Volatile solvent-free solid-state polymer-sensitized TiO$_2$ solar cells with poly(3,4-ethylenedioxythiophene) as a hole-transporting medium

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Novel, volatile solvent free, solid-state solar cells were fabricated with mesoporous TiO$_2$ electrodes sensitized using thiophene derivatives containing carboxyl groups and *in situ* electropolymerized poly(3,4-ethylenedioxythiophene) as a hole-transporting material together with the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide and lithium bis(trifluoromethanesulfone)imide as additives for charge transport promotion

Dye sensitized photo-electrochemical solar cells (DSCs) based on wide band gap nanoporous oxide semiconductors are of great interest as some of them have shown efficiencies comparable to their silicon counterpart.[1,2] However, all theses devices generally consist of expensive sensitizers such as ruthenium(II) polypyridyl complexes (with carboxylated ligands) and electrolytes with volatile solvents.[1,2] These factors, especially the fact that the liquid electrolyte causes significant technological problems associated with device sealing and stability, affect the commercial application of DSCs. Therefore, there is considerable interest in both the development of a solid-state electrolyte for these devices and replacement of expensive dyes with inexpensive and readily available materials.[3–5] In this context, inexpensive conductive polymer materials (CP), which behave either as sensitizers or hole-conductors, are of practical interest as possible replacements for the liquid electrolyte and the sensitizers in these devices.[4–17] However, one of the challenges in devising DSCs with CPs is the identification of suitable polymers with the requisite properties, such as appropriate band gaps, band positions, and methods for their deposition. Deposition techniques need to ensure firm and permanent contact of the hole-conducting polymer with the sensitizing polymer surfaces and also good intermolecular contacts. Recently we succeeded in the fabrication of DSCs comprising carboxyl groups bearing CPs, poly(3-thiophenyl acetic acid) (P3TAA) and poly(3-thiophenyl malonic acid) (P3TMA) as sensitizers.[17,18] The polymers were thus covalently attached onto TiO$_2$ nanoparticles *via* the carboxylic groups, which enable the necessary electronic coupling between the polymer and the semiconductor surface, leading to a satisfactorily high photo conversion efficiency. However, sensitizing either by P3TAA or P3TMA did not work as hole-transporting materials. Taking into account the poor conductivity of these polymers, we successfully attempted to fabricate a volatile solvent free solid-state solar devices (SSSD) comprising of either P3TAA or P3TMA as

sensitizers for TiO$_2$ and another CP, poly(3,4-ethylenedioxythiophene) (PEDOT) as the hole-conducting material together with ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (EMImTf$_2$N) and lithium bis(trifluoromethanesulfone)imide (LiTf$_2$N) as additives to promote the cell performances. PEDOT was selected due to its universal properties such as higher mobility, stability and transparency in the visible light region compared to the other hole-conducting polymers. To the best of our knowledge such a device has not yet been reported in the literature. Therefore this study indicates that thiophene derivative conducting polymers can be used effectively as sensitizers and hole-conductors in SSSDs showing the highest efficiencies ever published for volatile solvent free polymer sensitized solar cells.

In the fabrication of an SSSD, short-circuiting of the cell is often observed when using solid-state hole-transporting materials. In order to avoid this, dense (compact) $\sim$100 nm thick films of TiO$_2$ were coated on fluorine-doped conducting tin oxide (FTO) glasses (sheet resistance $\sim$16 Ω square^{-1}) as reported elsewhere.[16] Mesoporous TiO$_2$ films were then deposited on this compact layer by the "doctor blade" method using a TiO$_2$ paste from Solaronix nanoxide (Solaronix T) and then sintered at 500 °C for 1 h. The thickness of the TiO$_2$ electrodes were found to be $\sim$4–5 µm (Dektak profilometer (Veeco, Dektack 3). P3TAA (Mw = 1.7 × 10^4 g mol^{-1}) (MALDI-TOFMS Shimadzu Axima-CFR) and P3TMA (Mw = 1.0 × 10^4 g mol^{-1}) were synthesized by methods described elsewhere[15–19] starting from their monomers and confirmed by ^{1}H NMR (JEOL EX-270, 270 MHz) and IR (Perkin Elmer system 2000 FT-IR). Polymers were then dissolved in dimethyl sulfoxide and the optical absorption spectra of the solutions were obtained from JASCO (V-570) UV-Vis-NIR spectrophotometer. The electrodes were then dipped in the polymer solutions at least for 48 h, washed with dried ethanol and dried under N$_2$ and used as the working electrode in the polymerization cell. *In situ* photoelectrochemical polymerization of PEDOT was carried out in a standard three-electrode quartz cell equipped with a Ag/AgCl reference electrode and a Pt counter electrode filled with 0.1 M LiClO$_4$ acetonitrile solution containing the dimer, (0.01 M bis-EDOT) under potentiostatic conditions. The working electrode was illuminated with 500 W Xe lamp (λ > 390 nm) during the polymerization. The potential of the TiO$_2$ electrode was maintained at +200 mV *vs.* Ag/AgCl for 5 min (25 mC cm^{-2}). After the polymerisation electrodes were rinsed with dimer free 0.1 M LiClO$_4$ acetonitrile solution and dried under a N$_2$ atmosphere. Since the imidazolium salts improve the electronic properties of π-conjugated polymers and also the imidazolium cations are indispensable for the effective electron

