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Enhanced photoresponses of polypyrrole on surface modified TiO_2 with self-assembled monolayers

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Abstract

Photodevices comprising covalently grafted polypyrrole films on surface modified mesoporous TiO_2 substrates via 3-(trimethoxysilyl) propyl methacrylate were fabricated and tested their performances with a counter electrode having a thin layer of gold. Significant photoresponses were observed with the addition of an ionic liquid, l-ethyl-3-methylimidazolium bis-trifluoromethylsulfonyl amide containing 0.2 M LiTf2N and painting a layer of graphite on the surface of PPY. The cell TiO_2/PPY-C/Au cell delivered a short circuit current of ∼600 $\mu A\,cm^{-2}$ with an open circuit voltage of ∼500 mV under the irradiation of 100 $mW\,cm^{-2}$ (AM 1.5). The average corresponding fill factors and the efficiencies were 0.51 and ∼0.2%, respectively.

Keywords: TiO_2; Polypyrrole; Solid-state photocells; Hole transport materials

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1. Introduction

Dye sensitized solar cells (DSC) based on high band-gap semiconductors namely with TiO_2, have been showing great promises as a low cost method of converting light to electricity with overall efficiency exceeding 10%. Generally, these DSCs based on the solar excitation of ruthenium dyes, followed by injection of electrons into the conduction band of the semiconductor, which the dye is attached. To complete the charge transfer mechanism, these DSCs consist with a redox couple usually iodide/triiodide in an electrolyte which regenerates the oxidized dye. The oxidized state of the redox couple is subsequently reduced at the counter electrode [1–4]. Although these DSCs are promising in terms of power efficiencies, still there are some problems to be addressed. Some of the disadvantages of these cells, which limits their practical applications, are use of expensive dyes and the liquid electrolyte containing volatile solvents [5–20]. Therefore, numerous efforts have been done to search for suitable new materials as sensitizers and also to solidify the electrolytes without volatile solvents [6–13]. In this context π-conjugated conducting polymers, a new class of semiconducting materials, have attracted considerable interest nowadays for use as active component in photocells due to their high absorption coefficients in the visible part of the spectrum and the high mobilities of charge carriers. Nevertheless, recent efforts in this regard are more focusing on replacing both the dye and the electrolyte with suitable semiconducting polymer layer, bringing together the functions of light absorption and the hole transport in a single material [21–28]. The ideal sensitizer for a single junction photocell should adsorb all light below a threshold wavelength of about 900 nm. In addition it should be firmly grafted to the semiconductor oxide surface and inject electrons to the conduction band of the semiconductor. To use these materials effectively as sensitizers in these devices, rigid bonding, such as carboxylic moieties in ruthenium based dyes with inorganic semiconductors are required [1,2]. However, due to the difficulties encountered in the synthesis of these materials with suitable carboxylic moieties, it is generally accepted that self-assembled monolayers are highly promising to construct such a molecular architecture on metals and semiconducting surfaces. This approach has several advantages such as; it permits the fabrication of highly ordered, appropriatively oriented 2D and 3D structures at a fraction of

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the cost over traditional band-gap engineering like molecular beam epitaxy [29–31]. Recently we have succeeded in fabrication of organic solvent free polyaniline/TiO_2 heterojunction with enhanced photovoltaic properties by covalently grafting polymer via sialane-bearing aniline compound [31]. However, there the polymer was connected to the semiconductor surface via nitrogen molecules with no or poor conjugated chain (single and double bonding). Apart from polyaniline, conducting polymer polypyrrole, with band-gap of approximately 2–2.5 eV in its neutral state appears to be better photo-conducting candidate possessing strong intrinsic absorption in the visible range, and could be connected to the metal oxide surfaces via meta position of the monomer and connecting the rest of the polymer chain with good π-conjugation [8–10]. Therefore, here we have attempted to explore the possibilities of fabricating PPY/TiO_2 heterojunction using less expensive self-assembled monolayers of 3-(trimethoxysilyl) propyl methacrylate with enhanced photoresponses.

