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PII: S1572-6657(12)00293-7

DOI: <http://dx.doi.org/10.1016/j.jelechem.2012.07.032>

Reference: JEAC 945

To appear in: *Journal of Electroanalytical Chemistry*

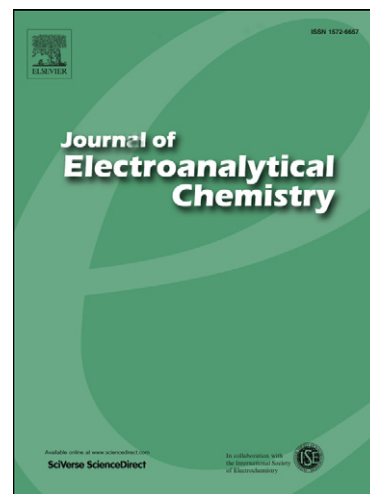
Received Date: 5 June 2012

Revised Date: 20 July 2012

Accepted Date: 24 July 2012

Please cite this article as: J. Durantini, P.P. Boix, M. Gervaldo, G.M. Morales, L. Otero, J. Bisquert, E.M. Barea, Photocurrent Enhancement in Dye-Sensitized Photovoltaic Devices with Titania-GrapheneComposite Electrodes, *Journal of Electroanalytical Chemistry* (2012), doi: <http://dx.doi.org/10.1016/j.jelechem.2012.07.032>

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# Photocurrent Enhancement in Dye-Sensitized Photovoltaic Devices with Titania-Graphene Composite Electrodes.

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## Abstract

Photovoltaic performance of dye-sensitized solar cell (DSC) devices based on a new titania-graphene paste has been investigated using Impedance Spectroscopy (IS) technique. The results provide key information about device performance, clarifying that photocurrent increment is not related to lower charge transfer resistance, neither with a downshift of the Fermi level of the graphene titania semiconductor. The DSC devices constructed using titania-graphene paste and graphene thin films reach higher photocurrent and therefore higher efficiency than devices made with a commercial paste due to extra photocurrent generation, because the titania-graphene paste presents higher light harvesting in the visible region of the solar spectra combined with large scatter effect than the commercial titania paste.

## Introduction

Nanocrystalline semiconductor-based dye-sensitized solar cells (DSC) have attracted significant attention as a low cost alternative to conventional solid-state photovoltaic devices.<sup>1</sup> The most successful dye sensitizers employed so far in these cells are polypyridyl-type ruthenium complexes<sup>2, 3</sup> yielding overall AM 1.5 solar to electric power conversion efficiencies (PCE) up to 11.7%<sup>4</sup>. Further improvements are still necessary and new materials as well as novel device fabrications need to be thoroughly explored. Several efforts are focused on improving the overall efficiency of DSCs, such as the exploration of new dyes to extend the solar irradiation absorption to the infrared and near infrared regions,<sup>5-7</sup> materials for counterelectrodes to improve charge extraction,<sup>8</sup> new redox mediators that can get higher open circuit potential<sup>9</sup> and new semiconductor materials. Composite metal oxides with different bandgaps<sup>10</sup> have been widely studied, as well as porous structures ordered in a perpendicular fashion to the conducting substrate<sup>11,12-14</sup>

Recently, the reduced graphene oxide (rGO), one type of graphene derivative, has been extensively used for biosensors,<sup>15</sup> memories,<sup>16</sup> transistors<sup>17</sup> and in DSCs.<sup>18</sup> The use of graphene in the DSC increases the overall conversion efficiency, but its function in the solar cell is still under investigation because there are many functional factors that are still unclear. It was suggested that graphene can absorb molecules (hydrocarbons)<sup>19</sup> or atoms (hydrogen) and the defects act as a conducting channel.<sup>19</sup> In general, an increase of the photocurrent has been observed when using graphene in a DSC, and it should be clarified which mechanism is causing this effect that promotes the overall power conversion efficiency.

In this paper we report photoelectrochemical and Impedance Spectroscopy (IS) studies of two different sets of TiO<sub>2</sub>-graphene DSCs, in addition to control devices. The first one consists in an active nanostructured electrode made by a mixture of titania-graphene paste fabricated by hydrothermal synthesis. In the second set a commercial titania paste is deposited onto a graphene layers deposited by spin coated on fluorine tin oxide (FTO) conducting glass. In both cases, the DSC containing graphene (composite or layered) present higher conversion efficiency than the reference device without graphene due to a large increase in the photocurrent.

