PEDOT Nanotube Arrays as High Performing Counter Electrodes for Dye Sensitized Solar Cells. Study of the Interactions Among Electrolytes and Counter Electrodes

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Dye sensitized solar cells (DSCs)[1] have received an increasing attention in the last two decades as efficient alternative to low cost photovoltaic devices. In DSCs a molecular dye is used for light harvesting. Photoexcited electrons are injected into a nanostructured wide bang gap semiconductor (i.e. TiO_2, ZnO). The oxidized dye is regenerated by the donor species of a redox couple solved in an electrolyte. Finally, the electrolyte is regenerated in turn at the counter electrode by the complementary redox reaction. To maximize the solar cell performance, each part of the device has to be optimized, from the nanostructured electrode to the counter electrode (CE). The most commonly utilized CE for DSCs is platinized transparent conductive oxide. Pt acts as a catalyst for the reductive reaction with the I^-/I_3^- redox couple that takes place at the CE. Nowadays, big effort is being carried out to replace the platinum by other CEs that are more versatile (including flexible DSC applications) and inexpensive.[2–4] In this communication, we demonstrate that nanostructured poly(3,4-ethylenedioxythiophene) (PEDOT) nanotube (NT) arrays **(Figure 1)** improve the counter electrode efficiency compared with their dense and flat counterparts. Furthermore, PEDOT NT counter electrodes present a performance comparable with platinized CE, or even better depending of the employed electrolyte. The resulting power conversion efficiencies of 8.3% is to our best knowledge the highest efficiency achieved for a PEDOT CE so far. The main effect of a good CE on the final performance of a DSC is a series resistance that affects the cell fill factor (FF).[5] However, bad performing counter electrodes can limit the solar cell photocurrent and photovoltage.[5] In this work, we argue that the contribution of the CE to the series resistance occurs in two ways: i) by a charge transfer resistance at the counter electrode, R_{CE}, and ii) by an ohmic layer resistance that contributes to the total contact resistance, R_S. We observe that R_{CE} resistances depend on the type of CE and on the type of electrolyte, while the presence of PEDOT increases R_S independently of the electrolyte. Recently, very promising results have been reported for DSCs using alternative redox couples.[6–8] Grätzel announced a record efficiency with a Co-redox of 12.3%.[9] In this paper, we show that the optimization of the counter electrode material depends on the electrolyte and we study how the CE performance can be properly analyzed. These results might have some important implications in the optimization process of CEs for different electrolytes.

Different kinds of CEs have been studied for DSCs: platinum, graphite, activated carbon, carbon black, single-wall carbon nanotubes, PEDOT, polypyrrole, and polyaniline.[3,4,10–14] In general, the best performances were obtained for platinized electrodes. Carbon electrodes and carbon derivative CEs are extensively employed in industrial applications of DSCs, in spite of their lower performances but due to their reduced costs.[15] On the other hand, polymer based composite films also present a very attractive type of low cost CE materials as they can be easily integrated into flexible devices.[3,14] Among these materials, PEDOT is especially interesting due to its high stability, electrical conductivity and catalytic capability.[2,8,11–14] Very recently, it has been shown that the performance of CEs can be improved by the addition of carbon nanotubes into the PEDOT CE[13] or by the introduction of nanostructures into the CE.[2] However, CEs based on ordered one-dimensional PEDOT nanostructures have not been explored yet. In this work, we applied PEDOT NT array electrodes[16] which exhibited a higher performance than flat PEDOT CEs due to their higher effective area.

Two sets of electrodes, in the following named A and B, were prepared and sensitized with N719 dye. Both sets were manufactured with two different layers of TiO_2, a transparent and a scattering layer. The TiO_2 electrodes showed a total thickness of 19 and 12 μm for A and B cells, respectively. Solar cells prepared with A electrodes were filled with a I^-/I_3^- redox electrolyte (E-A) in acetonotrile:valeronitrile (85:15 vol%). The B electrodes (E-B) were prepared with methoxypropionitrile as a solvent. The current-potential (J-V) curves obtained for both sets of cells assembled with different CEs are plotted in **Figure 2**. The solar cells' parameters extracted from these curves are indicated in **Table 1**.

The cells prepared with E-A exhibited a higher performance than the cells prepared with E-B. Photocurrent, J_{sc}, photovoltage, V_{oc}, and FF were higher for cells A than for cells B, independently of the CE. The lower J_{sc} and V_{oc} observed for the cells of

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COMMUNICATION

TiO$_2$ electrodes and dye sensitization: The general procedure for the preparation of the DSC devices, according to a sandwich-type structure, consisted in a double TiO$_2$ layer deposited on glass/FTO (Pilkington TEC15, ~15Ω/sq resistance) using the Screen printing technique. The resulting photo-electrodes were sintered at 450 °C and then immersed into a 0.04M TiCl$_4$ solution for 30 min at 70 °C followed by calcination at 450 °C for 30 min to obtain good electrical contact between the nanoparticles. After cooling to 40 °C, the electrodes were immersed into the dye solutions overnight. Two sets of electrodes were employed depending on the electrolyte used. For set A, the TiO$_2$ electrodes were prepared with a 12 μm thick (HT/SP Solaronix) +7μm thick scatter layer (WER4_O Dyesol), the photoelectrodes were sensitized for 24 hours in a N719 dye solution (0.5 mM N719 and 0.5mM of chenodeoxycholic acid as a coadsorbent in acetonitrile/tert-buthanol 1/1 (v/v)). For set B, the electrodes were prepared with a 8 μm thick (18NR-T Dyesol 20 nm) + 4 μm thick scatter layer (WER4_O Dyesol), sensitized for 16 hours in a dye solution (0.5 mM N719 in acetonitrile/tert-butanol (v/v = 1:1)). After the adsorption of the dye on the TiO$_2$ films, the working electrodes were rinsed with the same solvent used for the dye solution.

