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Nanostructured TiO_2 and PEDOT Electrodes with Photovoltaic Application

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Abstract: In this work, nanostructured TiO_2 and poly-3,4-ethylenedioxythiophene (PEDOT) layers were electrochemically prepared over transparent electrodes. Morphological characterization evidenced the presence of nanostructures as planed with 50-nm-wide TiO_2 rod formations followed by 30-nm-wide PEDOT wires. Different characterizations were made to the deposits, establishing their composition and optic properties of the deposits. Finally, photovoltaic cells were prepared using this modified electrode, proving that the presence of PEDOT nanowires in the cell achieves almost double the efficiency of its bulk analogue.

Keywords: dye-sensitized solar cell; electropolymerization; poly(3,4-ethylenedioxythiophene); polymer nanowires; solar cell; titanium dioxide

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1. Introduction

Global warming is a current global concern known to be, in part, tightly linked to the large dependence of humans on non-renewable fossil-fuel-based energy sources involving the release of greenhouse gases. If renewable clean energy sources remain expensive, it will not be possible to reduce or stop global warming and its consequences. A valid strategy to lower the costs of clean-energy-harvesting devices, such as photovoltaic cells, could be to incorporate low-cost and more efficient materials, such as conducting polymers (CPs). This class of polymers has shown interesting electronic and optical properties, while maintaining feasible handling of plastics [1], with applications in supercapacitors, light-emitting diodes, electrochromic and photosensitive devices, sensors, batteries, transistors, fuel cells, electrocatalysis, and photovoltaics, among others [2–17].

CPs have proven their potential usefulness in energy-harvesting devices, and could be enhanced by a higher control of their morphology. A method using solely electrochemical perturbations has been developed ([18–22]; 10.1007/s11581-016-1796-9) as a solution for controlling the deposition process and electrode morphology, suitable for the reproducible construction of nanostructured semiconducting polymer layers.

With respect to CP application in solar cells, most successful outcome corresponds to the incorporation of a doped poly-3,4-ethylenedioxythiophene (PEDOT) coating in a multiple-layer organic solar cell configuration. PEDOT is recognized as an excellent buffer layer material and some studies have revealed that it is possible to use it as an

anode in a multiple-layer solar cell configuration [23]. Nevertheless, the performance of cells using this type of material, and other CPs, is limited by the imperfect connections (empty spaces) of a multiple-layer configuration. Short cuts, misguided excitons, and energy loss due to dissipative forces are some of the failure sources encountered when assembling these types of device [24,25]. A way to solve this problem is the incorporation of a nanostructured heterojunction assembly; nanostructured or nanowired (nw) assembly provides an enhanced surface-contact area while avoiding empty spaces between layers, and directs exciton movement correctly [26].

In previous studies, we have verified that PEDOT-nw displays better performance on other types of device, such as fuel cells [16]. Thus, it seems convenient to further test PEDOT-nw incorporation in the design of anodes for solar cells. In addition, some reports indicate that the previous addition of a semiconducting oxide layer as anatase (TiO_2) followed by an appropriate sensitizer dye can enhance multiple-layer solar cell performance [27].

In the present study, transparent indium-doped tin oxide (ITO) electrodes are sequentially modified with layers of TiO_2, sensitizer dye, mesoporous silica template, and nanowired PEDOT. Then, these electrodes are employed in the design of multiple-layer photovoltaic cells [28,29]. It is worth noting that most preparative methods are based on electrochemical techniques which ensures low cost and reproducible results. The main objective of the present report is to demonstrate that the electrochemical method enables sufficient control to produce a nanostructured conducting polymer layer over electrodes and to check if these deposits have advantages in terms of the performance of photovoltaic cells constructed with them [30].

2. Materials and Methods

2.1. Electrode Modification

Electrochemical studies were carried out in a high-purity Ar atmosphere at room temperature (20 °C), in a three-compartment anchor cell, using a Pt wire with an area 20 times greater than that of the respective working electrodes. A reference wire of Ag | AgCl in tetramethylammonium chloride solution, with potential adjustment to that of the saturated calomel electrode (SCE) was used as the reference electrode [31]. The working electrode was glass coated with indium-doped tin oxide (ITO) of 0.21 cm^2 geometric area and sheet resistance of $\leq$10 Ω sq^{-1}.

