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Solid state dye sensitized solar cells applying conducting organic polymers as hole conductors

Youhai Yu and Monica Lira-Cantu*

Centre de Investigaciò en Nanociencia i Nanotecnologia, Campus UAB, Edifici ETSE 2nd Floor. Bellaterra (Barcelona), E-08193, Spain.

Abstract

Solid-state dye sensitized solar cells (SSDSCs) applying mesoporous TiO_2 electrodes sensitized with Ru complex dye Z907 and conducting organic polymers as the hole transport material (HTM) are prepared. We employ the *in-situ* photo-electrochemically polymerization technique (PEP)[1-3] in order to obtain, in a single step, the conducting organic polymer on the TiO_2/Dye electrode. We developed a modification of reported method [2] which allows the polymer poly(3,4-ethylenedioxythiophene) (PEDOT) by different electrochemical techniques applying constant-voltage and constant-current methods. Polymer morphology and its influence on solar cell performance were studied. Overall conversion efficiency above 2% (AM 1.5, 100 mW cm^{-2}) was obtained.

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Keywords: dye sensitized solar cell; solid state; electrochemical; conducting polymer; PEDOT.

1. Introduction

Since the discovery of nanocrystalline Dye-sensitized solar cells (DSC) in 1991[4], great efforts have been taken in order to improve the performance of the DSC. Although efficiencies up to 12% have been reported for DSCs applying liquid electrolytes, several technological challenges must be overcome before DSC can reach large-scale production. A major problem for these systems is the application of liquid electrolytes (containing the iodine/iodide redox couple) and the technological issues associated with them like device sealing and solvent evaporation which limits device stability and lifetime. The substitution of the liquid electrolyte in DSC by solid or semisolid (gel) hole conductor materials have led to what is call as the solid-state dye-sensitized solar cell (ss-DSC). In recent years, researchers have developed several types of hole transport materials (HTM) to replace the iodine based liquid electrolyte. For example, the application of a kind of p-type inorganic semiconductor of a Cu(I)-based compound

* Corresponding author. Tel.: +34-93580185 3; fax: +34-93580185 3.
E-mail address: monica.lira@cin2.es.

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such as CuI or CuSCN[5,6] has shown the existence of imidazolium thiocyanate, a crystal inhibitor which can improve the cells' stability[7]. Moreover, the most promising results so far are related to the application of 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-spirobifluorene (spiro-OMeTAD) reported by the group of Grätzel[8,9]. Another possibility is the application of p-type organic semiconductors such as conducting organic polymers polypyrrole[10], polyaniline[11], polydiacetylenes[12], or poly(3-octylthiopehene)[13,14]. Among conjugated polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is proved to be a promising hole transport polymer (HTP) for ss-DSCs[12,15], because it has high transparency in the visible range with high conductivity and good stability at room temperature[16].

The first reports of using polypyrrole as hole conductor in 1997 by Prof. Yanagida[10]. In order to enhance the efficiency by improve the pore filling of HTM, his group developed a new technique called in situ photoelectropolymerization (PEP) where a careful design of the dye properties and the strategically selected monomer oxidation potential was taken into consideration as already described[15]. For this purpose, the monomer 2,2'-bis(3,4-ethylenedioxythiophene) (bis-EDOT) was employed in order to form the conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) by photoelectrochemical oxidation[1,15,17-19]. Promising results in their group demonstrated a >2% iodine-free ss-DSC efficiency by the application of the PEP technique together with the use of a novel hybrid Ru complex dye (HRS-1)[19], and already reach 2.8% recently[1]. In this work, we have modified the PEP method and have developed a new thin layer photo-electrolytic cell based on the modification of our previous reported method.[2] Our work aims for the synthesis of the polymers by different electrochemical techniques: constant-voltage[1-3] and constant-current[20] with the possibility to simplify the methodology and be able to improve reproducibility of the technique.

2. Experimental

2.1. Materials

Deoxycholic acid, lithium bis-trifluoromethanesulfonylimide (LiTFSI), 4-tert-butylpyridine (tBP) and Guanidinium thiocyanate (GSCN) were obtained from Aldrich and used as received. Cis-bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(2,2'-bipyridyl-4,4'-di-nonyl) ruthenium(II) (known as Z907), Nanoxide-T paste and 3-ethyl-1-methylimidazolium dicyanoamide (EMIDCA) were obtained from Solaronix, tertbutyl alcohol were purchased from Fluka, acetonitrile and ethanol were purchased from Panreac and used as received. H_2O was purified by distillation. 2,2'-Bis(3,4-ethylenedioxythiophene) (Bis-EDOT) was synthesized according to the literature method[21].

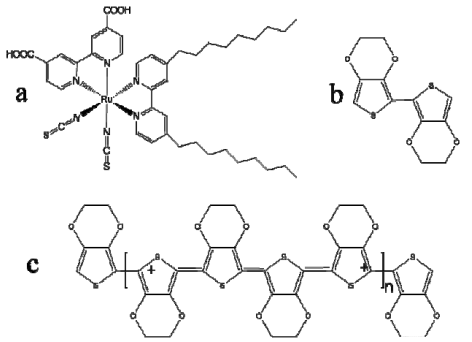

Figure 1. The chemical structures of Z907(a), bis-EDOT(b) and PEDOT(c).