Cell assembling: The DSC devices were assembled with the CEs using a thermoplastic frame (Surlyn 25 μm thick). The electrolyte was introduced though a hole previously drilled into the working electrode and sealed afterwards. In all these cells the hole was not in the CE as in normal cells in order to avoid damage of the PEDOT film. The hole was introduced into the working electrode, before the deposition of the titania film. The prepared solar cells had a 0.2 cm^2 area, the masking solar cell 0.125 cm^2.

Electrode and cell characterization: The morphology of the samples was analyzed using a Scanning Electron Microscope (JSM-5500LV). *J–V* curves were measured using a solar simulator equipped with a 1000W ozone-free Xenon lamp and AM 1.5 G filter (Oriel), and the light intensity was adjusted according to an NREL-calibrated Si solar cell with a KG-5 filter to one-sun intensity (100 mW cm^{-2}). IS measurements were carried out under same illumination conditions than *J–V* curves, and different bias potentials that ranged from zero to open circuit voltage and frequencies between 1 MHz and 0.1 Hz, with an AC perturbation of 20 mV. Measurements were carried out with cell positioned on a reflecting metallic surface.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

[1] B. O' Regan, M. Grätzel, *Nature* **1991**, *353*, 737.

[2] S. Ahmad, J.-H. Yum, Z. Xianxi, M. Grätzel, H.-J. Butt, M. K. Nazeeruddin, *J. Mater. Chem.* **2010**, *20*, 1654.

[3] T. Miyasaka, *J. Phys. Chem. Lett.* **2011**, *2*, 262.

[4] T. N. Murakami, M. Grätzel, *Inorg. Chim. Acta* **2008**, *361*, 572.

[5] I. Hod, Z. Tachan, M. Shalom, A. Zaban, *J. Phys. Chemis. Lett.* **2011**, *2*, 1032.

[6] T. Daeneke, T.-H. Kwon, A. B. Holmes, N. W. Duffy, U. Bach, L. Spiccia, *Nat. Chem.* **2011**, *3*, 211.

[7] E. A. Gibson, A. L. Smeigh, L. L. Pleux, L. Hammarstrm, F. Odobel, G. Boschloo, A. Hagfeldt, *J. Am. Chem. Soc.* **2011**, *115*, 9772.

[8] H. Tian, Z. Yu, A. Hagfeldt, L. Kloo, L. Sun, *J. Am. Chem. Soc.* **2011**, *DOI: 10.1021/ja2030933*.

[9] Grätzel, M., HOPV11, 3rd international Conference on Hybrid and Organic Photovoltaics, Valencia (Spain), May **2011**.

[10] P. Joshi, L. Zhang, Q. Chen, D. Galipeau, H. Fong, Q. Qiao, *ACS Appl. Surf. Interfaces* **2010**, *2*, 3572.

[11] K. S. Lee, H. K. Lee, D. H. Wang, N.-G. Park, J. Y. Lee, O. O. Park, J. H. Park, *Chem. Comm.* **2010**, *46*, 4505.

[12] Y. Saito, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, *J. Photochem. Photobio. A: Chem.* **2004**, *164*, 153.

[13] J. Zhang, X. Li, W. Guo, T. Hreid, H. Hou, H. Su, Z. Yuan, *Electrochimica Acta* **2011**, *56*, 3147.

[14] J. M. Pringle, V. Armel, D. R. MacFarlane, *Chem. Comm.* **2010**, *46*, 5367.

[15] A. Hinsch, S. Behrens, M. Berginc, H. Bnnemann, H. Brandt, A. Drewitz, F. Einsele, D. Faßler, D. Gerhard, H. Gores, R. Haag, T. Herzig, S. Himmler, G. Khelashvili, D. Koch, G. Nazmutdinova, U. Opara-Krasovec, P. Putyra, U. Rau, R. Sastrawan, T. Schauer, Schreiner, S. Sensfuss, C. Siegers, K. Skupien, P. Wachter, J. Walter, P. Wasserscheid, U. Würfel, M. Zistler, *Prog. Photovoltaics: Research and Applications* **2008**, *16*, 489.

[16] M. Döbbelin, R. Tena-Zaera, P. M. Carrasco, J.-R. Sarasua, D. Mecerreyes, *J. Polym Sci: A* **2010**, *48*, 4648.

[17] F. Fabregat-Santiago, G. Garcia-Belmonte, I. Mora-Seró, J. Bisquert, *Phys. Chem. Chem. Phys.* **2011**, *13*, 9083.

[18] J. Halme, P. Vahermaa, K. Miettunen, P. Lund, *Adv. Mater.* **2010**, *22*, E210.

[19] F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo, A. Hagfeldt *Sol. Energy Mater. Sol. Cells* **2005**, *87*, 117.

[20] Y. I. Kharkats, H. Nielsen, J. Ulstrup, *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *169*, 47.

[21] S. Peulon, D. Lincot, *Adv. Mater.* **1996**, *8*, 166.

[22] R. Tena-Zaera, J. Elias, C. Lévy-Clément, I. Mora-Seró, Y. Luo, J. Bisquert, *Phys. Status Solidi A* **2008**, *205*, 2345.