ITO modification with TiO_2 was done in a single compartment cell, from titanium oxysulfate 0.020 mol L^{-1} ($TiOSO_4$ 99.9%, Aldrich, Santiago, Chile), as a precursor to titanium oxide; hydrogen peroxide 0.030 mol L^{-1} (H_2O_2 30% v/v, Merck, Santiago, Chile) and potassium nitrate (KNO_3, 99.0%, Merck), as a supporting electrolyte, in Milli-Q water, at pH 1.8 at 10 °C. The electro-obtaining of TiO_2 was carried out by potentiostatic perturbance at −1.1 V for 300 s. Subsequently, the modified electrode was heat-treated at 500 °C for 1 h, following the heating ramp at 8 °C min^{-1}. Then, the ITO | TiO_2 electrodes were modified by immersing the electrode in a 1.0×10^{-4} mol L^{-1} N3 dye solution, for 24 h and then washed with acetone. N3 solutions corresponded to commercial cis-bis(isothiocyanate)-bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) ($C_{26}H_{16}N_6O_8RuS_2$, N3) in ethanol. Thus, ITO | TiO_2 | N3 electrodes were obtained.

Incorporation of nanowired (PEDOT-nw) conducting polymer requires an early silica template preparation stage [10.1016/j.elecom.2020.106896] over the ITO | TiO_2 | N3 electrodes. Precursor solution for the silica template was prepared as follows: sodium nitrate 0.1 mol L^{-1} ($NaNO_3$ 99.0%, Merck) as supporting electrolyte, tetraethyl orthosilicate 0.0034 mol L^{-1} ($(C_2H_5O)_4Si$, 99.999%, Aldrich) as a precursor to silicon oxide and hexadecyltrimethylammonium bromide 0.115 mol L^{-1} as surfactant (CTAB, $C_{19}H_{42}BrN$, 95%, Aldrich), in ethanol 50% *v/v* (ethanol/Milli-Q = 1:1) under vigorous stirring for 2.5 h. Mesoporous silica template was prepared by immersing the ITO | TiO_2 | N3 electrodes in this solution and application of a potential step between −1.100 and −1.400 V. This modified electrode was washed with abundant Milli-Q water and dried in an oven

for 24 h at 130 °C, to generate a thin film of SiO_2. Next, the CTAB micelles were removed by immersing the electrodes for 15 min in acidified ethanolic solution under stirring. Then, the electrochemical growth of PEDOT nanowires took place inside the nano-channels of this template-modified electrode ([18–22]; 10.1007/s11581-016-1796-9). The electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) was performed in a working solution containing monomer 0.010 mol L^{-1} (Aldrich) and support electrolyte 0.100 mol L^{-1} (tetrabutylammonium hexafluorophosphate, $TBAPF_6$, Aldrich 99%), in acetonitrile (CH_3CN 99.9%, Merck); the technique employed in this case was cyclic voltammetry (CV). Successive potentiodynamic scans were applied between −1.000 and 1.600 V on electrodes with and without the silica template for preparation of bulk and nanowired polymeric deposits. A scan rate of 0.1 V s^{-1} was used considering 5 and 1 potentiodynamic cycles for production of bulk PEDOT and PEDOT-nw, respectively. To remove the silica template and expose the nanowires, electrodes were immersed in 0.5 mol L^{-1} NaOH solution for 15 min, rinsed with 5% m/v $NaHCO_3$ and finally with distilled water. Therefore, the ITO | TiO_2 | N3 | PEDOT and ITO | TiO_2 | N3 | PEDOT-nw electrodes were obtained. A schematic summary of the preparative methods can be seen in Figure 1.