## Experimental Section

### Synthesis and characterization of TiO<sub>2</sub>-Graphene composite material.

The synthesis method used to obtain the titania-graphene composite was based on a modification of the Kang's procedure.<sup>20</sup> Briefly, 4 mg of graphene oxide dispersed in 12ml of H<sub>2</sub>O and 4 ml of glacial acetic acid were poured into a conical flask immersed into an ice bath, stirred and then allowed to cool. Afterwards, 0.45 ml of isopropanol (Aldrich, 99.5%) is added

to a dropping funnel followed by 1.80 ml of titanium isopropoxide (Aldrich, 97%). The titanium isopropoxide/isopropanol solution was dripped into the acetic acid solution at a rate of approximately 1–2 drops per second with vigorous stirring. Then the mixture is kept between 4–8 h under reflux to achieve the peptisation. The obtained colloidal suspension was loaded in Teflon-lined stainless steel autoclave and heat at 200°C for 12 h. The titania-graphene was dispersed by ultrasound for 30 seconds to disperse the aggregates, followed by a concentration until 13% wt of titania nanoparticles was reached. In order to obtain the final paste, the titania-graphene composite are mixed with 20 wt% polyethylene glycol (Fluka, MW 20,000) and 20 wt% polyethylene oxide (Aldrich, MW 100,000).

The titania-graphene paste were characterized by X-ray diffraction spectroscopy using D4 Endeavor, Bruker-AXS (Figure 1 in SI), where it is clearly observed that the  $\text{TiO}_2$  present in the composite is obtained in the anatase phase. The less intensity of the peak and the broadness is due to the defects generated in the 3-dimensional framework by the graphene flakes. In addition, graphene shows peaks close to the anatase phase of titania which broadness the XRD spectra.

All the prepared materials were characterized by Transmission Electron Microscopy (TEM) using a Philips CM200 UT microscope operating at 200 kV and room temperature and by Atomic force microscopy (AFM), that were performed using an Agilent 5500 SPM microscope (Agilent Technologies, Inc.) working in Acoustic AC Mode. Commercial silicon cantilever probes, with aluminum backside coating, and nominal tip radius of 10 nm (Mikro Masch, NSC15/Al BS/15, spring constant ranging 20–75  $\text{N m}^{-1}$ ), were employed just under their fundamental resonance frequencies of about 325 kHz. Height and phase images were acquired simultaneously under ambient conditions. Scan rates were set between 0.5 to 2 Hz depending on the size of the images. Figure 1 shows a typical TEM and high resolution TEM image of the synthesized titania-graphene paste. It is apparent that the composites consisted of uniform  $\text{TiO}_2$  nanoparticles with diameters of about 15 nm grow on the graphene flakes. It is observed that both components, graphene and semiconductor  $\text{TiO}_2$ , have been integrated in an intimate interfacial contact.<sup>21</sup>

The surface morphologies of the prepared composite electrodes were examined with AFM in order to observe their topology, Figure 2 in SI shows a typical Acoustic AC Mode AFM height mode image of the deposited titania-graphene on FTO. No significant differences in topological features were found for the electrodes prepared by using  $\text{TiO}_2$  with and without graphene. As can be seen, the films present a highly rough and open surface, with the presence of small features assigned to the presence of  $\text{TiO}_2$  nanoparticles. The observed microstructure must be a consequence of the nucleation, and further  $\text{TiO}_2$  growing process over graphene flakes in agreement with the observed in TEM images.

### DSC fabrication and characterization

Two sets of electrodes, named GP (graphene paste, titania-graphene paste fabricated by hydrothermal synthesis) and GF (graphene film, commercial titania paste is deposited onto a graphene oxide layers deposited by spin coating on fluorine tin oxide (FTO) conducting glass) were prepared and sensitized with N719 dye (0.5 mM acetonitrile/tert-butanol N719 and 0.5 mM chenodeoxycholic acid 98% solution) for 24 hours. Both sets were manufactured by Doctor Blade technique on FTO (Pilkington TEC15,  $\sim 15 \Omega/\text{sq}$  resistance) or on a spin coated film of graphene oxide deposited on TCO. All the electrodes were made with two different layers of  $\text{TiO}_2$ , a transparent commercial paste and a scattering layer (commercial paste and graphene paste) calcined at  $450^\circ\text{C}$  under  $\text{N}_2$  atmosphere during 30 minutes, with a 19-20  $\mu\text{m}$  thickness total. The solar cells were assembled with counter electrode thermally platinized using a thermoplastic frame (Surlyn 25  $\mu\text{m}$  thick). The redox electrolyte [0.6 M methyl propyl imidazolium iodide, 0.03 M  $\text{I}_2$  (99,9%) and 0.5 M 4-tert-butylpyridine in acetonitrile/valeronitrile (85:15)] was introduced through a hole drilled in the counter electrode that was sealed afterwards. Prepared solar cells (0.3  $\text{cm}^2$  size, masking solar cell to 0.25  $\text{cm}^2$ ) were characterized by current–voltage characteristics and incident photon to current efficiency (IPCE). UV/Vis data was obtained using a Cary 300 Bio Spectrophotometer with the adequate setup for thin-film analysis. Photocurrent and voltage were measured using a solar simulator equipped with a 1000 W ozone-free Xenon lamp and AM 1.5 G filter (Oriel), where the light intensity was adjusted with an NREL-calibrated Si solar cell with a KG-5 filter to 1 sunlight intensity ( $100 \text{ mW cm}^{-2}$ ) and a 250 W Xenon arc lamp (Oriel) served as a light source for IPCE. Impedance Spectroscopy measurements (IS) were carried out under 1 sun illumination (AM 1.5 conditions) at different applied bias potentials, ranged from zero to open-circuit photovoltage, with frequencies varying between 1 MHz and 0.01 Hz.

