltage (Voc), electrical current density (Jsc), conversion efficiency ( $\eta$ ) and form factor or fill factor (FF) associated with the composition of the DSSC were analyzed. Cells with upper electrode of Pt NP's deposited by deep coating, Pt film by sputter deposition, the TiO<sub>2</sub> layer by the Dr. Blade method, TiO<sub>2</sub> by spin coating and the types of dye: Rhodamine B and Anthocyanin, were compared. (See table 1).

Variable	A)	Parameters	B)	Parameters
Pt	Deep coating	10 seconds and dry by 5 minutes.	Sputtering	25scm of Ar, 3 mTorr and 8% power of DC source
TiO <sub>2</sub>	Deep coating	Mascaraed	Spin coating	3000 rpm by 40 seconds
Dye	Rhodamine B	80°C by 24 hours	Anthocyanin	80°C by 24 hours

Table 1 Variables compared in the manufacture of DSSC's cells

After two hours of stirring a colloidal solution of 2 g of TiO<sub>2</sub> NPs in 96 ml of methanol and 4 ml of 0.1 M nitric acid; ITO/Glass is dipped. Figure 4 shows the result of the deposit by the dip coating method of the mesoporous layer made up of TiO<sub>2</sub> NPs on a glass-supported ITO film. In c) a pair of micrographs taken in an optical microscope of the TiO<sub>2</sub> layer with a very uniform appearance is observed, and in d) the roughness of the surface between 1  $\mu$ m and 3  $\mu$ m is observed by AFM with scans of 15 $\mu$ m x 15 $\mu$ m.

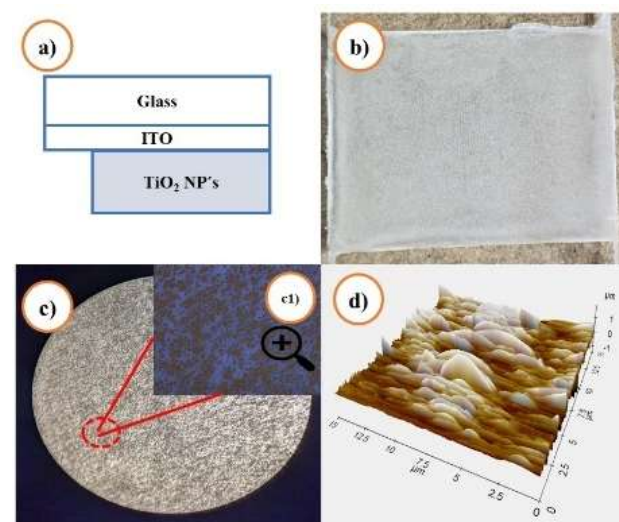
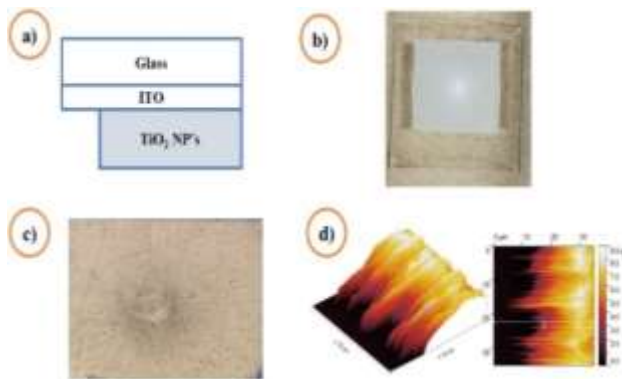


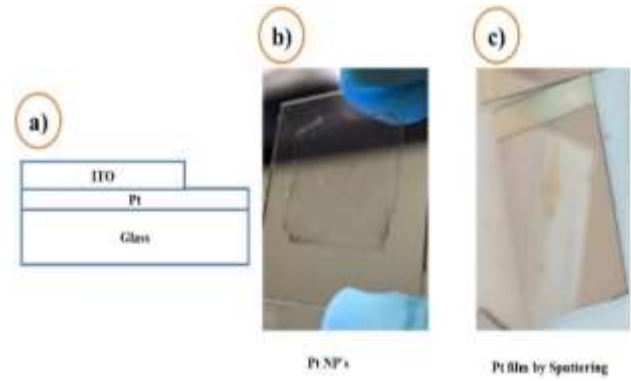
Figure 4 Deposit by the dip coating method. a) shows top electrode schematic, b) photograph of TiO<sub>2</sub> NP's deposition on a glass-supported ITO film, c) 10X optical micrograph and c1) 50X zoom, and d) NP's surface topography of TiO<sub>2</sub> by AFM of 15 $\mu$ m x 15 $\mu$ m

Figure 5 shows the result of the deposit by the spin coating method of the mesoporous layer made up of  $\text{TiO}_2$  NPs on a glass-supported ITO film. 100  $\mu\text{l}$  of a solution of 2 g  $\text{TiO}_2$  NP's + 0.05 g of PEG + 0.5 ml of Triton X-100 was placed in 6 ml of 1M  $\text{HNO}_3$ . The equipment was programmed at 3000 rpm for 40 seconds. In c) a micrograph taken in an optical microscope of the  $\text{TiO}_2$  layer with a very compact and uniform appearance is observed, and in d) the AFM scan of  $35\mu\text{m} \times 35\mu\text{m}$  is observed, a step can be seen with which an average thickness of 7.68  $\mu\text{m}$ .



