Utilization of conducting polymer as a sensitizer in solid-state photocells

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Solvent-free, solid-state solar cells were fabricated with mesoporous TiO$_2$ sensitized by electronically conducting polymer; poly(3-thiophenylethenedicarboxylic acid) (P3TAA) and reasonably high photocurrents were observed for the first time in polymer sensitized solid-state photovoltaic devices. When CuI was employed as the hole transporting material together with an ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide (EMImTf$_2$N) and LiTf$_2$N as additives for charge transport promotion, the cell TiO$_2$/P3TAA/Cul delivered a respectable short circuit photocurrent of ~1.2 mA cm$^{-2}$ with an open-circuit voltage of ~275 mV under the irradiance of 100 mW cm$^{-2}$ (1.5 Air Mass).

*DYE-SENSITIZED mesoporous TiO$_2$ photoelectrochemical solar cells (DSC) emerged recently as legitimate alternati-
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tives to conventional photovoltaic devices. The highest efficiency reported for this device is around 10% under AM 1.5 (100 mW cm⁻²) radiation. Although the DSCs show such a good performance, it has not yet found significant commercial applications because of problems like evaporation of the electrolyte, stability or degradation of the electrolyte or dye. Many efforts were directed towards improving the stability by replacing the liquid electrolyte by a polymer gel electrolyte, or by organic or inorganic hole conductors. Additionally, investigations were widened to test different sensitizers like ruthenium complexes, coumars. The best performing sensitizers were carboxyl group-bearing Ru complexes such as cis-dithiocyanato(4,4'-dicarboxy-2,2'-bipyridine) ruthenium(II). However, from the point of view of cost reduction and mass production of DSCs, ruthenium dyes have several disadvantages, such as their high cost and long-term non-availability. In this context, owing to their high light absorption coefficient in the visible part of the spectrum and the high mobilities of charge carriers, conjugated polymer (CP) films are promising candidates for application in molecular opto-electronic devices. Even though many researchers have demonstrated the possibility of making p-n heterojunctions between CPs and inorganic semiconductors, little work has been done to demonstrate these CPs as photo-sensitizers ('dye' molecules) in the TiO₂ devices with respectable performances. Our strategy towards higher efficiencies in these conjugated polymer sensitized TiO₂ solar cells is the improved surface contacts between the sensitizing polymer molecules and the mesoporous TiO₂ surface. In this context, poly(3-thienylacetic acid) (P3TAA) is one of the promising candidates having COOH groups covalently bound to the polymer which enable the necessary electronic coupling between the polymer and the semiconductor surface. As a result of visible light absorption, dye species (polymer) are electronically excited resulting in efficient electron transfer from the carboxylic groups to the semiconductor. On the other hand, use of some ammonium salts like imidazolium salts, particularly in polymers, have attracted much attention as ionic liquids in the improvement of physical properties of the CPs. By taking into account these factors, we successfully attempted to fabricate volatile solvent-free quasi-solid solar device comprised of P3TAA as the sensitizer for TiO₂ and the well-known inorganic hole conductor CuI as the hole conducting material together with ionic liquid 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)amide (EMImTf₂N) and LiTf₂N.