### Results and Discussion

The current-potential ( $j$ - $V$ ) curves obtained for both sets of cells assembled with different working electrode are plotted in Figure 2. The solar cells parameters extracted from these curves are indicated in Table 1. Note that for sets GP and GF, the main difference is observed in the photocurrent, with an increase of  $3 \text{ mA/cm}^2$  for the DSC with GP and  $2.4 \text{ mA/cm}^2$  for GF DSC, that enhance the overall conversion efficiency of the cell by around 20%. The increase in the photocurrent is also observed in the incident photon-to-current conversion efficiency (IPCE) (Figure 3).

To clarify the mechanism governing the performance of the devices IS measurements were performed on the DSCs at different bias potentials (from zero to open circuit potential, step 0.05

volts) under 1 sun irradiation in a frequency range from 1MHz to 10 mHz. These measurements were analyzed using the impedance model developed by Bisquert and co-workers,<sup>22, 23</sup> allowing to isolate the recombination resistance from other resistive contributions in the cell. The aim of IS measurements here is to identify variations in the devices concerning the changes of the rate of transport and recombination and also shift in the capacitance due to the presence of graphene that could strongly influence the performance.<sup>24</sup> Details about the methodology and the interpretation of IS results in connection to the performance of DSCs are provided in recent papers.<sup>25-29</sup> The chemical capacitance and recombination resistance are plotted vs  $V_F$  (Fermi level voltage), that corresponds to remove from the bias voltage the effect of ohmic drops in the solar cell. IS enables extracting the voltage drop in the sensitized electrode,  $V_F$ , at each applied potential,  $V_{app}$ , by subtracting the effect of the series resistance on both  $R_{rec}$  and  $C_{\mu}$  as follows:  $V_F = V_{app} - V_s - V_{ce}$ , where  $V_s$  and  $V_{ce}$  are potential drops at the series resistance and at the counter-electrode, respectively.  $V_F$  is proportional to the rise of the Fermi level of electrons in  $TiO_2$ ,  $V_F = (E_{Fn} - E_{F0})/q$ , where  $q$  is the positive elementary charge and  $E_{Fn}$  and  $E_{F0}$  are the electron quasi-Fermi level and the electron Fermi level at the equilibrium.

Figure 4 shows a similar chemical capacitance and recombination resistance in both set of samples, with and without graphene. This clearly indicates that graphene does not shift the conduction band of  $TiO_2$  and neither influences the recombination process. The electron conductivity in the semiconductor, usually measured by the reciprocal of the transport resistance, was too large to be measured, being the transport resistance negligible in both sets of samples (GP and GF). This indicates that the current limitation in the case of commercial titania DSC is not due to low transport rate in  $TiO_2$ .<sup>27</sup>

The interpretation of IS measurements therefore shows that a number of features usually employed to explain the increase in the photocurrent in DSC can be ruled out in the present investigation, namely: lower recombination rate, a down shift of the capacitance that could increase the injection from the LUMO level of the dye, or larger electron conductivity. Therefore, the increase in the photocurrent and its associated increase in the efficiency could be related to a combination of two factors. (1) Increase in the light harvesting from 400 to 800nm<sup>30</sup> due to the scatter effect by presence of graphene flakes (Figure 5), combined with an increase in the absorption compared with the reference titania commercial paste (Figure 6). (2) Extra electron injection under illumination from the graphene in the composite and from the graphene film, due to the fact that the extra electrons of six-membered ring concentrate in the LUMO level,<sup>31</sup> also because the defects of the graphene act as a conducting channel,<sup>19</sup> or some plasmon effect that cannot be rule out and has been reported recently in the bibliography.<sup>32,33</sup> Our results therefore show that the extra current obtained in DSC made with GP or GF is due to the nature of graphene, its light absorption and scattering properties in the

visible region. As a consequence, this work opens a new path in the improvement of the DSC, in particular an increase of photocurrent using titania-graphene composites.

### Conclusions

In summary, graphene is a material of general interest for optoelectronic devices, and we introduced it into the working electrode of DSC successfully. The short-circuit current density and the conversion efficiency of the DSC was increased. The enhancement of the light harvesting and higher scatter effect of the naked graphene titania paste is what generate extra photocurrent without any energetic and structural change in the semiconductor. This is confirmed by impedance spectroscopy results that show the same recombination resistance and no downshift of the conduction band of titania.