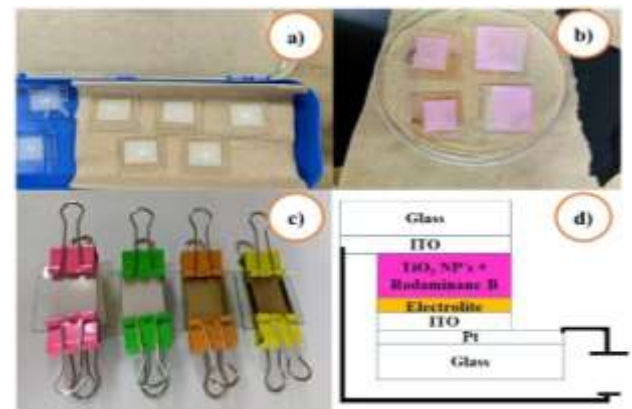
**Figure 5** Deposit by the spin coating method. a) shows top electrode schematic, b) photograph of  $\text{TiO}_2$  NPs deposition on a glass-supported ITO film, c) 10X optical micrograph, and d) surface topography of  $\text{TiO}_2$  NPs by  $35\mu\text{m}$  AFM x 35

Figure 6 shows the manufacture of the bottom electrode. For this, it was tested to deposit a layer of Pt NP's and a uniform Pt film by sputter deposition on Glass and later ITO on the Pt NP's/Glass and Ptfilm/Glass correspondingly. In b) a photograph of the ITO/Pt NP's/Glass film with a slightly opaque and translucent appearance is observed. The Pt NP's were synthesized from 134.14  $\mu\text{l}$  of 6.09 mM chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) in 30 ml of deionized water + 10.75 mg of polyvinylpyrrolidone (PVP) as protective agent + 1 ml of 1% sodium borohydride ( $\text{NaBH}_4$ ), 127.5  $\mu\text{l}$  of the Pt NP's solution were added on the Glass and allowed to dry, subsequently heated to  $400^\circ\text{C}$  to activate the surface of the Pt NP's. In c) a very uniform Ptfilm/Glass film. The sputter deposition equipment was operated at a DC source power of 8%, Ar gas flow of 25 sccm and 3 mTorr.



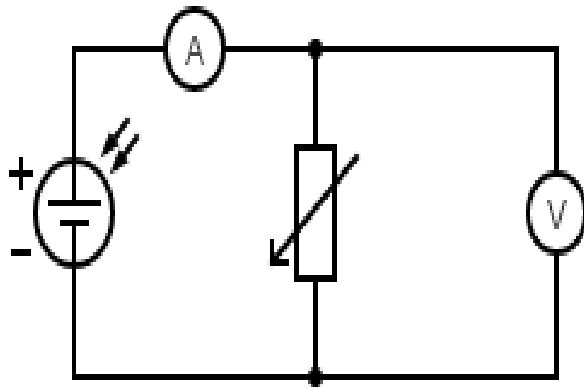
**Figure 6** Deposit of the bottom electrode. a) shows diagram of bottom electrode, b) bottom electrode ITO/Pt NP's/Glass, and c) ITO/Ptfilm/Glass

Figure 7 shows the assembly of the DSSC's, in a) the top electrodes of  $\text{TiO}_2$  NP's/ITO/Glass are prepared, in b) they are subsequently impregnated with the dye, in c) the electrolyte is added, and it is connected to the bottom electrodes of ITO/Pt NP's/Glass and ITO/Ptfilm/Glass (they were fixed with metallic tweezers to avoid movement). In d) a complete schematic of the DSSC's is observed.



**Figure 7** Assembly of the DSSC's. a)  $\text{TiO}_2$  NP's/ITO/Glass top electrode, b)  $\text{TiO}_2$  NP's/ITO/Glass upper electrode + dye, c) top and bottom electrode assembly, d) complete schematic of a DSSC cell

Figure 8 shows the electrical circuit model that allows the measurement of the current and voltage of a solar cell contains a variable resistor, ranging from 3  $\Omega$  to 10,000  $\Omega$ , which is connected in parallel with the solar cell. For the measurement of the variables, a current meter is placed in series with the cell and the resistance, and a voltage meter is placed in parallel.



**Figure 8** Circuit diagram for the measurement of the electrical variables of the DSSC

In annexes section is the table 2 with variations of solar cells and their measured electrical variables. The table 3 show results about photovoltaic performance of DSSC's using Rhodamine B and Anthocyanin.

Dye	Jsc (mA/cm <sup>2</sup> )	Voc (mV)	Mpp (μW)	FF	η (%)
Rhodamine B	0.02285	505	11.41	0.3043	0.0037
Anthocyanin	0.3812	380	78.8	0.2166	0.0145*

\* For the efficiency of the anthocyanin cell 1.5AMG illumination was assumed.