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diffusion in nanoporous TiO_2 electrodes,[16–18,20,21] the PEDOT coated electrodes were then treated with ionic liquid, 0.2 M $LiTf_2N$ in $EMImTf_2N$ for 24 h. Then the solutions of ionic liquid on the electrode surfaces were wiped off and thin layers of graphite (C) were applied onto the wiped electrodes. The electrodes with and without graphite layers were then topped with FTO glasses coated with a thin layer of gold as the counter electrode (Fig. 3) and the cell performances were measured (poor contacts between the gold plated FTO glass and the PEDOT limit the photocurrent to several microamperes). The painting of the outer surface of the electrodes with graphite drastically enhanced the performances of the devices both in the dark and under illumination. Current–voltage measurements were performed using a computer controlled voltage current sourcemeter (R6246, Advantest) under standard solar irradiation of 100 mW cm^{-2} (AM1.5) (solar simulator, YSS-50A, Yamashita Denso) at 25 °C. The incident photon to current conversion efficiency (IPCE) was estimated using a commercial set-up for IPCE measurement (PV-25DYE, JASCO) under 5 mW cm^{-2} monochromatic light illuminations. In order to characterize the physical properties of PEDOT, polymerization was carried out on FTO glasses by electropolymerization under the same conditions as in the previous case. After the polymerization PEDOT films were removed from the FTO using double-sided adhesive tapes[22,23] and the conductivity measurements were performed by the four-probe conductivity measuring method.

The current–voltage (I–V) characteristics of the cells, fabricated with $\sim$5 µm thick TiO_2 films sensitized by different polymer dyes in the dark and under illumination are shown in Fig. 1. Curves (a) and (b) show the dark I–V characteristics of the cell sensitized with P3TMA (TiO$_2$/P3TMA/C/PEDOT) before and after the insertion of additives. Curves (c) and (d) show the same characteristics of the cell sensitized with P3TAA (TiO$_2$/P3TAA/C/PEDOT) before and after treatment with additives respectively. The curves (e) and (f) show the photoresponses of the above treated cells sensitised either
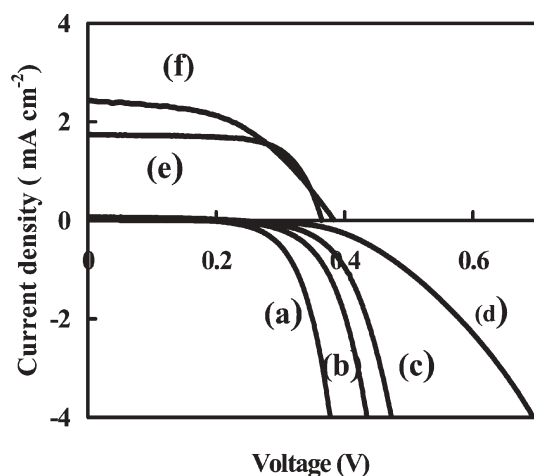
with P3TMA or P3TAA respectively, under an illumination of 100 mW cm^{-2}.

The corresponding values (average of five) obtained for the main cell parameters such as short-circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and the overall efficiency (η) of the cell sensitized with P3TAA (Fig. 1, curve (f)) are $\sim$2.5 mA cm^{-2}, 365 mV, 0.54 and 0.50%. The corresponding values of the cell sensitized by P3TMA (Fig. 1, curve (e)) are 1.75 mA cm^{-2}, 385 mV, 0.62 and 0.42% respectively. As is evident, better performances can be achieved with P3TAA than the P3TMA. However, significant improvements in the dark and photo characteristics of these cells were observed with the additives. One of the reasons for this improvement could be associated with the prevention of short-circuiting between PEDOT and the conducting glass where TiO_2 was deposited. Further the improvement of the surface contacts between the polymer dyes and the PEDOT might have also contributed to this enhancement. Especially the ionic liquid $EMImTf_2N$, possibly can improve the physical properties of both polymer dyes and PEDOT resulting in better cell performances.[20] To our knowledge, these values are the first and highest obtained so far for solar cells consisting of the thiophene polymers as sensitizers and another thiophene polymer as a hole-conductor.[13,14] Since the parameters of the cell assembly have not yet been optimized, further improvements are presently being investigated especially for V_{oc} and structures of labyrinthine TiO_2 layers for polymeric molecules. The average value of the conductivity of PEDOT polymerized on FTO under the same conditions was about 15 ($\pm$05) S cm^{-1}. This value is very much higher than that of the I^-/I_3^- in the liquid electrolytes used in the DSCs.[21] Therefore, the efficiencies of the cells could be improved by optimizing the aforementioned factors.