P3TAA was synthesized according to the methods described elsewhere. Formation of P3TAA was confirmed by 'H NMR (JEOL EX-270, 270 MHz); in DMSO, δ 12.53 ppm (s, -COOH, 1H), 7.49–7.28 ppm (m, thiophene ring proton, 1H), 3.78–3.35 ppm (m, thiophene ring –CH₂–, 2H) and FT-IR (Perkin Elmer system 2000 FT-IR) spectra: (Kbr, cm⁻¹) 3400–2400 (OH, carboxylic acid), 1624 (υC–H, thiophene ring), 2890 (υC–H, aliphatic), 1696 (υC=O, carboxylic acid), 1621 (υC–O), 832 (υC–H out of plane, thiophene ring). Since nano-structured electrodes used in the DSCs with electrolytes meet some difficulty on using in solid-state DSCs, specially due to the penetration of hole conducting materials through nano-size voids to the bottom of the porous photo-electrode, it is necessary to use a compact layer to avoid unnecessary short-circuiting of the cells. Therefore, compact and thin TiO₂ layer was first applied on glass substrates having F-doped SnO₂ conducting layer (FTO, 16 Ω sq⁻¹) using an ethanolic solution of titanium tetra-1-methylethoxide (Ti(O’Pr)₄) containing a few drops of HNO₃ (pH = 2) by spin-coating at 1000 rpm for 1 min. The films were then sintered at 500°C for 1 h and cooled down to the room temperature. The above procedure was then repeated to obtain ~100 nm thick denseless porous compact TiO₂ layer. Mesoporous films of TiO₂ were deposited on the above substrates by the following method. TiO₂ (Nippon Aerosil P-25, 0.5 g) was added to a mortar containing 50 drops (2 ml) of acetic acid and ground well for 1 min. Then, 0.5 ml of titanium tetra-1-methylethoxide (Ti(O’Pr)₄) was added. Mixture was ground and 0.1 ml of deionized water was added to the above mixture. Surfactant Triton X-100 (Aldrich) was then added (0.1 ml) and the mixture was ground thoroughly. Ethanol (100 ml) was then added to the mixture and sonicated for 10 min. Finally the solution was further diluted by ethanol (1 : 4 v/v) and sprayed onto a preheated FTO-coated glass with the compact TiO₂ layer placed on a digital hotplate at 300 ± 5°C. The electrodes were then sintered at 500°C for 1 h.

P3TAA was dissolved in dimethyl sulphoxide (DMSO). TiO₂ electrodes were then immersed in polymer solution for 48 h. The dyed electrodes were then rinsed with ethanol and dried under N₂. Junction properties of TiO₂/P3TAA were tested by sandwiching these electrodes with a gold-plated FTO. However, sensitizing by P3TAA did not work as the hole transporting material. CuI deposition on the dyed electrodes was carried out as follows: A solution of CuI was prepared by dissolving 0.3 g of CuI in 10 ml of moisture-free acetonitrile. The dye-coated electrodes were placed on a hot surface (80–100°C) and filtered CuI solution was lightly spread over the dyed film using a dropper. This process was repeated until all the pores were filled and the thickness of CuI extended up to ~6 μm. The electrical contact to the CuI was made by pressing a gold-coated FTO glass plate onto the CuI surface.

To improve the electron diffusion of TiO₂ and at the same time to see the effect of ionic liquid on CuI, 0.2 M LiTf₂N in EMImTf₂N (1.7 mg/ml) was added to CuI solution and spread on the TiO₂ electrodes as in the previous case. A schematic diagram illustrating the construction of the cell is shown in Figure 1a. Photo-energy conversion efficiency was evaluated using the standard solar irradiation of 100 mW cm⁻² (AM 1.5) with a solar simulator.
(YSS-50 A, Yamashita Denso) and a computer-controlled voltage current sourcemeter (R6246, Advantest) at 25°C. The power conversion efficiency (η) was calculated according to the following equation: η% = FF × Jsc × Voc/I, where Jsc is the short circuit photocurrent density in A cm⁻², Voc is the open circuit voltage in V, I is the intensity of the incident light in W cm⁻² and FF is the fill factor defined as FF = JscVoc × Voc/I. Jsc and Voc values are maximum photo current and voltage that can be extracted from the maximum power point of the I–V characteristics.