2. Experimental

Titanium tetra iso propoxide (Wako Pure Chemicals), actylactone (Tokyo Kaisai), pyrrole (Wako, P-Xylene (WAKO) and $3'$-(trimethoxysilyl) propyl methacrylate (TSM, Aldrich) were used without prior purification. Dense less porous (compact) nanoporous films of TiO_2 were coated on fluorine doped conducting tin oxide (FTO) glasses (sheet resistance ∼16 Ω sq^{-1}) by the method described in literature [22]. Nanoporous TiO_2 electrodes were then deposited on the compact layer by “doctor blade” method using a TiO_2 paste from Solaronix (Solaronix nano-oxide-T). Electrodes were then sintered at 500 °C for 1 h and cooled down to room temperature in the furnace. The thickness of the films on FTO substrates were determined by a Dektak profilometer (Veeco, Dektack 3) and found to be ∼4.5 μm.

2.1. Surface modification of substrates with sialane compound

TiO_2 films were treated with 7:3 (v/v) of concentrated H_2SO_4 and 30% H_2O_2 at 90 °C for 3 min to clean the surface and to produce terminal hydroxyl groups. The acid treated films were then rinsed thoroughly with distilled water and dried under N_2 for 12 h in a glove box. Dried plates were then put into a 100 ml round bottom flask and 70 ml of xylene solution containing 200 mmol of TSM was added. The mixture was refluxed for 24 h and methanol was removed through an 80 °C water condenser as described by Cho et al. [33] and washed several times with acetone and vacuum dried at 30 °C for 48 h. After dried above films were first vertically inserted into a 0.1 M aqueous solution of pyrrole monomer and then added 0.1 M aqueous solution of ammonium persulfate dropwise while stirring the solution and kept for 5 min. After the polymerization, polymer coated films were removed from the solution and rinsed with scopous amounts of deionized water and vacuum dried for 12 h. Fig. 1(A) describes the schematic illustration for the fabrication of a conducting polypyrrole film on a TSM modified substrate. Photocells were fabricated by sandwiching a counter electrode having a very thin layer of gold (Fig. 1(B)) and photoresponses were observed. Some of the above electrodes were treated with ionic liquid 0.2 M LiTf2N in EMImTf2N for 24 h. Then the excess solutions of ionic liquid on the PPY surfaces were wiped off and tested their photoresponses just by sandwiching with