Photocurrent action spectra of the cells and UV-visible absorption spectra of polymer dyes in DMSO are depicted in Fig. 2. While the absorption spectrum of the P3TAA (curve (a)) showed an intense absorption at $\sim$418 nm, P3TMA showed an intense band at $\sim$435 nm (curve (b)). As shown in curve (c) the IPCE versus wavelength for the TiO$_2$/P3TAA/C/PEDOT cell has a maximum around 425 nm with $\sim$15% IPCE and the cells having

Fig. 1 Current–voltage (I–V) curves of the polymer sensitized photocell with PEDOT. Dark I–V of TiO$_2$/P3TMA/C/PEDOT before (a) and after (b) treatment with additives, and the photoresponse (e) of the cell. Corresponding curves of the cell TiO$_2$/P3TAA/C/PEDOT before (c) and after (d) treatment with additives, together with the photoresponse (f) of the same cell.
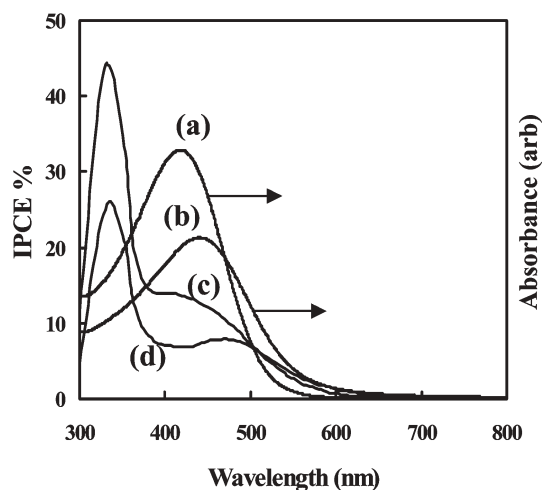

Fig. 2 UV-visible absorption spectra of P3TAA (a) and P3TMA (b) in DMSO, and the IPCE spectra of TiO$_2$/P3TAA/C/PEDOT (c) and TiO$_2$/P3TMA/C/PEDOT (d).
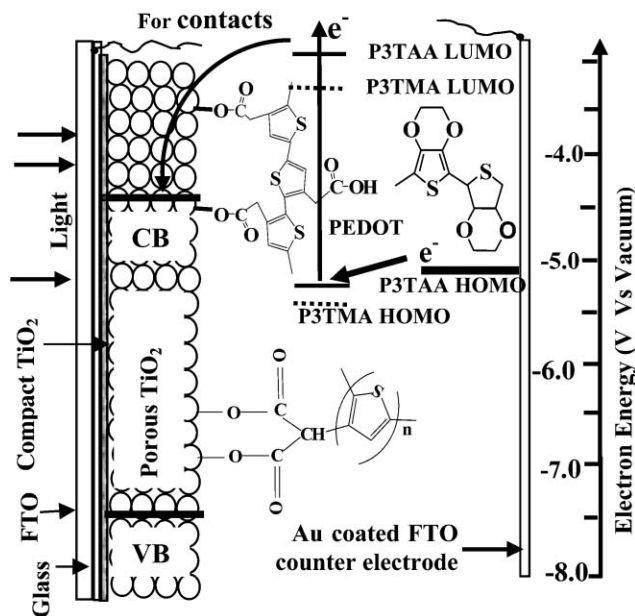
Fig. 3 Schematic diagram of the construction of photocells with polymers and energy level diagram of the materials involved.

P3TMA electrodes showed nearly ~10% maximum IPCE around 470 nm as shown in curve (d). All measured IPCE values were not corrected for the loss of incident light due to absorption and reflection by the conducting glass support. However, the close relationship and the red shifts of the action spectra with the optical absorption spectra reveal that the junctions between the polymers and the semiconductor are responsible for the photocurrent generation and also the chemical attachment of the polymers to the semiconductor.

The possible electron-transfer processes and the relative band positions of the materials employed are shown in Fig. 3. The HOMO and LUMO levels of P3TAA estimated from the oxidation potential and the band gap (π–π*) value are situated as shown at ~-5.27 eV and ~-2.951 eV vs. vacuum respectively. The corresponding values for P3TMA are evaluated to be at -5.49 eV and -3.34 eV on the same scale respectively. As reported in the literature, the conduction band (CB) of TiO$_2$ and the HOMO level of the PEDOT are situated at ~-4.4 V and ~-5.1 eV vs. vacuum respectively.[1,2,22] It should be noted that it is very difficult to evaluate the doping level and the redox potential of the PEDOT in the voids of TiO$_2$ films.

However, upon illumination polymers which are attached covalently to the TiO$_2$ electrodes transfer electrons to the conduction band of TiO$_2$, while the holes transfer to the valance band of the PEDOT possibly through the stacking of thiophene groups, thus producing a respectable photocurrent through an external circuit.

In conclusion we have successfully constructed a pseudo-cell of the "Grätzel-type" DSCs employing polymer sensitizers bearing carboxylic groups. The methodology we have demonstrated here would lead to the use of conducting polymers in solar cells more effectively.

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