### Acknowledgments

We acknowledge support by projects from Ministerio de Economía y Competitividad of Spain (Consolider HOPE CSD2007-00007, MAT2010-19827), and GeneralitatValenciana (PROMETEO/2009/058 and the “Institute of Nanotechnologies for Clean Energies”ISIC/2012/008.).Red Cyted - Red Temática 5511RT0416. The SCIC of University Jaume I (Spain) for providing the XRD facilities and M.S. Moreno, Centro AtómicoBariloche, by the TEM images.

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**Table caption**

**Table 1.** Photovoltaic Performances of DSCs fabricated with graphene and commercial paste and sensitized with N719,

**Figure captions**

**Figure 1.** TEM image of the as synthesized graphene-titania paste. GO is the graphene oxide..

**Figure 2.**  $j$ - $V$  curves for DSCs prepared with (a) graphene paste (GP) (b) graphene film (GF).

**Figure 3.** IPCE for DSCs set of (a) GP and (b) GF and the references DSC.

**Figure 4.** (a) Capacitance and (b) recombination resistance, with respect to the Fermi level voltage (removing the effect of series resistance) for GP set of DSC. (c) Capacitance and (d) recombination resistance respect to the Fermi level voltage for GF set of DSC.

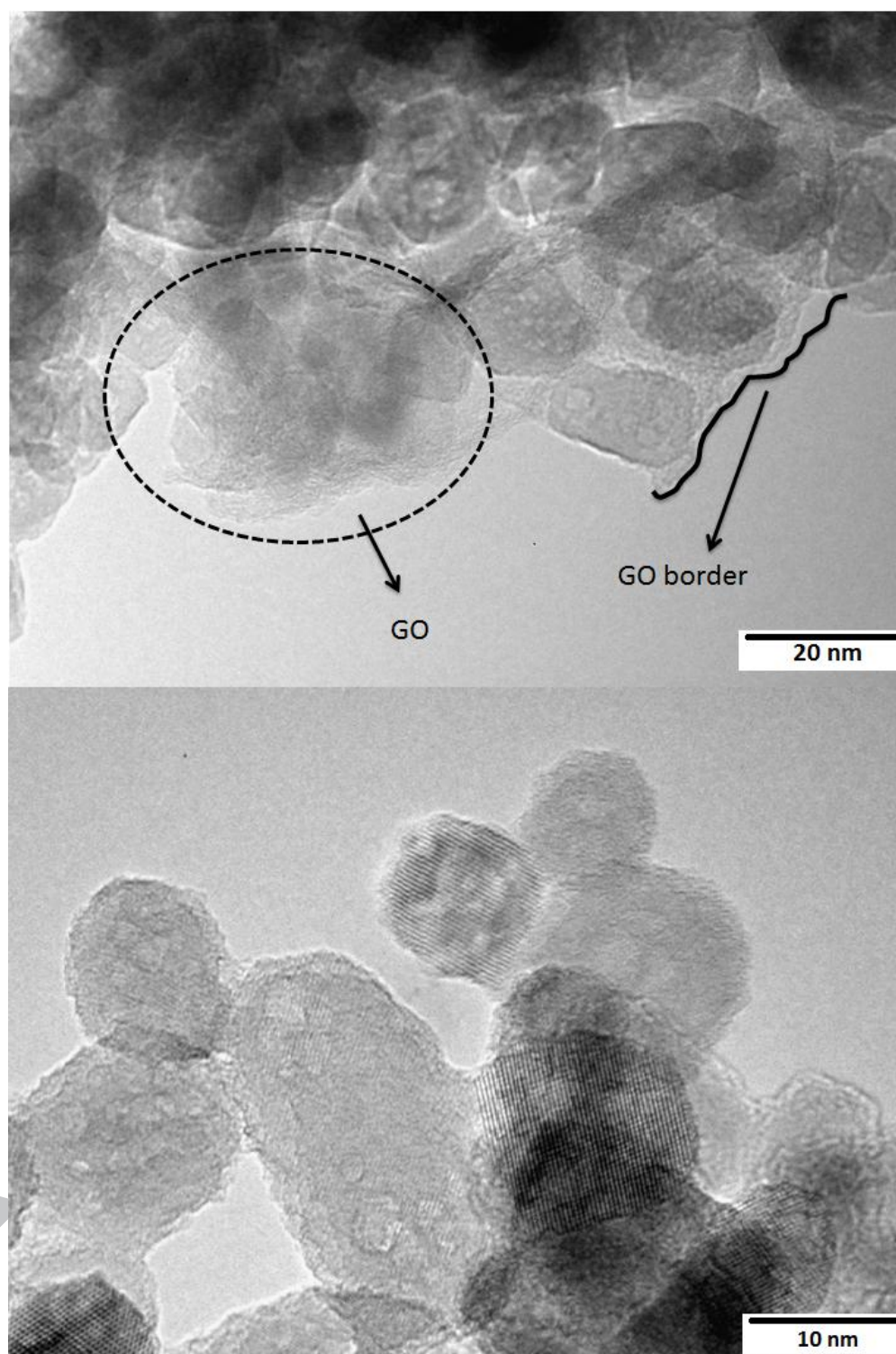
**Figure 5.** UV-vis spectra of the naked titania films made by commercial titania paste and graphene paste.

