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Improvement of photoelectrochemical and optical characteristics of MEH-PPV using titanium dioxide nanoparticles

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ABSTRACT

The use of bulk heterojunctions can increase the efficiency of exciton dissociation in polymer-based photovoltaics. We prepared and characterized bulk heterojunctions of poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) and titanium dioxide nanoparticles deposited by spin coating on indium tin oxide substrates. The surface morphology of the MEH-PPV+TiO_2 composite films revealed that addition of TiO_2 nanoparticles increased the film roughness. The effect of TiO_2 nanoparticles on the photoelectrochemical and optical characteristics of MEH-PPV polymer heterojunctions was studied. Addition of TiO_2 nanoparticles improved the absorbance of MEH-PPV composite films. Moreover, the photocurrent of the composite devices increased with the TiO_2 nanoparticle concentration. These observations provide an insight into new approaches to improve the light collection efficiency in photoconductive polymers.

1. Introduction

Photovoltaic cells based on organic–inorganic bulk heterojunction (BHJ) semiconductors have attracted much interest in the last two decades [1–4]. Based on intimate nanoscale mixing of an electron donor–usually a p-type conjugated polymer–and an electron acceptor–usually an n-type organic semiconductor–BHJs have shown regular improvements due to better control of the nanophase separation [5]. Research trends on this area are now focused on the development of new materials such as low-bandgap polymers [6,7] to absorb a greater fraction of the solar radiation spectrum.

Nanoparticles of a variety of inorganic materials such as CdSe [8–10], CdTe [11,12], silicon [13,14], InP [15], GaAs [16] and PbS [17,18] have been studied intensively for use in hybrid BHJ solar and photoelectrochemical cells. In particular, hybrid BHJs comprising transition metal oxide compounds and organic semiconductors have shown promising results. Among the metal oxides, titanium dioxide (TiO_2) [19,20] and zinc oxide (ZnO) [21–23] are of particular interest because of their easy fabrication, non-toxicity and relatively low production costs.

Poly[2-methoxy-5-(20-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) is a photoactive polymer that forms excitons on exposure to light [24]. Despite its low electron mobility, MEH-PPV has been utilized in solar cell research because of its high absorbance in the visible spectral range [25]. However, since MEH-PPV has high hole mobility, it is often paired with an electron carrier for the preparation of photovoltaic devices [26].

BHJ materials can be deposited via solution-based techniques or electrochemical polymerization onto printable, flexible and large-scale films for various industrial applications [27]. For solar cell applications, nanocrystalline TiO_2/indium tin oxide (ITO) electrodes are generally combined with a conjugated polymer such as MEH-PPV [28,29]. Hybrid polymer solar cells that use metal oxides as acceptors have been reviewed [30–32]. Here we report on the morphology of MEH-PPV films modified by addition of TiO_2 nanoparticles and on the enhanced device performance resulting from the increase in the active surface area.

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2. Experimental

2.1. Materials and film preparation

Commercial MEH-PPV (99%, Sigma-Aldrich) and TiO_2 nanoparticles (40–80 nm, 99%, Aldrich) were dissolved in chlorobenzene (99.8%, Sigma-Aldrich) and stirred for 24 h. ITO substrates (Merck; sheet resistance $\sim 10\,\Omega/\mu$) were successively cleaned with water and acetone for 20 min in an ultrasonic bath and finally dried at 120 °C. Once dissolved, the MEH-PPV+TiO_2 solution was deposited by spin coating on the ITO substrate at a spinner speed of $\sim$900 rpm for 40 s. Following deposition, films were dried at 80 °C for 15 min to remove the solvent.

2.2. Characterization

The morphology of MEH-PPV+TiO_2 films was examined by atomic force microscopy (AFM) using a Thermomicroscope AutoProbe LP Research instrument. The film thickness, measured with a Dektak profilometer, varied from 100 to 120 nm.