Figure 1b shows the I–V characteristics of the cell measured under illumination. The cell TiO₂/P3TAA/Cul delivered a short circuit current density of ~1.2 mA cm⁻² (Jsc), with an open-circuit voltage (Voc) of ~275 mV, under the irradiance of 100 mW cm⁻² (AM 1.5). The average energy conversion efficiency and the fill factors were ~0.2% and 0.45 respectively. The ionic liquid treatment to the solution of Cul significantly improved the cell performances in dark and an illumination condition resulting in the increase of fill factor and the Jsc. Therefore, the addition of LiTf₂N in EMLmTf₂N into the cell could have formed an electrical double layer at FTO/Cul or P3TAA/CUL at both the interfaces avoiding the inauspicious contact of the Cul at these interfaces which cause electron recombination in the cells. On the other hand, as reported by Lu et al., addition of ionic liquids improved the physical properties of conducting polymer P3TAA resulting in good performances in the device. The efficiency is not comparable to the ruthenium dye-sensitized solar cells, because of differences in light harvesting efficiency. However, to our knowledge, these values are the highest obtained so far in the solar cells consisting of a polymer as the sensitizer and inorganic semiconductor as a hole conductor. Since the parameters of the cell assembly have not yet been optimized, further improvements are presently being investigated especially for Voc and structures of labyrinthine TiO₂ layers for polymeric molecules.

Figure 2 shows the absorption spectrum (arbitrary units) of P3TAA (curve a), the action spectrum (curve b) and IPCE of the cell (curve c) TiO₂/P3TAA/Cul. The absorbance of P3TAA shows a peak around ~420 nm. The IPCE of the cell shows as high as ~8% (at 450 nm). (The peak around 350 nm originates from the direct band gap excitation of TiO₂) The IPCE spectrum of the cell resembles the absorption spectrum of the P3TAA, confirming the sensitization by the P3TAA. The rapid recombination of the carriers (i.e. electrons in the TiO₂ and the holes in the Cul) might be one of the reasons for this low IPCE.

The possible electron-transfer processes and the relative band positions of the materials employed are shown in Figure 3. The lowest unoccupied molecular orbital level
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(LUMO) of P3TAA estimated from the oxidation potential and the band gap (π-π*) value are situated \( \sim -2.95 \) eV vs vacuum. As reported in the literature, the conduction band (CB) of TiO₂ and the valence band level of CuI are situated at \( \sim -4.2 \) eV and \( \sim -4.85 \) eV vs vacuum respectively.\(^{2,10,16}\) Therefore, upon illumination a majority of the excited dye molecules attached covalently to the TiO₂ electrode transfer electrons to the conduction band of TiO₂, while the holes are transferred to the valence band of the CuI, thus producing a respectable photocurrent through an external circuit.

In conclusion, we have successfully constructed and demonstrated the possibilities of fabrication of volatile solvent-free polymer-sensitized solar cells composed of chemically attached thiophene polymer to an inorganic semiconductor TiO₂ with CuI as the hole transporting material. Even though these values are far from practical applications, we believe that the methodology demonstrated here would lead to the use of conducting polymers in solar cells more effectively.


Received 4 March 2004; revised accepted 14 June 2004

Induction of oxidative stress and ultrastructural changes in moss Taxithellum nepalense (Schwaegr.) Broth. under lead and arsenic phytotoxicity

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Changes in physiological, biochemical and ultrastructural level under lead (Pb) and arsenic (As) phytotoxicity were investigated in moss, Taxithellum nepalense. Decrease in dry matter and total chlorophyll was observed in moss under metal treatment. Increase in lipid peroxidation, hydrogen peroxide and superoxide anion radical were visible under Pb compared to As. Accumulation of Pb was found to be maximum compared to As. An increase in superoxide dismutase activity with a concomitant decrease in catalase, peroxidase and glutathione reductase activity was recorded. Both ascorbate and glutathione accumulated to a greater extent under Pb treatment in moss. A distortion in thylakoid ultrastructure in moss chloroplast was noticed under Pb compared to As and control.

THE living organism possesses the ability to withstand specific quantity of essential and non-essential elements present in the environment, and utilize them for their growth and development. These elements are toxic if taken up at a higher concentration than required. In contrast to the essential elements which serve as metabolic resources for plants, the non-essential elements do not have any known metabolic function. Non-essential elements are grouped together into one major category termed as heavy metals. Heavy metals are the integrated component

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