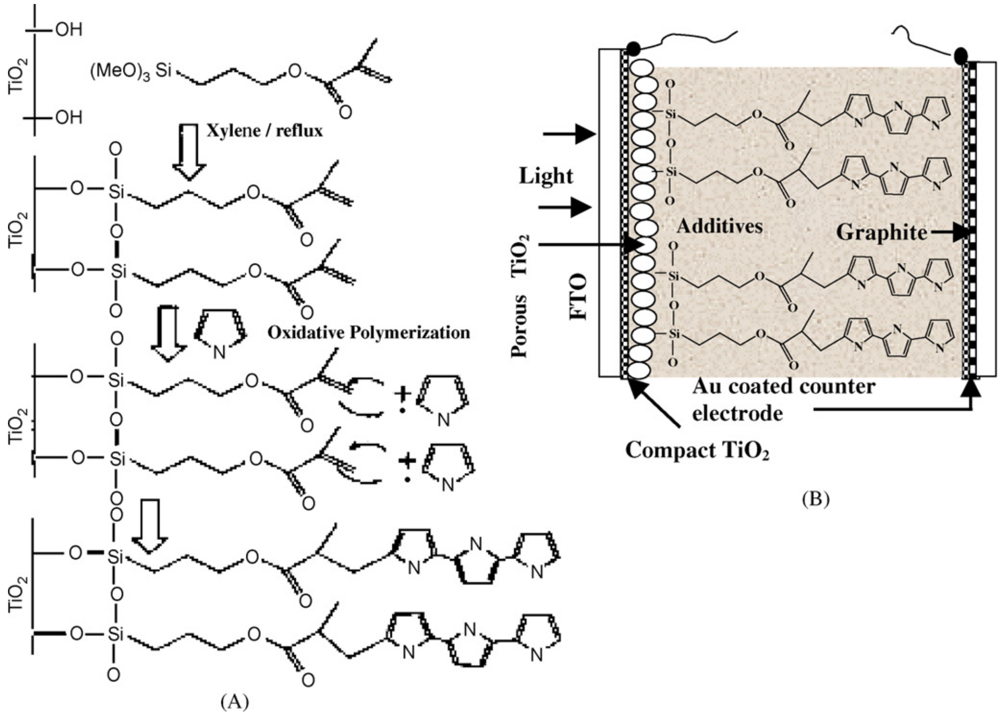

Fig. 1. (A) Scheme of grafting of polypyrrole to the surface of TiO_2 and (B) schematic view of fabrication of the cell.

same counter electrode. Finally, a thin layer of carbon (C) was applied very carefully on the surface of PPY and measured their photoresponses using the same counter electrode. Before applying the carbon the cell performances were poor and several microamperes were obtained as photocurrent. However, application of graphite shoots up the photocurrent to several hundreds of microamperes.

2.2. Characterization of electrodes

In order to check whether the grafting sites (vinyl group of TSM) had not reacted themselves during the surface modification, diffuse reflection FT-IR (Perkin-Elmer system 2000) spectra of TSM treated and non-treated substrates were compared. Further, X-ray photoelectron spectroscopy (XPS) measurements for the TSM treated substrates were performed using a PHI ESCA 5700 spectrometer with monochromated Al Kα radiation (1486.6 eV). The samples were placed on a standard sample holder and the spectra were recorded at take-off angle of 45° with respect to the surface of the sample. All binding energies were referred to the C 1s peak of an adventitious contamination hydrocarbon at 285.0 eV. IR measurements of bare TiO_2 and SAM modified TiO_2 in the range from 5000 to 500 cm^{-1} were performed using Perkin-Elmer system 2000 FT-IR spectrometer. The optical absorption spectrum of the polymer was recorded on a JASCO (V-570) UV–vis–NIR spectrophotometer. Film thickness and roughness were measured with a Dektak 30330 profilometer.

2.3. Solar cell fabrication and characterization

Photocells were constructed as depicted in Fig. 1(B), by sandwiching a gold coated FTO glass and TiO_2/TSM-PPY electrodes (cell area ~ 0.25 cm^{-2}). Photo-energy conversion efficiency was evaluated using standard solar irradiation of 100 mW cm^{-2} (AM 1.5) with a solar simulator (YSS-50A, Yamashita Denso) and a computer controlled voltage current sourcemeter (R6246, Advantest) at 25 °C. The effectiveness of the cell to convert light of various wavelengths into electrical current was measured as the incident photon to current conversion efficiency (IPCE) defined as the number of electrons generated by light per number of photons incident on the cell, formulated by IPCE (%) = $1240\,J_{sc}/\lambda W_i$, where J_{sc} is the short circuit current density (μA cm^{-2}), λ the excitation wavelength (nm) and W_i is the photon flux (W m^{-2}) [1,31,32] using a commercial setup for IPCE measurements (PV-25DYE, JASCO). UV–visible spectra of the PPY films deposited on FTO was measured with a Varian Cray spectrophotometer.

