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Surface ligand effects in MEH-PPV/TiO_2 hybrid solar cells

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ABSTRACT

TiO_2 nanorods (NRs) were synthesized by hydrolysis of titanium tetraisopropoxide (TTIP) using oleic acid (99%) as surfactant at low temperatures (80–100 °C) and are modified with different ligands: oleic acid (OLA), *n*-octyl-phosphonic acid (OPA) and thiophenol (TP) in order to investigate the effect of surface ligand on the excition dissociation and the charge transport in hybrid MEH-PPV/TiO_2 photovoltaic (PV) cells. The morphology and crystalline form of as-prepared TiO_2 NRs are examined by transmission electron microscopy (TEM), high-resolution TEM (HRTEM), X-ray diffraction (XRD) and Raman spectrometer (RS). The FTIR analysis confirms all the ligands coordinated with the Ti center of TiO_2 NRs. The optical properties of the modified TiO_2 NRs are characterized by UV–vis absorption spectra and photoluminescence (PL) spectra. Thiophenol modified TiO_2 NRs quench the PL of MEH-PPV more effectively than OLA-TiO_2 NRs and OPA-TiO_2 NRs. The power conversion efficiency of hybrid PV cells from thiophenol modified TiO_2 NRs and MEH-PPV is the highest among the investigated TiO_2 NRs.

1. Introduction

Hybrid organic/inorganic materials are promising candidates in photovoltaic (PV) cells [1]. In this PV cells, inorganic nanocrystals are used to replace the PCBM molecules of the polymer-PCBM PV cells with the similar device architecture. It combines the electrical properties of semiconductor organic polymers with the optical peculiarities of inorganic nanocrystals. Nanocrystals in hybrid PV cells can absorb visible light and its band gap can be adjusted by variation of their size and surface passivation. Moreover, nanocrystals can be controlled to get one-dimensional morphology resulting in better pathways for electron transport.

Up to now, different kinds of inorganic nanocrystals such as CdSe [2], CdS [3], ZnO [4], TiO_2 [5] are reported as charge acceptor in the hybrid PV cells. In the fabrication of hybrid PV cells, organic ligands that envelop the NR surface are necessary to stabilize and disperse nanocrystals. That is one of the limiting factors for the efficiency of these devices [6]. Pyridine is used extensively to exchange the surface ligands of CdSe nanocrystals for fabrication of a hybrid PV device [7]. Chen et al. [8] reported thiophenol as a surface ligand for enhancing photoluminescence quenching and PV properties in hybrid CdSe PV cells.

TiO_2 nanocrystals are environmentally friendly and can be patterned into a continuous network for electron transport [9]. Because of the polarity difference between the hydrophobic polymer and hydrophilic TiO_2, TiO_2 nanocrystals and conjugated polymer are mostly fabricated into a bilayer or multilayer PV cells [10]. Fabricating TiO_2/polymer bulk heterojunction structures is an effective way to improve the exciton dissociation in hybrid PV cells. Petrella et al. [11] reported the photoinduced charge transfer and recombination of MEH-PPV and TiO_2 nanorods (NRs) capped with oleic acid (OLA), but the power transfer efficiency is not reported. Subsequently Su et al. [12] reported a power conversion efficiency of 0.49% of MEH-PPV/TiO_2 hybrid PV device was obtained by inserting a thin layer of TiO_2 NRs on top of TiO_2/MEH-PPV hybrid layer. For further improving the property of hybrid polymer/TiO_2 NRs, it is very important to choose an appropriate ligand to exchange the OLA in the surface of TiO_2 NRs.

In this paper, we report comparable studies of PV properties of bulk heterojunction device from MEH-PPV and TiO_2 NRs modified by different ligands: OLA, *n*-octyl-phosphonic (OPA), thiophenol (TP) and as-prepared TiO_2 with thoroughly cleaned surface. Different ligands (OLA, OPA, TP) capped TiO_2 NRs are obtained by a facile ligand exchange process. The photoinduced electron and hole transfer has been investigated between MEH-PPV and surfactant-capped TiO_2 NRs. It is shown that the thiophenol is best for exciton dissociation in the MEH-PPV/TiO_2 NRs interfaces. Consequently, the power conversion efficiency of hybrid PV cell is improved when TiO_2 NRs modified by thiophenol is used as an acceptor.