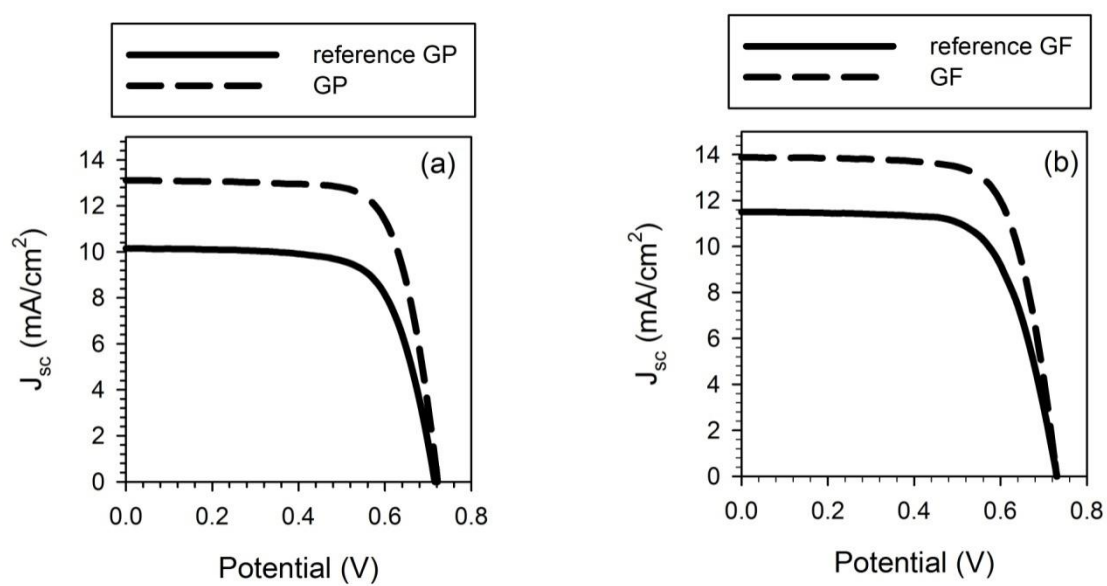
**Figure 6.** UV-vis spectra normalized to thickness films for the sensitized graphene based electrode and commercial paste based electrode

**Table 1**

| <b>DSC</b>       | <b>V<sub>oc</sub> (V)</b> | <b>J<sub>sc</sub> (mA/cm<sup>2</sup>)</b> | <b>FF</b> | <b>Efficiency (%)</b> |
|------------------|---------------------------|-------------------------------------------|-----------|-----------------------|
| GP               | 0.72                      | 13.2                                      | 0.73      | 7.1                   |
| Reference for GP | 0.71                      | 10.2                                      | 0.70      | 5.1                   |
| GF               | 0.73                      | 14.0                                      | 0.72      | 7.3                   |
| Reference for GF | 0.73                      | 11.6                                      | 0.70      | 5.8                   |

V<sub>oc</sub> is the open circuit voltage, J<sub>sc</sub> is the density current, FF is the Fill Factor. Values are obtained at steady-state measurement under 100 mW·cm<sup>-2</sup> light intensity and AM 1.5 global radiation.