2.2. Fabrication of nanoporous-TiO_2 electrodes

TiO_2 compact layer or blocking layer was prepared according to previous report[18]. The FTO glass (Nippon Sheet Glass, SnO_2:F, 10 ohm/sq) was first cleaned in a detergent solution using an ultrasonic bath for 20 min, and then rinsed with water and ethanol. After clean with a UV-O_3 system (PSD-UV, Novascan, IA, USA) for 20 min, A compact TiO_2 film was then deposited onto FTO substrate by span-coating. The FTO glass with compact TiO_2 film was annealed at 450 °C for 30 min in air. After cooling down, a film of nanoporous TiO_2 electrodes were prepared on the FTO from the colloidal Nanoxide-T paste (Solaronix) by doctor-blade techniques. The films were annealed at 450 °C for 30 min in air again. The resulting TiO_2 films were cut into pieces. Then, the electrodes were immersed into a 0.3 mM Z907 solution with 0.6 mM deoxycholic acid added as the co-adsorbent in a mixture of acetonitrile and tertbutyl alcohol (volume ratio, 1:1) and kept at room temperature for 20-24 h to assure complete sensitizer uptake. The dye-sensitized TiO_2 films were rinsed with acetone and dried under nitrogen before being used for PEP.

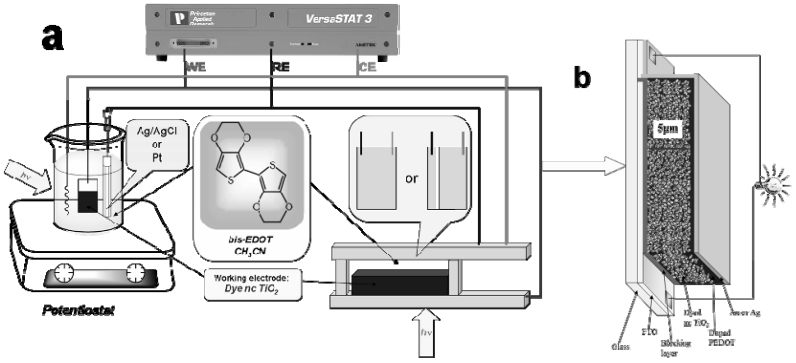

Figure 2. a: The scheme of four kinds of Photo-electrochemical Polymerization (PEP) of bis-EDOT. b: The structure of ss-DSC with PEDOT as HTM

2.2.1. Constant Voltage PEP.

Constant Voltage PEP was performed at a standard three-electrode electrochemical cell with Princeton Versa Stat 3 electrochemical working station (Figure 2a left part). The dye-sensitized TiO_2 film was used as a working electrode and a platinum foil as a counter electrode and Ag/AgCl electrode as reference electrode or Pt as pseudo-reference were employed. A concentration of 0.01 M bis-EDOT and 0.1 M LiTFSI in acetonitrile was used for the PEP. The PEP was achieved by applying the constant potential (+0.2 V vs ref)[1] under light irradiation of a 300 W Xe lamp (22 mW cm^{-2}, $\lambda > 520$ nm) for 20 min.

2.2.2. Constant Current PEP.

After applying a small drop of acetonitrile solution containing 35 mM bis-EDOT and 0.15 M LiTFSI onto the dye-sensitized TiO_2 photoelectrode, a piece of integrated or a divided conducing surface pyrolyzed Pt/FTO electrode was clipped with the dye-sensitized TiO_2 photoelectrode to assemble a thin layer electrolytic cell using parafilm as the spacer and sealant(Figure 2a right part). Filtered (> 520 nm) light of a 300 W Xe lamp (22 mW cm^{-2}), was used to illuminate the thin layer cell from the TiO_2/FTO side. The polymerization lasted for 1500 seconds with the current density maintained at 10 $\mu A/cm^2$ (Versa Stat 3).

After in-situ PEP, the resulting TiO_2/dye/PEDOT electrode was rinsed by acetonitrile and then dried. After that, 1 drop of EMIDCA with 0.2 M of tBP and 0.2 M of LiTFSI was added on the surface. The sandwich-type devices were finished by coated with a layer of silver paste(Figure 2b). Typical areas of the electrodes were around 0.20 cm^2.

2.3. Measurements

The light to power conversion efficiency of the the sealed type cells (sealed with thermal adhesive film (SX1170-25) and glass) were recorded using a computer-controlled source-measure-unit (Keithley 2601) under illumination of AM1.5 (1 Sun; 100 mW/cm^2) by using a Solarconstant 575 (Steuernagel, Germany) and respective AM 1.5 filters.

The incident photon to current conversion efficiency (IPCE) was measured by using a QE/IPCE Measurement Kit (QE-PV-SI, Newport). The scanning electron microscopy images were taken using Hitachi Model S-570 SEM at 20 kV beam voltage.