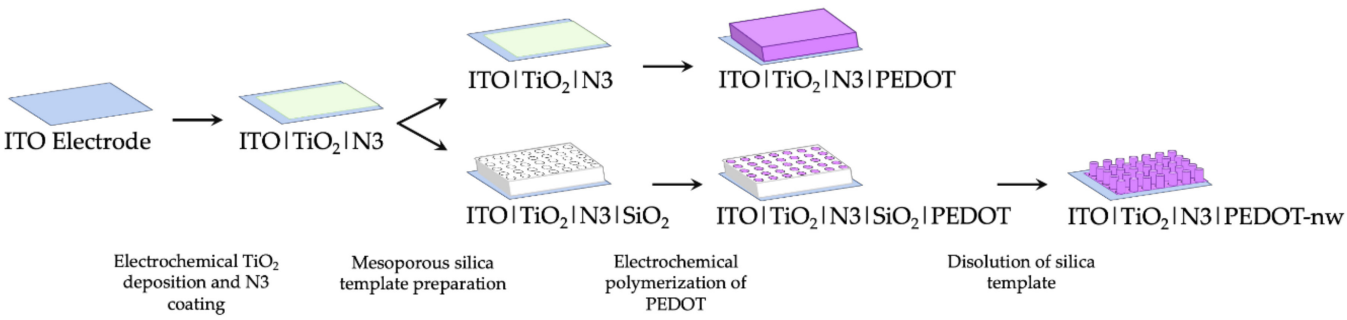

Figure 1. Schematic representation of preparative methods.

2.2. Characterization

Surface morphology of the prepared electrodes was studied using scanning electron microscopy (SEM) Inspect F50 SEM or JOEL model 7600F (Nantes, France).

Identification of TiO_2 deposit in its anatase form was confirmed by X-ray diffractometry (XRD) obtained on a Siemens D5000 spectrometer (Nantes, France) using Cu radiation (λKα 0.15406 nm) in an interval of 20 to 60 2θ and X-ray photoelectron spectroscopy using a Kratos Analytical AXIS Nova spectrometer, with an Al excitation line (Kα 14.866 eV) in an interval between 0 and 1.200 eV, analyzing the data with CasaXPS software (Nantes, France).

Electrochemical modifications and characterization of electrodes were made using a CH Instruments potentiostat/galvanostat controlled by CH750D software. UV-Vis spectra were recorded on a Specord 40 spectrophotometer (Analytik Jena, Thuringia, Germany), between 300 and 800 nm.

Solar cells were assembled following the methodology proposed by Bernéde et al. [29,30]. The photovoltaic characterization of the solar cells was carried out in an unautomated I–V under darkness and lighting, using a global solar simulator AM1.5 (Oriel 300 W, Nantes, France), with an intensity of 100 mW cm^{-2}, which was adjusted with a reference photovoltaic cell (CIGS 0.5 cm^2 PV, calibrated in NREL, Denver, CO, USA).

3. Results and Discussion

Before template and nanowire deposition, a layer of TiO_2 in its anatase form was required to enhance the photocell performance. Morphological characterization is presented in Figure 2.

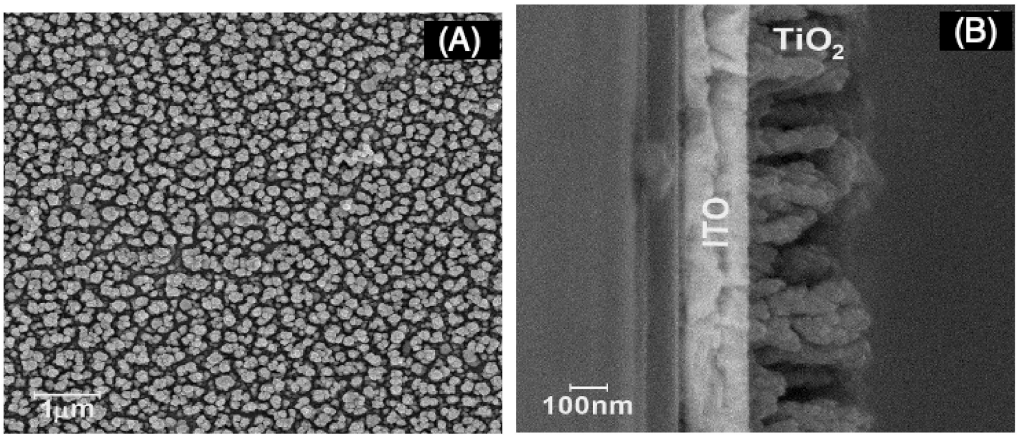

Figure 2. Scanning electron microscopy (SEM) micrographs of indium-doped tin oxide (ITO) | TiO_2 after 300 s electrosynthesis time (**A**) top view and (**B**) cross section.