**Figure 1**

**Figure 2**

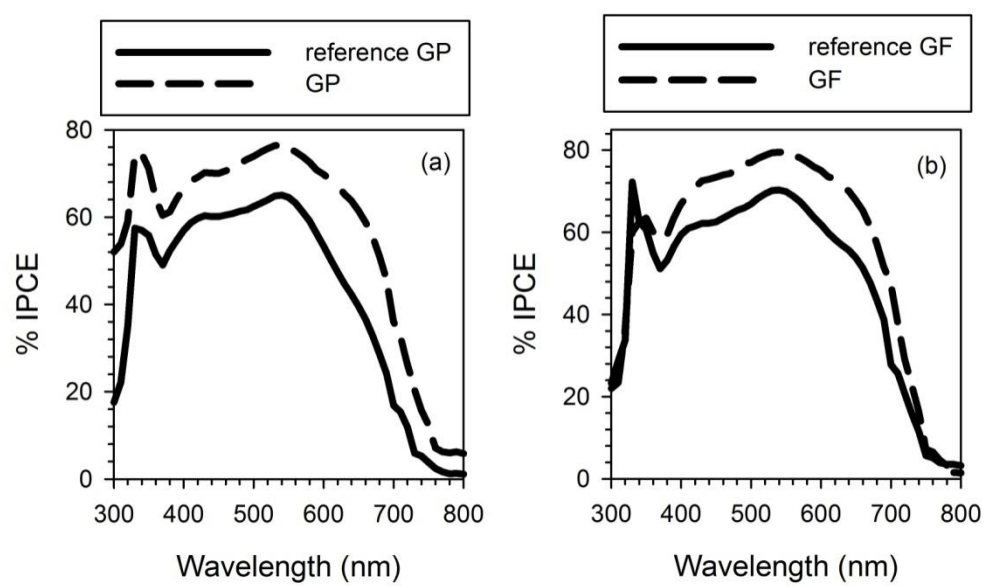
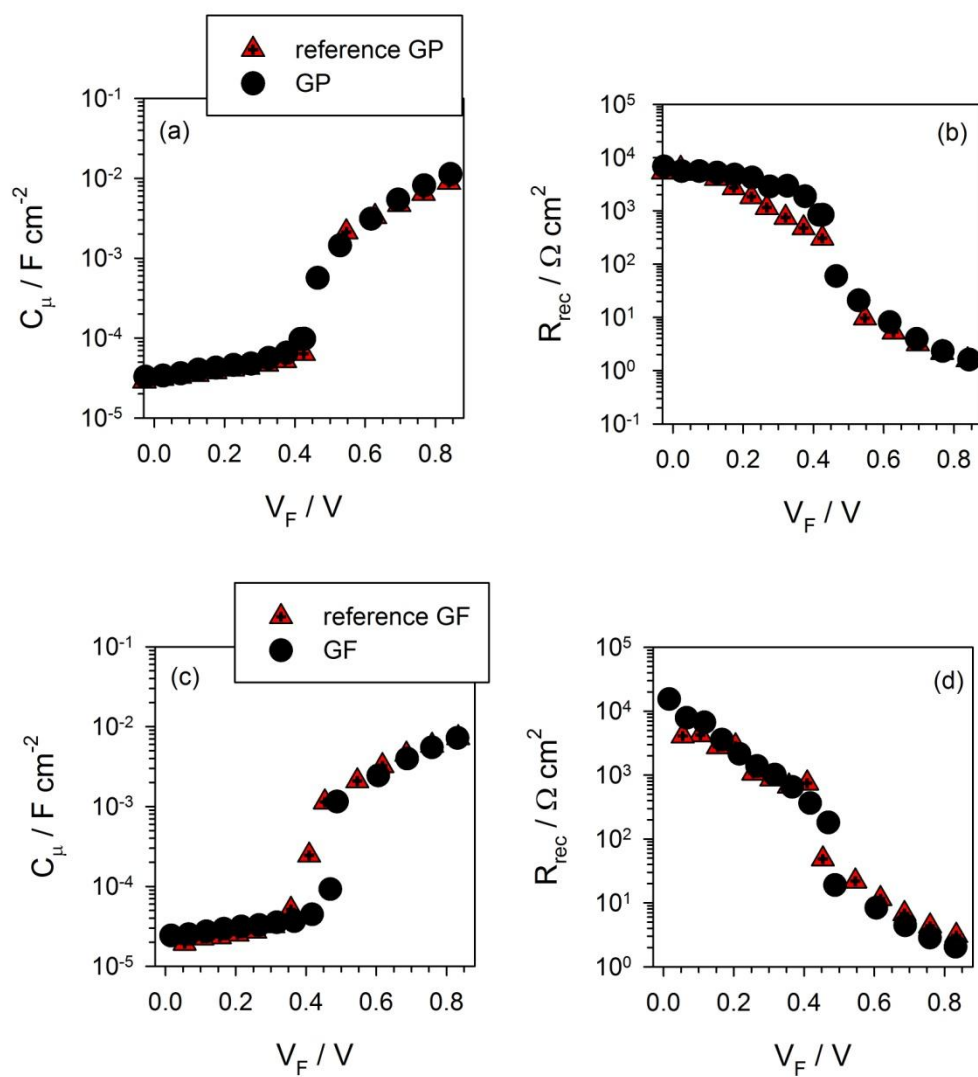
**Figure 3**