3. Results and discussion

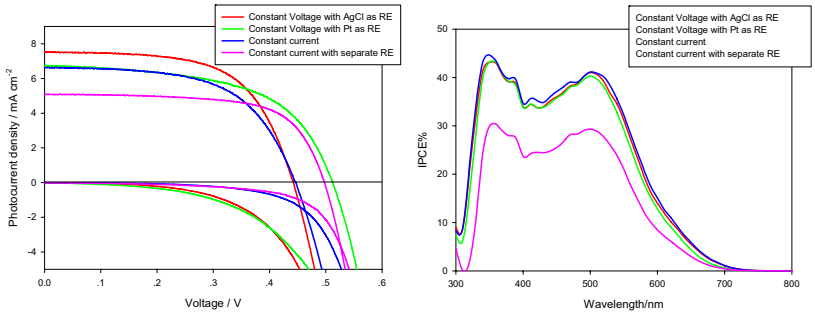

Figure 3. Photocurrent-voltage characteristics and ICPE spectra for ss-DSCs applying PEDOT as HTM.

Table 1. Performance of ss-DSCs with different PEP methods and solar cell performance observed.

Method	V_{oc}(V)	J_{sc}(mA)	ff	η(%)
Constant Voltage & Ag/AgCl as RE	0.444	7.52	60.8	2.03
Constant Voltage & Pt as RE	0.510	6.75	56.9	1.96
Constant Current	0.447	6.64	57.9	1.72
Constant Current & separate RE	0.497	5.08	66.9	1.69

Here we have compared four kinds of in-situ PEP methods. Figure 3 show the photocurrent-voltage curves and the corresponding IPCE spectra of the PEDOT ss-DSCs of four kinds of PEP method. For comparison purposes Table 1 shows detailed solar cells parameters obtained for each case. As seen from table 1, the ss-DSCs with PEDOT as HTM gave a good overall conversion efficiency about 2% at AM 1.5 illumination (100 mW cm^{-2}).

The typical SEM images of the photoelectrode before and after PEP are shown in Figure 4. The changes in the surface morphology indicate that a PEDOT layer has been polymerized on the dye-sensitized photoelectrode. we can see almost all the surface were covered with PEDOT polymer and the surface morphology of all four kinds of PEP method were almost the same, and the overall conversion efficiency of the cells made from them also show the similar result. It indicated that all the technique were successful. In constant-voltage method we have used Pt as pseudo-reference and we found it also works as well as Ag/AgCl electrode. It means we can simplify the constant-voltage PEP method by avoiding the frangible Ag/AgCl electrode or simile reference electrode. As compared to the method of using a three-electrode system for PEP of bis-EDOT under a constant voltage, using constant-current method with a thin layer electrolytic cell only need a small quantity of bis-EDOT solution for polymerization. It is very economical for commercial production. Another advantage is the thin layer cell can be easily sealed to separate

air and prevent evaporation of the electrolyte during polymerization and the thin layer cell can generate the parallel electric field easily, which is beneficial to the formation of a PEDOT layer with even thickness.

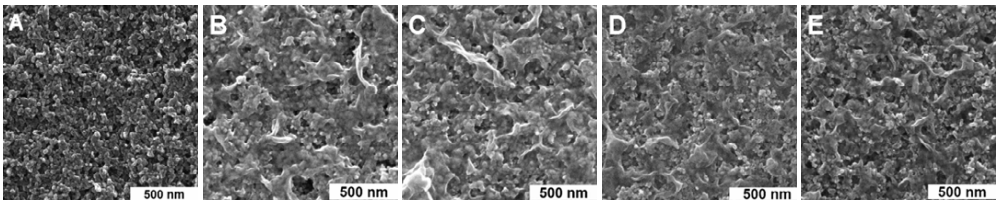

Figure 4. SEM image of Z907 dye-sensitized TiO_2 photoelectrode before (A) and after (B-E) polymerization to form a PEDOT layer. B) Constant Voltage & Ag/AgCl as RE. C) Constant Voltage & Pt as RE. D) Constant Current. E) Constant Current & separate RE.

4. Conclusions

The initial results shown here support that we have successfully developed a new thin layer photo-electrolytic cell based on the modification of in-situ photo-electrochemically polymerization technique which allow us to synthesize the polymers by two electrochemical techniques: constant-voltage and constant-current. We employed four kinds of PEP method to fabricate poly(3,4-ethylenedioxythiophene) (PEDOT) based iodine-free SSDSSCs. By applying Ru complex dye Z907 as the sensitizer, the light response of around 2%(η) at AM 1.5 illumination (100 mW cm^{-2}) for all ss-DSSCs were reached. From the SEM images we can see not all the pores of the TiO_2 nano-paticles were filling with PEDOT, we believe that we can improve the ss-DSCs performance with the optimization of PEP condition. Further efforts such as change other kinds of dye or polymer, preparing more porous TiO_2 films, and optimizing the PEP condition are in progress.

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