Morphological characterization revealed rod-like formations of TiO_2 over ITO surface after 300 s electrolysis time. From the pictures (Figure 2A,B), the rods were on average 50 and 300 nm in width and height, respectively, and rod density was calculated as being near 2.1×10^7 per mm^2.

Other characterizations were considered. XRD characterization (Figure S1 in Supplementary Materials) showed expected results for the formation of anatase after 60 s deposition time displaying typical crystallographic signals [32], and the (101) phase became favored with electrolysis time. There was a small shift of TiO_2 signals at the diffractograms, attributed in the literature to a strain resulting from planar stress very likely in thin-layer electrochemical deposits [33]. XPS analysis of the samples (Figure S2 in Supplementary Materials) showed signals of around 459.5 (Ti $2p^{1/2}$) and 465.5 (Ti $2p^{3/2}$) eV from the Ti–O interaction.

Afterwards, these electrodes were further modified with a dye to improve contact between TiO_2 and the subsequent PEDOT layers. Bulk PEDOT and PEDOT nanowires were then electrochemically polymerized using a methodology published in past reports [16–18,20] (Figure 3). From the micrographs (Figure 3A,B), it can be seen that the polymer grows between the TiO_2 structures with excellent cohesion for the hetero junction. Bulk PEDOT (Figure 3A) displays a homogeneous morphology, fills gaps between the TiO_2 rods, and finishes with a smooth surface. On the other hand, nanostructured PEDOT, or PEDOT-nw (Figure 3B), displays nanometric wire morphology. PEDOT-nw shows wires with an average 30-nm width and, from micrograph analysis, a nanowire density of approximately 90,000 wires per μm^2 can be calculated.

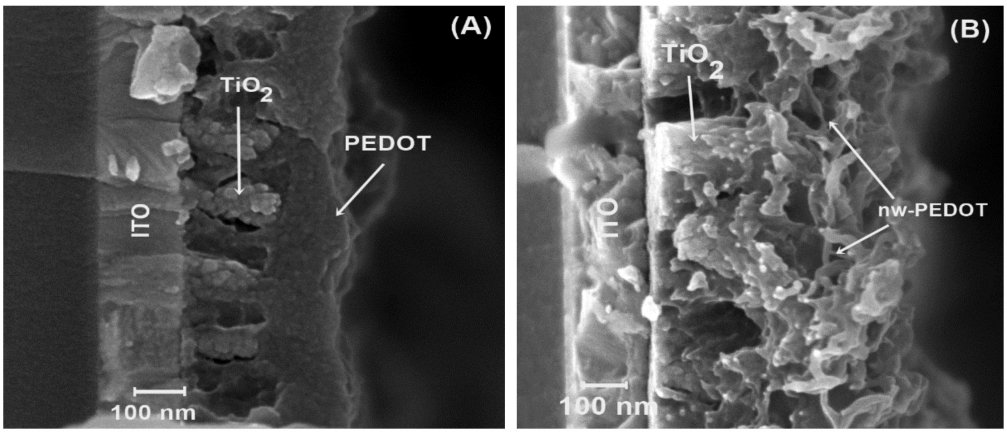

Figure 3. Electrodes' morphological characterization. (**A**) ITO | TiO_2 | PEDOT and (**B**) ITO | TiO_2 | PEDOT-nw.