**Table 3** Photovoltaic performance of DSSC's using two different dyes

## Conclusions

During the development of the manufacturing of the different cells, methods such as Deep coating were tested, which is a simple and cheap technique, however, when testing the Sputtering process, the results were similar among its variants, uniform on the surface eye and resistant to the manipulation.

All the results with illumination with the Sun show similar values of states of polarization related to Voc (open circuit voltage) and the comparison with illumination under a solar simulator, it presents values twice as high as those with the sun. The values of the current flow Jsc were also observed different in relation to lighting, however, what stands out is the difference between the cells manufactured with Rhodamine B and Anthocyanin, where the latter presents better values in general in relation to efficiency.

Consequently, the results of this work provide a description and comparison of the various methods that offer an excellent alternative for the manufacture of DSSC's cells, and derived from these results many proposals arise to develop innovation in the manufacture of photovoltaic devices (modification of the dye, manufacture of DSSC's devices with microfluidics to vary or exchange the dye, among others) and the versatility of its applications in relation to architecture, ergonomics in work areas in relation to lighting, remote control of DSSC's devices (IoT), among others.

## References

- [1] REN21. 2019. Renewables 2019 Global status report. Recuperado el 20 de marzo de 2020, a partir de <https://core.ac.uk/download/pdf/328806729.pdf>
- [2] Arjunan, T. v y Senthil, T. S. 2013. Review: Dye sensitised solar cells. *Materials Technology*. Taylor & Francis, 28(1–2), 9–14. <https://doi.org/10.1179/1753555712Y.0000000040>
- [3] Lamberti, A., Sacco, A., Bianco, S., Giuri, E., Quaglio, M., Chiodoni, A., & Tresso, E. (2011). Microfluidic sealing and housing system for innovative dye-sensitized solar cell architecture. *Microelectronic engineering*, 88(8), 2308-2310. <https://doi.org/10.1016/j.mee.2010.12.114>
- [4] Ali, N., Hussain, A., Ahmed, R., Wang, M. K., Zhao, C., Haq, B. U., & Fu, Y. Q. (2016). Advances in nanostructured thin film materials for solar cell applications. *Renewable and Sustainable Energy Reviews*, 59, 726-737. <https://doi.org/10.1016/j.rser.2015.12.268>
- [5] Gong, J., Liang, J., & Sumathy, K. (2012). Review on dye-sensitized solar cells (DSSCs): Fundamental concepts and novel materials. *Renewable and Sustainable Energy Reviews*, 16(8), 5848-5860. <https://doi.org/10.1016/j.rser.2012.04.044>
- [6] Li, G., Sheng, L., Li, T., Hu, J., Li, P., & Wang, K. (2019). Engineering flexible dye-sensitized solar cells for portable electronics. *solar energy*, 177, 80-98. <https://doi.org/10.1016/j.solener.2018.11.017>

[7] Zhang, L., Zhang, J., Tang, X., Chen, Y., Wang, X., Deng, Z., ... & Sun, B. (2023). Densely Packed D- $\pi$ -A Photosensitizers on TiO<sub>2</sub> Enable Efficient Dye-Sensitized Solar Cells. *ACS Applied Energy Materials*, 6(8), 4229-4237.

<https://doi.org/10.1021/acsaem.3c00072>

[8] Aslam, A., Mehmood, U., Arshad, M. H., Ishfaq, A., Zaheer, J., Khan, A. U. H., & Sufyan, M. (2020). Dye-sensitized solar cells (DSSCs) as a potential photovoltaic technology for the self-powered internet of things (IoTs) applications. *Solar Energy*, 207, 874-892. <https://doi.org/10.1016/j.solener.2020.07.029>

[9] Devadiga, D., Selvakumar, M., Shetty, P., y Santosh, M. S. (2021). Dye-sensitized solar cell for indoor applications: A mini-review. *Journal of Electronic Materials*, 50(6), 3187-3206. <https://doi.org/10.1007/s11664-021-08854-3>

[10] Bifari, E. N., Almeida, P., & El-Shishtawy, R. M. (2023). Advancing Panchromatic Effect for Efficient Sensitization of Cyanine and Hemicyanine-based Dye-Sensitized Solar Cells. *Materials Today Energy*, 101337. <https://doi.org/10.1016/j.mtener.2023.101337>

[11] Calogero, G., Citro, I., Crupi, C., Carini, G., Arigò, D., Spinella, G., Bartolotta, A., y di Marco, G. (2019). Absorption spectra, thermal analysis, photoelectrochemical characterization and stability test of vegetable-based dye-sensitized solar cells. *Optical Materials*, 88, 24-29.

<https://doi.org/10.1016/j.optmat.2018.11.005>

[12] Lau, K. K., & Soroush, M. (2019). Overview of dye-sensitized solar cells. *Dye-Sensitized Solar Cells*, 1-49. <https://doi.org/10.1016/B978-0-12-814541-8.00001-X>

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