3. Results and discussion

3.1. PPY on TiO_2

Fig. 2 shows the diffuse reflection FT-IR spectra of TiO_2 films before (a) and after (b) the TSM treatments. As can be seen in the spectrum of TSM treated TiO_2, a characteristic band appears at 1712 cm^{-1} corresponding to the carbonyl peak. This indicates that the vinyl group of TSM had not reacted. If it had reacted a peak could have observed at ~1700 cm^{-1} because the characteristic IR band position of the TSM is at 1690 cm^{-1} [33,34]. IR spectra of TiO_2 before (a) and after (b) the treatments of TSM are shown in Fig. 3. Chemical anchoring of TSM onto TiO_2 surfaces can be identified by the bands assigned to the various functional groups as follows. Complete disappearance of the peak around 820 cm^{-1} in the TSM/TiO_2 shows splitting of Si–O–CH_3 groups during grafting processes. In addition to that appearance of new bands at 1029 cm^{-1} corresponding to Si–O–Si and absorption arising from C–H stretching occurs in the region 3000–2840 cm^{-1}($\nu_a(CH_2)$ 2919 cm^{-1}, $\nu_b(CH_2)$ 2840 cm^{-1}) also an indication for this grafting. Further, the appearance of new bands ($\delta(CH_2)$ 1404 cm^{-1}, 1469 cm^{-1}) in the spectra of the TSM treated TiO_2 further supports to this phenomenon [33,34]. In addition to that, X-ray photoelectron studies (XPS) of TSM modified TiO_2 further confirmed the presence of the sialane on the substrate (103 and 151 eV) as shown in Fig. 4. Peaks centered at ca. 285 and 532 eV corresponds to C 1s and O 1s could be observed in the spectra. Therefore, based on the above experimental results, we can confirm that TSM is anchored on the glass surface through covalent bonds as a monolayer and the vinyl group of TSM is present as a reactive site on the surface. To determine whether the polypyrrole was chemically bonded or physically attached to the TiO_2 surface, similar investigations were performed as reported by Cho et al. [33]. In this context, PPY was deposited either on TSM treated and non-treated substrates and tried to peel off them using scotch tapes.

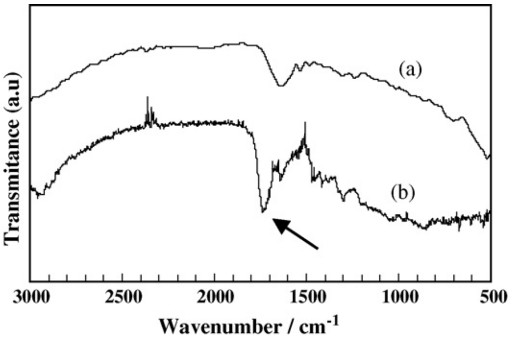

Fig. 2. The diffuse reflection FT-IR spectra of TiO_2 films before (a) and after (b) the TSM treatments.

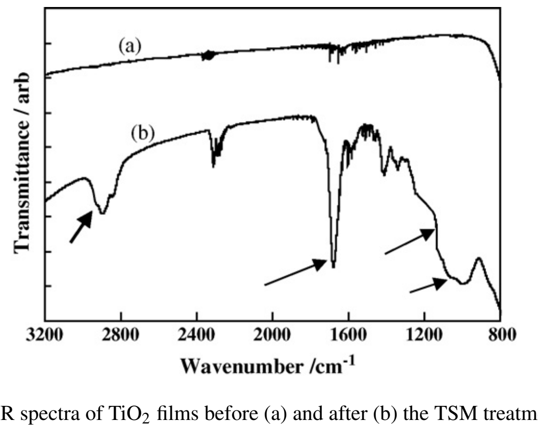

Fig. 3. IR spectra of TiO_2 films before (a) and after (b) the TSM treatments.

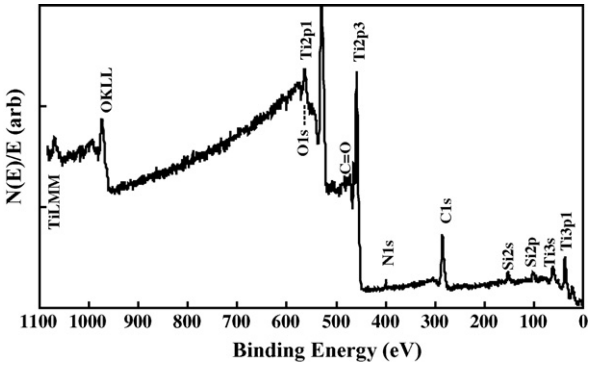

Fig. 4. XPS spectrum of TSM treated TiO_2.