To predict the behavior of the photocells, the energy diagrams of the respective modified electrodes, ITO | TiO_2 | PEDOT and ITO | TiO_2 | PEDOT-nw, were constructed (Figure S3 in Supplementary Materials) [34]. Electrochemical impedance spectroscopy measurements were made on electrodes in 0.1 mol L^{-1} LiCl solution, at 1 kHz to obtain Mott–Schottky graphs where flat band potential, Vfb, was calculated for TiO_2, PEDOT and PEDOT-nw, finding values of −0.58, 0.674 and 0.113 V vs. SCE, respectively, which are consistent with those reported in the literature [35–37]. Thus, TiO_2 showed a positive slope, which indicates the presence of an n-type semiconductor. On the other hand, PEDOT and PEDOT-nw negative slopes were found, accounting for a p-type semi-conductor. From these slopes, using Equations (1) and (2) [34], it is possible to calculate the apparent density of carriers, for the different semi-conductors, where N_D and N_A are the number of donors and acceptors for *n*-type and *p*-type semi-conductors, respectively.

$$N_D = \frac{2}{\varepsilon \cdot \varepsilon_0 \cdot e \cdot A^2 \cdot P_{MS}} \quad (1)$$

$$N_A = -\frac{2}{\varepsilon \cdot \varepsilon_0 \cdot e \cdot A^2 \cdot P_{MS}} \quad (2)$$

Here, P_{MS} is the value of the slope, e is the charge of the electron, ε_0 and ε are the dielectric constant in vacuum and the dielectric constant of the semiconductor, considering values of 100 and 600,000 for TiO_2 [38] and PEDOT [39], respectively, and A is the area. Therefore, the calculated values of 6.057×10^{19}, 8.246×10^{17} and 1.107×10^{17} cm^{-3} are obtained for the respective TiO_2, PEDOT and PEDOT-nw electrodes. These values are also consistent with those reported for these semiconductors [40–42]. Using the Tauc transformation [43], from the UV-Vis spectra (Figure S3, inserts at D,E,F in Supplementary Materials) the band gaps of the respective modified electrodes are determined, obtaining values of 3.65, 2.31 and 2.56 eV for TiO_2, PEDOT and PEDOT-nw, respectively. The increase in the band gap of PEDOT-nw with respect to PEDOT is attributed or accounts for the quantum confinement of the nano-structured material.

As has been proven in past reports [44], direct electro-synthesized conducting polymer deposit may show an imperfect connection between the semiconducting layers (short circuit). To improve cell performance, a layer of N3 dye was placed between the TiO_2 and conducting polymer; this dye would also inject a significant amount of electron-hole pairs into the system, generating better efficiency as described in the literature [45]. The V values for each layer were transformed into eV in vacuum [46]. It should be noted here that organic semiconductors have flat band potential, corresponding to the bipolaron band, 0.70 eV above the HOMO level, unlike inorganic semiconductors, which have flat bands at 0.06 eV [34,47]. The energy level for N3 was taken from the literature [48], with −5.89 and −5.22 eV for HOMO and LUMO levels, respectively. With this information, band diagrams were constructed (Figure S4 in Supplementary Materials). These cells were then characterized based on their J-V performance, as shown in Figure 4.

At first sight, ITO | TiO_2 | N3 | PEDOT-nw | Al electrodes show a higher current density than the modified ITO | TiO_2 | N3 | PEDOT | Al electrodes. Table 1 summarizes the values corresponding to the photovoltaic characterization of these cells.

Table 1. Current-voltage (J-V) characterization photocells using bulk and nanowired PEDOT layers.

Deposited Layer	V_{OC}/V	J_{SC}/mA cm^{-2}	% FF	% η
PEDOT	0.48	6.0×10^{-3}	16.1	4.9×10^{-4}
PEDOT-nw	0.39	1.0×10^{-2}	25.7	1.0×10^{-3}

The values in Table 1 show that nanowired PEDOT-based photovoltaic devices are practically twice as efficient as bulk polymer. Therefore, the selection of nanostructured presents advantages over bulk PEDOT deposits. Despite the fact that solar cell performance

was not good, further studies will attempt optimizing through variation of nanowire length and/or diameter.