Figure 4



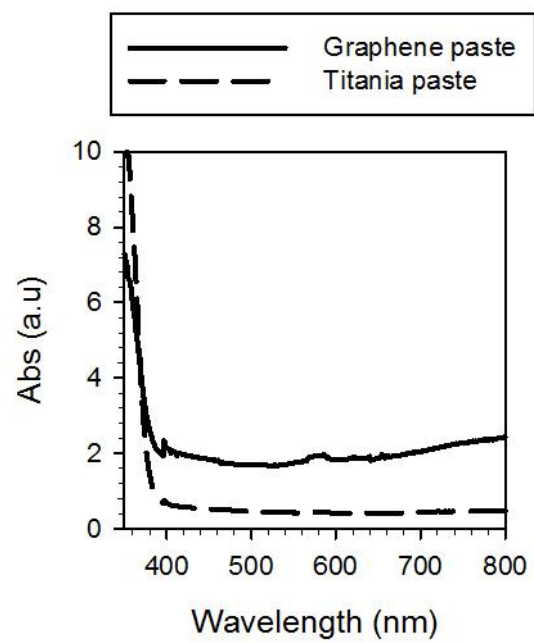
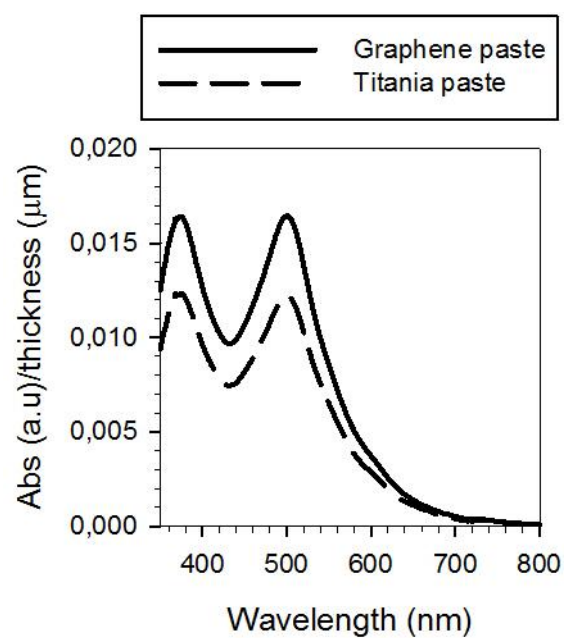
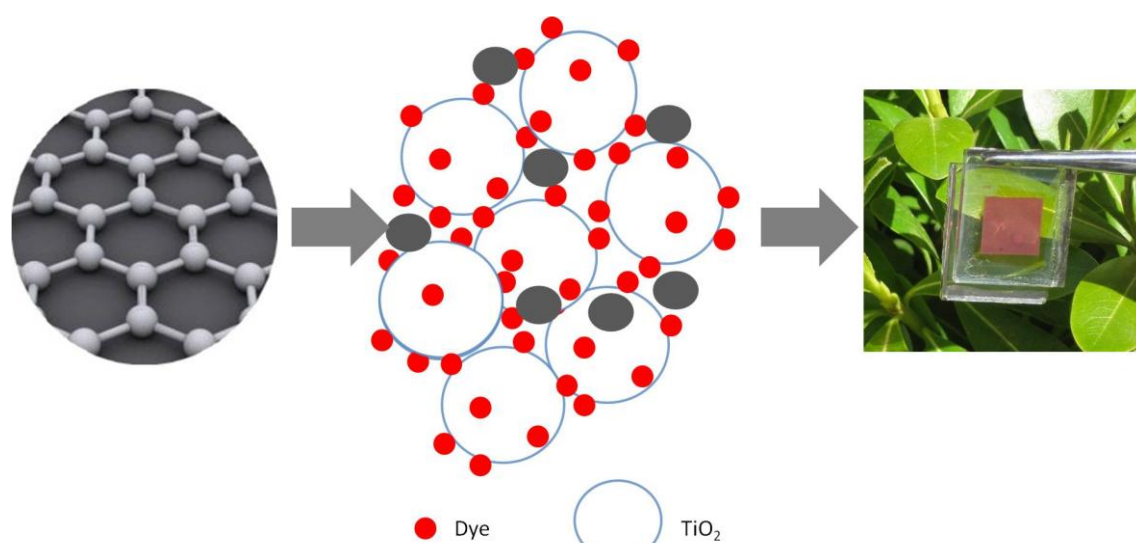
**Figure 5**

