Morphology and Photoelectrochemical Characterization of MEH-PPV/PCBM Composite Film Doped with TiO₂ Nanoparticles

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Poly[2-methoxy-5-(20-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV), [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and titanium dioxide (TiO₂) nanoparticles (n-type) were dissolved, mixed and deposited by physical methods (spin-coating) on indium tin-oxide (ITO) substrate. The incorporation of the titanium dioxide nanoparticles changed the morphology and increased the roughness of polymers film (MEH-PPV/PCBM), and the photocurrent density of the composite (MEH-PPV/PCBM + n-TiO₂) was higher than that of single MEH-PPV/PCBM film. The study showed that the presence of n-TiO₂ particles in the polymeric film improves the photoelectrochemical properties of MEH-PPV/PCBM composite.

KEY WORDS: Photocurrent density; Electrochemical property; Hybrid coating;
Conducting polymer; Titanium dioxide; Organic nanostructures

1. Introduction

The performance of the photovoltaic devices with a light absorber consisting of a single-type conjugated polymer is poor, due to a low photo-generation yield of charge carriers, strong radiative recombinations and low mobility of charge carriers^[1]. Conjugated polymer photovoltaic devices have many positive properties that may provide the means to overcome the current hurdles toward low-cost photovoltaics.

However, polymer-based organic photovoltaic are presently limited in their power efficiency due to a number of device and material parameters that have yet to be optimized. The first such limitation is that the band gap of the conjugated polymers needs to be decreased in order to absorb a larger portion of the solar spectrum and increase the photocurrent. The

photovoltage could be increased by the proper optimization of the band offsets, where the lowest unoccupied molecular orbital of the donor and the valence band of the acceptor are close in energy, but still allow for efficient electron transfer. If the band alignment between donor and acceptor materials was more appropriately engineered through the proper selection and design of active materials, this lost energy could be utilized resulting in improved device performance^[2–5].

Conducting polymers have been examined so far for stability in solar cells, mainly the poly[2-methoxy-5-(20-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV)^[6], P3HT^[7] and P3CT^[8].

MEH-PPV is a photoactive polymer known to form excitons upon exposure to light^[9]. Despite low electron mobility, MEH-PPV has been utilized in solar cells research due to high absorbance in the visible region^[10]. Because MEH-PPV possess high hole mobility, it is often paired with an electron carrier to generate photovoltaic devices^[11].

At the same time, the concept of the photovoltaic (PV) device structure has also evolved from single

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Fig. 1 Sketch of the molecular structures of poly[2-methoxy-5-(2-ethylhexyl-oxy)-p-phenylenevinylene] (MEH-PPV) and the fullerene 1-(3-methoxycarbonylpropyl)-1-phenyl-[6.6]C₆₀ (PCBM)

layer^[12], double layer^[13] to bulk heterojunction (BHJ)^[14], which is now the most successful and widely adopted organic PV device structure. The active layer of bulk heterojunction is typically composed of a conjugated polymer (electron donating molecule) and fullerene derivative such as C₆₀ or PCBM (electron accepting molecule)^[15–17].

Recently, it has been shown that ultra-fast photoinduced charge transfer can also occur between a conjugated polymer and a metal oxide semiconductor such as SnO₂, TiO₂, ZnO, Nb₂O₅, *etc.*^[18,19]. This has led to the fabrication of photovoltaic devices based on composites of oxide semiconductor nanoparticles embedded in a conjugated polymer matrix^[20]. Polymeric materials could be deposited by the solution-based technique or electrochemical polymerization onto printable, flexible and large-scale film promising for various applications and commercialization of solar cells^[21].

In this work, we present the results of the enhancement of photoelectrochemical properties of bulk conjugated polymers, MEH-PPV and PCBM (Fig. 1) by the addition of n-TiO₂ nanoparticles (acceptor), which improve the performance of this photovoltaic device.