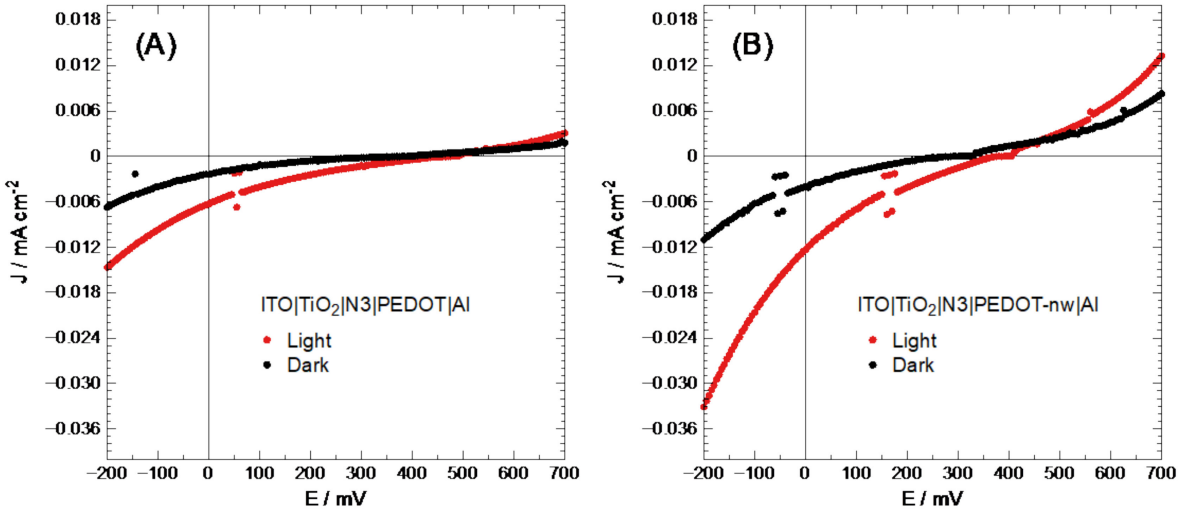

Figure 4. Solar cell J-V characterization of (**A**) ITO | TiO_2 | N3 | PEDOT | Al and (**B**) ITO | TiO_2 | N3 | PEDOT-nw | Al.

4. Conclusions

Electrochemical techniques are useful for the construction of nanostructured layers of photovoltaic cells such as TiO_2 and PEDOT. The TiO_2 layer was identified in its anatase form and showed a nanorod-ordered formation. Bulk and nanowired PEDOT deposits were successfully prepared over the initial TiO_2 layer. In particular, PEDOT nanowire showed expected morphology and disposition as presented in past reports.

To use these electrodes in photovoltaics, a layer of N3 dye was added between the TiO_2 layer and the conducting polymer. The photocell architecture ITO | TiO_2 | N3 | PEDOT-nw | Al showed the best current density–potential performance during characterization, meaning that the use of a nanostructured heterojunction in multiple-layer solar cells improves the overall performance.

5. Patents

The authors applied for an international patent called "Electrosynthesis of polymeric nanowires directly on solid surfaces (electrodes)", with application numbers PCT/CL2018/050116 and reference 273176-WO.

Supplementary Materials: The following are available online at https://www.mdpi.com/2079-4991/11/1/107/s1, Figure S1: X-Ray diffractograms of ITO | TiO2 electrodes prepared by potential step of −1.100 during: (A) 60; (B) 180; (C) 300, and (D) 600 s; Figure S2: XPS analysis of ITO | TiO2 electrodes prepared by potential step of −1.100 V during 300 s: (A) Scan interval; (B) Maximum level of Ti 2p, and (C) Core level; Figure S3: Mott-Schottky graphics measured at 1 kHz: (A) TiO2; (B) PEDOT, and (C) PEDOT-nw obtained in absence of light. Graphics of (hν α L)2 vs. hν of: (D) TiO2; (E) PEDOT, and (F) PEDOT-nw; Figure S4: Energy diagram of (A) ITO | TiO2 | N3 | PEDOT and (B) ITO | TiO_2 | N3 | PEDOT | PEDOT-nw.

Author Contributions: Methodology, formal analysis, investigation, and writing-original draft preparation, A.M.R.; supervision, formal analysis, and investigation, L.C., J.-C.B. and F.R.D.; formal analysis, data curation, and writing-original draft preparation, M.A.G.; conceptualization, investigation, writing-review and editing, funding adquisition, and project administration, M.A.d.V. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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