Figure 6



TOC



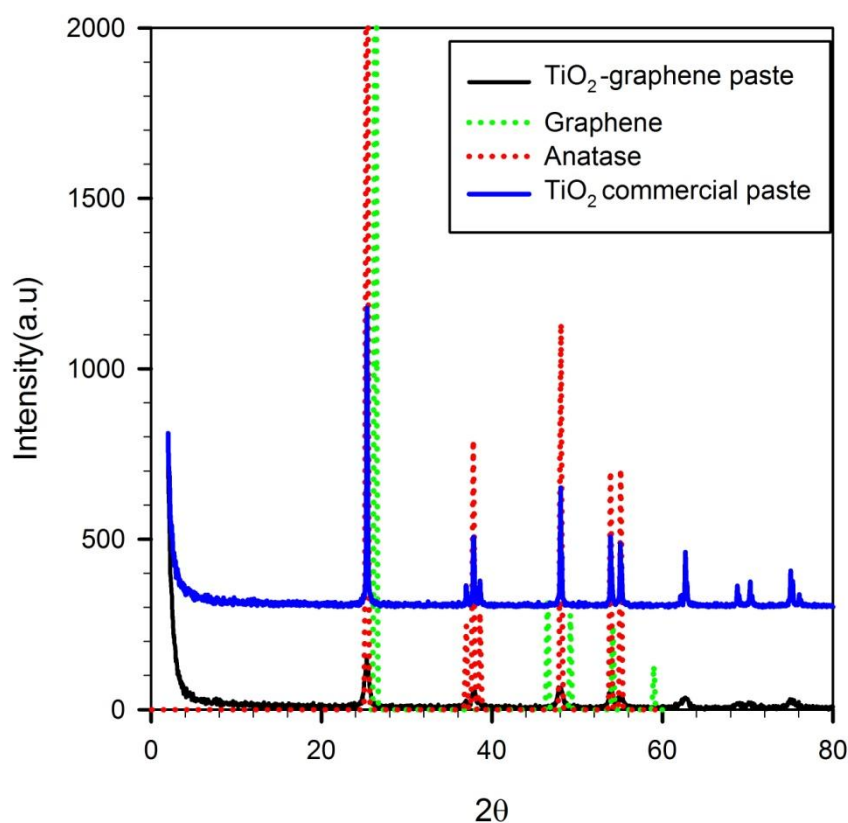
## Supporting Information

# Photocurrent Enhancement in Dye-Sensitized Photovoltaic Devices with Titania-Graphene Composite Electrodes.

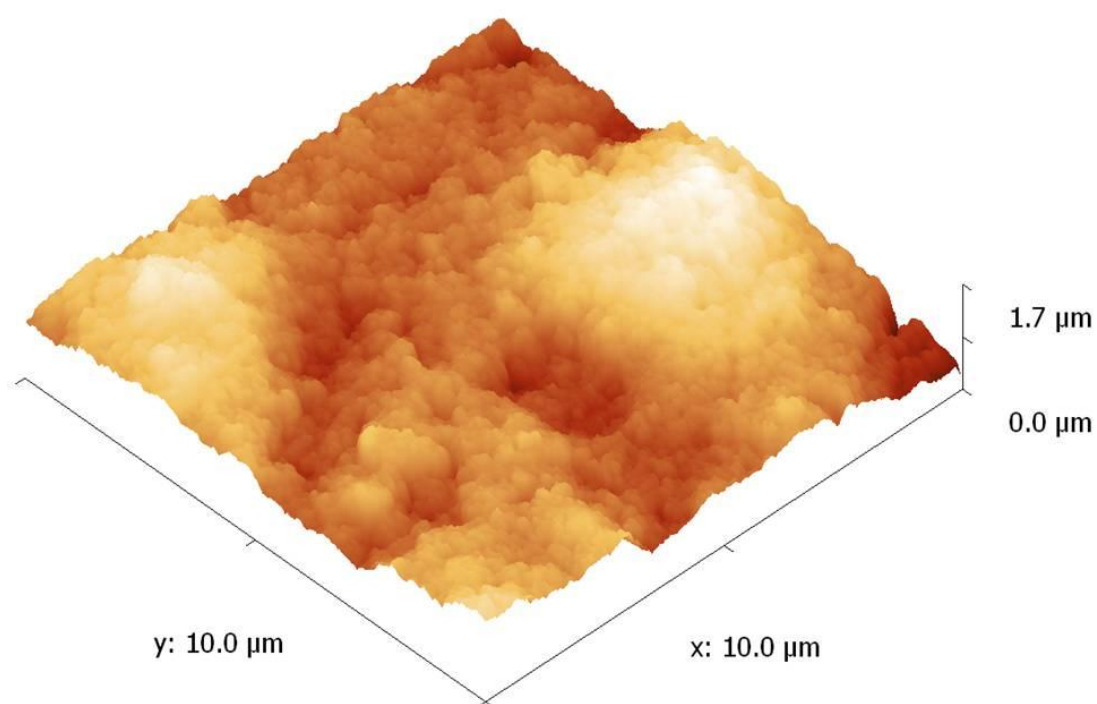
Javier Durantini,<sup>b</sup> Pablo P. Boix,<sup>a</sup> Miguel Gervaldó,<sup>b</sup> Gustavo M. Morales,<sup>b</sup> Luis Otero,<sup>b</sup> Juan Bisquert,<sup>a\*</sup> and Eva M. Barea<sup>a\*</sup>

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**Figure 1.** DRX of commercial opaque titania and synthesized graphene-titania paste.



**Figure 2.** AFM images of the as synthesized graphene-titania paste.

#### Research Highlights:

DSC devices constructed using titania-graphene paste and graphene thin films reach higher photocurrent and therefore higher efficiency than devices made with a commercial paste has been studied.

Impedance Spectroscopy characterization has been studied in order to identify the role of the graphene in the increment of the current and efficiency of the DSC, observing that there is not any change in the Capacitance, neither in the charge transfer resistance of the cell.

The increase in the photocurrent and its associated increase in the efficiency could be related to a combination of two factors.

- (1) Increase in the light harvesting from 400 to 800nm due to the scatter effect by presence of graphene flakes, combined with an increase in the absorption compared with the reference titania commercial paste.
- (2) Extra electron injection under illumination from the graphene in the composite and from the graphene film, due to the fact that the extra electrons of six-membered ring concentrate in the LUMO level or some Plasmon effect that cannot be rule out and has been reported recently in the bibliography