The PPY films deposited on non-treated substrates were easily and completely peeled off while complete removal was not possible for the PPY films, which were deposited on the TSM treated TiO_2 substrates. Based on our investigations and the available information [33] it could be speculated that due to the hydrophobic properties of the TSM modified TiO_2 surface, monomer, pyrrole could be condensed on it and consequently polymerized it due to the addition of ammonium persulfate as oxidant.

3.2. Current–voltage characteristics

Fig. 5(A) shows the dark current–voltage behavior of the TiO_2/TSM-PPY-C/Au cell before (i) and after (ii) the addition of EMImTf2n/LiTf2N. The TiO_2/TSM-PPY-C/Au junction showed strongly rectifying characteristics very similar to that of the conventional p–n junction. Improved dark current properties were observed in the cells fabricated with the above additives in PPY. Fig. 5(B) shows the average *I–V* curves of the TiO_2PPY devices under the illuminated conditions (AM 1.5, 100 mW cm^{-2}). Curve (a) shows the performances of the cell fabricated with no additives to the PPY. Curves (b) and (c) show the performances of the above devices with (b) EMImTf2n/LiTf2N and (c) carbon layer on PPY. As it is evident from the figure significant enhancement in overall photoresponses could be observed when the additives were available. The addition of carbon layer to PPY, further enhanced the cell performances of the above electrodes as shown in curve (c). The corresponding values (average of five samples) for the short circuit current density (J_{sc}), open circuit voltage (V_{oc}) fill factor (FF) and overall solar to electrical energy conversion efficiency (η) are tabulated in Table 1. Even though the values obtained here are unexpectedly small, they are significant and much higher than the reported devices with TiO_2/PPY. As generally observed the addition of $EMImTf_2N$ and $LiTf_2N$ further improved the cell performances. This could be due to the reduction of the charge recombination at the interfaces and improvement in the surface contacts of the material interfaces [12,18,22,35]. One of the possible reasons for the lower device voltage observed in the cells with the carbon layer could be attributed with the physical damage of PPY in the application processes of carbon by hand which could eventually short circuiting of the cells and increase the degree of recombination of the electrons. In order to check whether the adhesion of PPY onto TSM treated TiO_2 affected in the photoresponses, pilot experiment was carried out as follows. In this, PPY films were deposited on the non-treated TiO_2 surfaces using aforementioned method and photoresponses were observed. As observed by the others very poor photoresponses were observed with ~50 μA cm^{-2} short circuit current density and 300 mV voltage. Therefore, PPY should have chemically grafted onto TSM and eventually improved the photoresponses and the electron transformation from PPY to TiO_2.

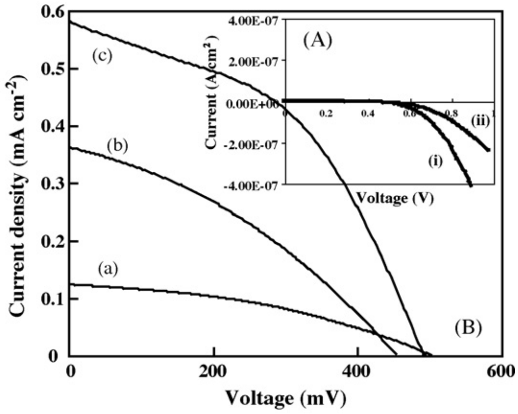

Fig. 5. (A) Dark current–voltage (*I–V*) responses of the cells TiO_2/TSM-PPY-C/Au: (i) without additives and (ii) with additives. (B) Photo *I–V* responses of the cells: (a) without additives, (b) with additives and (c) with additives and a graphite layer.