2. Experimental

Soluble MEH-PPV (Aldrich), PCBM and n-TiO₂ nanoparticles (40–80 nm) were dissolved in chlorobenzene and stirred during 12 h (Fig. 2). The indium tin-oxide (ITO, from Merck with a sheet resistance ~10 Ω/K) substrates were successively cleaned for 20 min in water and acetone in an ultrasonic bath and finally dried at 120 °C. Once dissolved, MEH-PPV/PCBM+n-TiO₂ solution was dropped on ITO substrate (step 1) and spin-coated by using spinner

speed of about 900 r/min for 40 s (step 2). Following deposition, films are dried at 80 °C for 15 min to evaporate the solvent (step 3). The thickness of the film, measured *via* an Ambios Technology XP-2 surface profiler, varied from 100 to 120 nm.

Morphology of the coated active layer MEH-PPV/PCBM+ n-TiO₂ composite was examined by means of atomic force microscopy (AFM), using an electron microscope ULTRA 55 (Zeiss, France).

The electrochemical analysis including cyclic voltammetry of the single-layer MEH-PPV/PCBM or MEH-PPV/PCBM+n-TiO₂ composite film deposited on ITO (working electrode) by spin-coating were carried out in a one-compartment cell connected to a potentiostat/galvanostat (PGZ-301 Voltalab) coupled with a computer equipped with software (voltamaster 4) which makes it possible to select the electrochemical technique and to fix the parameters desired. The reference electrode is a saturated calomel electrode with KCl (SCE), and the auxiliary electrode is a platinum plate. The supporting electrolyte was 0.1 mol/L lithium perchlorate (LiClO₄, Fluka) dissolved in acetonitrile solvent (CH₃CN, Aldrich).

The cyclic voltammogram (CV) was recorded at scan rate of $v=50$ mV/s in the potential range of –1.5 to 1.8 V (*vs.* SCE). The identical cell used in the photocurrent measurements and was recorded with a 500 W halogen lamp as polychromatic light source, and the illumination intensity is 100 mW/cm². All measurements were taken at the atmosphere and room temperature.

3. Results and Discussion

3.1 Atomic force microscopy

The surface topography of MEH-PPV/PCBM+n-TiO₂ composites film (~100 nm of thickness)

Fig. 2 Schema of experimental preparation methods

Fig. 3 AFM images of MEH-PPV/PCBM (a) and MEH-PPV/PCBM+n-TiO₂ (b) composite films

revealed contact-mode atomic force microscopy, as shown in Fig. 3. Generally, AFM image can give information about the height differences and also about the constituency of the composite thin film at the surface because the hard nanoparticle can easily be distinguished from the soft polymer. And it's shown the addition of titanium dioxide (n-TiO₂) nanoparticles increases the roughness (root mean square) of polymer film^[22], from 7.63 nm of (MEH-PPV/PCBM) to 19.76 nm of (MEH-PPV/PCBM+n-TiO₂). A feature of a dispersion of n-TiO₂ nanoparticle structure is found and inevitably leads to provide more organic/inorganic interfaces forming their own networks in the active layer.

The results indicate that the interpenetrating network and the small feature size the MEH-PPV/PCBM+n-TiO₂ film will facilitate more effi-

cient exciton dissociation, provide more conducting channels for charge transfer and then lead to enhance device performance.

3.2 Cyclic voltammetry

The cyclic voltammograms (CVs) of composite materials (MEH-PPV/PCBM), obtained for different concentration of n-TiO₂ nanoparticle deposited an ITO electrode, in CH₃CN/LiClO₄ (0.1 mol/L) electrolyte solution (Fig. 4) shows for all CVs tow peak of oxidation at 0.5 and 0.8 V (*vs.* SCE) correspondents to first and second oxidation of MEH-PPV respectively, another peak at 1.22 V (*vs.* SCE) correspondent to the oxidation of PCBM.