Electrochemical analysis, including cyclic voltammetry, of MEH-PPV and MEH-PPV+TiO_2 films deposited on ITO (working electrode) was carried out in a one-compartment cell connected to a potentiostat/galvanostat (PGZ-301 Voltalab) connected to a computer equipped with Voltamaster 4 software to select the electrochemical technique and set suitable parameters. The reference electrode was a saturated calomel electrode (SCE) with KCl and the auxiliary electrode was a platinum plate. The supporting electrolyte was 10^{-1} mol l^{-1} lithium perchlorate dissolved in acetonitrile.

Cyclic voltammograms were recorded at a scan rate of 50 mV s^{-1} in the potential range from 0 to +1500 mV vs. SCE. The same cell used in current density measurements was used for photoelectrochemical experiments. A 500-W halogen lamp was used as a polychromatic light source and the illumination intensity was 100 mW cm^{-2}. All measurements were made at room temperature.

3. Results and discussion

3.1. Atomic force microscopy

In general, AFM images provide information about height differences and the constituency of composite thin films at the surface because hard nanoparticles can easily

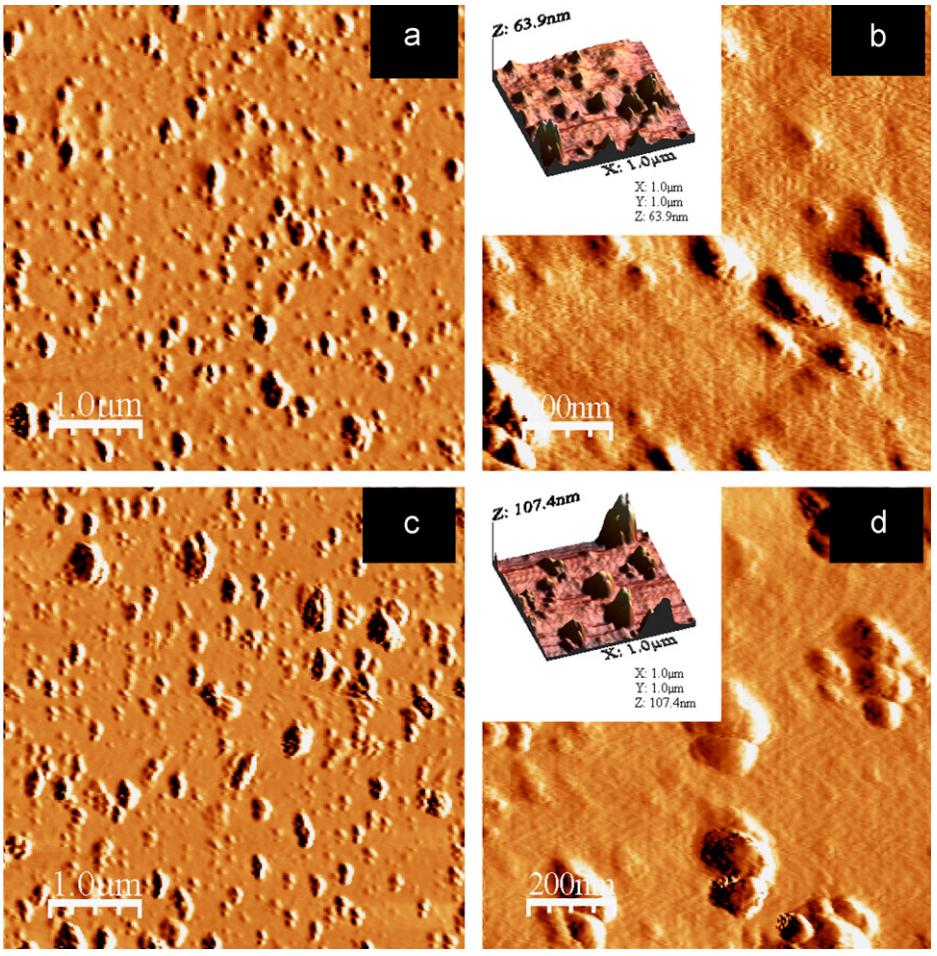

Fig. 1. AFM images of (a,b) MEH-PPV and (c,d) MEH-PPV+TiO_2 (8%) films.