Table 1

	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
(a) TiO_2/TSM-PPY/Au	0.587	493	0.51	0.15
(b) TiO_2/TSM-PPY-additives/Au	0.362	453	0.47	0.08
(c) TiO_2/TSM-PPY-additives-C/Au	0.125	501	0.36	0.03

3.3. Absorption and action spectral studies

The action spectrum (IPCE%) (a) of the cell TiO_2/TSM-PPY-C/Au is shown in Fig. 6 together with the UV–visible absorbance of PPY film (b). Losses of the light reflection and absorption by the conducting glasses were not corrected in the calculation of

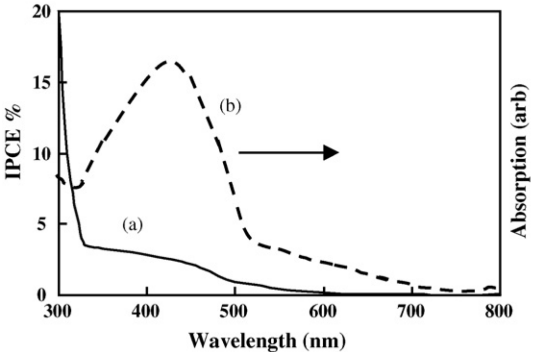

Fig. 6. Action spectra of the cell (a) and the absorbance of PPY (b).

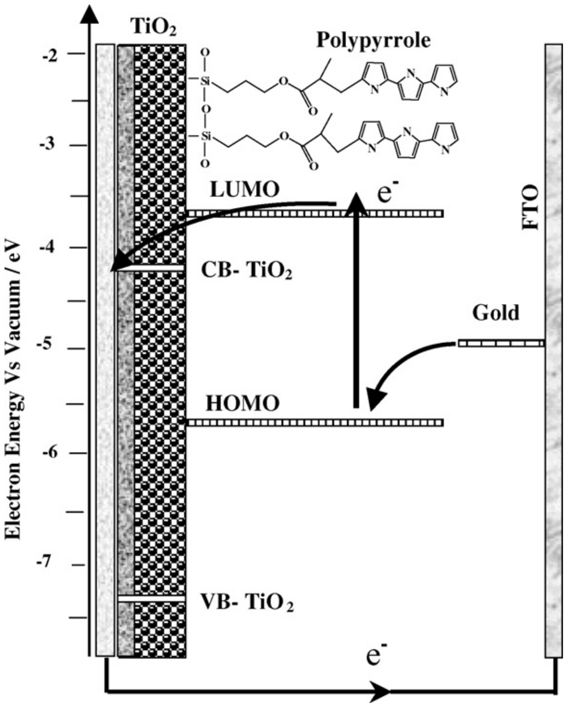

Fig. 7. Energy band diagram of the materials used in the fabrication of TiO$_2$/TSM-PPY-C/Au.

IPCE. The peak around 300 nm corresponds to the absorption of the TiO$_2$. However, slightly improved photoresponses in the visible region could be observed. The action spectrum and the absorption spectrum closely matched each other indicating the responsibility of the photocarrier generation of the PPY. In order to further clarify this photoelectron generation, relative energy values of the materials used in this study were arranged in the standard way as shown in Fig. 7. The reported values of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) of PPY and the work function of gold were considered [9]. As can be seen from the figure, the LUMO level of PPY is situated in an energetically higher position than the conduction band edge of TiO$_2$. Therefore, when the cell is illuminated PPY could absorb the photons and the excited electrons in the HOMO level could be moved to the LUMO level of it and these electrons could then be transferred into the conduction band of the TiO$_2$ delivering significant photoresponses from this junction.

4. Conclusion

In order to explore the possibilities of devising PPY with TiO$_2$ in solid-state nature, photovoltaic junctions were performed by covalently grafting PPY on TiO$_2$ via molecular self-assembly. Contrary to the expectation, poor performances were observed in these devices. However, significant enhancement in photoresponses was observed with the above additives in PPY than the reported devices comprising TiO$_2$/PPY. According to these observations, it could be concluded that, PPY could be used more efficiently as a sensitizer for TiO$_2$ when covalently attached to a surface of a nanoparticle inorganic semiconductor via carboxylic groups as in the case of ruthenium dyes. Further studies are being carried out on this phenomenon.

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