In the return scan, it was observed that three peaks at 0.2, 0.75 and -0.9 V (*vs.* SCE) which corre-

Fig. 4 Cyclic voltammograms of MEH-PPV/PCBM film and MEH-PPV/PCBM+TiO₂ composites in CH₃CN/LiClO₄ solution

spondent to the first and second reduction of MEH-PPV and the reduction of PCBM respectively. Currents densities of oxidation and reduction peaks increase with the content of n-TiO₂. The absence of another peak in the CVs of the composite materials (MEH-PPV/PCBM+ n-TiO₂) can be explained by the fact that the inorganic semiconductor (TiO₂) is electrochemical but not electro activated because of its insolubility in the medium in the experimental conditions.

The observed electrochemical stability of the composite material (MEH-PPV/PCBM+ n-TiO₂) is in good agreement with the cyclic voltammograms of other organic/inorganic composites given in the literature^[23–26].

3.3 Photo-electrochemistry

MEH-PPV/PCBM and MEH-PPV/PCBM + n-TiO₂ composite films deposited ITO sub-

strate (Fig. 5(a)) used as working electrode in photoelectrochemical cell (Fig. 5(b)) containing acetonitrile/LiClO₄ (0.1 mol/L) electrolyte solution.

Typical photocurrent-time curves are given in Fig. 6 upon switching the light on and off, with an applied potential of -0.6 V (*vs.* SCE). It can be seen that the polymers and the composite film featured a pronounced cathodic photocurrent and it has been shown that polymers modified with n-TiO₂ (6 wt.%) semiconductor particles could feature higher photocurrents as compared to the pure polymers (MEH-PPV/PCBM) by a factor of 5 (0.5 μ A to 2.5 μ A).

Fig. 7 shows the photocurrent density as function of applied potential (-1 to 1 V (*vs.* SCE)) of MEH-PPV/PCBM +(6 wt.% n-TiO₂)/ITO electrode obtained at light intensity of 100 mW/cm². It was observed that the photocurrent of the composite with inorganic semiconductor nanoparticles (TiO₂) at all range of potential was negative and higher than of non-modified polymers^[25,27]. This response indicates that recombination processes occur in the film, probably due to the presence of charge carriers in the polymer bulk, mainly due to structural disorder. The presence of the space-charge region suggests that these polymers may produce photocurrent when illuminated. Furthermore, it has been shown that polymers modified with n-TiO₂ semiconductor particles could feature higher photocurrents as compared to the pure polymers, MEH-PPV/PCBM.

As expected, the addition of the inorganic semiconductor nanoparticles into the polymers film (MEH-PPV+PCBM) increases the photocurrent, assuring more efficient exciton dissociation, and provide more conducting channels for charge transfer and then lead to enhance the polymer photovoltaic proprieties^[25–28].

Fig. 5 (MEH-PPV/PCBM+n-TiO₂) ITO photovoltaic structure (a) and schematic of photoelectrochemical experimental technique (b)

Fig. 6 Photocurrent density–time dependencies obtained with (MEH-PPV/PCBM)/ITO and (MEH-PPV/PCBM+TiO₂)/ITO electrode in CH₃CN/LiClO₄ (0.1 mol/L) at a negative potential of -0.6 V observed under illumination and obscurity

Fig. 7 Photocurrent density as function of applied potential of MEH-PPV/PCBM /ITO electrode doped or undoped with TiO₂ nanoparticles in CH₃CN/LiClO₄ solution at light intensity of 100 mW/cm²

4. Conclusions

MEH-PPV, PCBM and inorganic semiconductor nanoparticles (n-TiO₂) were dissolved, mixed and spin-coated on indium tin-oxide (ITO) substrate. The incorporation of the n-TiO₂ nanoparticles changes the morphology and increases the roughness of polymers film (MEH-PPV/PCBM). Characterization by cyclic voltammetry showed the electrochemical stability of the composites material, and the photocurrent density characteristic of the composite (MEH-PPV/PCBM+n-TiO₂) was higher than that of the single MEH-PPV/PCBM film.

The study showed that the presence of n-TiO₂ particles in the polymeric film improves the photoelectrochemical properties of MEH-PPV/PCBM and gives information on the possibility of application in organic–inorganic photovoltaic cells.

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