2. Experiment

2.1. Materials

Titanium tetraisopropoxide (Ti $(OPri)_4$ or TTIP, 99%), trimethylamino-*N*-oxide dihydrate [$(CH_3)_3NO \cdot 2H_2O$] and poly

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(styrenesulfonate/poly (2,3–dihydrothieno–(3,4–b)–1,4–dioxin (PEDOT/PSS) were purchased from Aldrich. Octyl-phosphonic acids ($C_8H_{17}PO$ $(OH)_2$ or OPA, 98%) were purchased from Alfa Aesar. Oleic acid (OLA, 99%) and thiophenol (TP, 99%) were purchased from Shanghai Reagent Cooperation, China.

All solvents were of analytical grade and purchased from Guangzhou Chemical Corporation, China. Conjugated polymer poly [2-methoxy-5- (2-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) was synthesized in our lab.

2.2. Synthesis and modification of TiO_2 NRs

OLA capped anatase TiO_2 NRs were synthesized by hydrolysis of TTIP using OLA (99%) as surfactant at low temperatures followed the modified method published in the literature [13]. Thirty-five milliliters of OLA were dried at 120 °C for 1 h under Ar flow in a 50 mL three-neck flask. After the temperature was lowered to 90 °C, 1.5 mL (5 mL) TTIP was injected into the OLA solvent under stirring. The reaction mixture was kept stirring for another 10 min. Then a 4 mL of 2 M aqueous trimethylamino-*N*-oxide (TMAO) solution was rapidly injected. The solution was maintained at 90 °C for 20 h. The as-synthesized TiO_2 NRs were precipitated upon addition of an excess of methanol to the reaction mixture at room temperature. Then the resulting precipitate was isolated by centrifugation and washed three times with ethanol. The OLA capped TiO_2 NRs (specimen a, OLA-TiO_2) were then redispersed in hexane. After the purified procedure was repeated more than 6 times, the TiO_2 NRs (specimen b, P-TiO_2) was redispersed in toluene for characterization and for hybrid solar cell fabrication.

TiO_2 NRs after purified for 6 times were dispersed in toluene and then added 0.2 M OPA solution in toluene to get clear solutions, and then the as-prepared solutions were precipitated by adding excess methanol. The OPA-capped TiO_2 NRs (specimen c, OPA-TiO_2) was then redispersed in toluene for further analysis and device fabrication.

The TiO_2 NRs purified for 6 times was added to thiophenol solvent. Then a refluxing procedure was carried out under Ar flow for 24 h. Excess hexane was added to the resulting solvents to isolate TiO_2 NRs. Then the thiophenol capped TiO_2 NRs (speciman d, TP-TiO_2) was redispersed in toluene for further characterization and device fabrication.

2.3. Fabrication of hybrid solar cells and PV property testing

The hybrid PV device was fabricated with a sandwich structure of ITO/PEDOT (50 nm)/MEH-PPV:TiO_2/Al (100 nm), as shown in Fig. 1. A 50 nm thick PEDOT:PSS was spin-cast on a cleaned ITO glass substrate and was followed by a baking at 80 °C in a vacuum oven for 8 h. The blends of MEH-PPV and TiO_2 NRs were prepared from an approximately 2% toluene solution by spin coating onto the PEDOT: PSS and ITO substrate. The thickness of the photo-active layer was approximately 200 nm monitored by Tencor Alpha-Step 500 surface profilometer. Aluminum cathodes were then thermally evaporated in vacuum chamber at a pressure below 3×10^{-4} Pa. Typically, $15 \times 15\,mm^2$ substrate was patterned with five 2 mm ITO strips (see Fig. 1). 1 short strip serves as anode, cross-area of ITO anode and Al cathode defines active area of five devices. The typical active area of the device was $0.17\,cm^2$. Thereby for each composition, five devices were fabricated and tested. Generally, the device was fabricated and encapsulated inside N-circulated (O_2 and H_2O level was below 5 ppm) dry box with cover glass sealed by UV epoxy. Then it was immediately moved out from dry box for measurement under solar simulator.

The current–voltage (*I*–*V*) characteristics of the encapsulated devices were measured with Keithley 2400 Source meter at room temperature in the ambient atmosphere. Power conversion efficiencies (PCE) were measured using a solar simulator (Oriel model 91192) to provide AM1.5 white illumination with an intensity of $100\,mW/cm^2$ calibrated by standard Si-photodiode. The power conversion efficiency (PCE) was calculated according to the report published elsewhere [14].

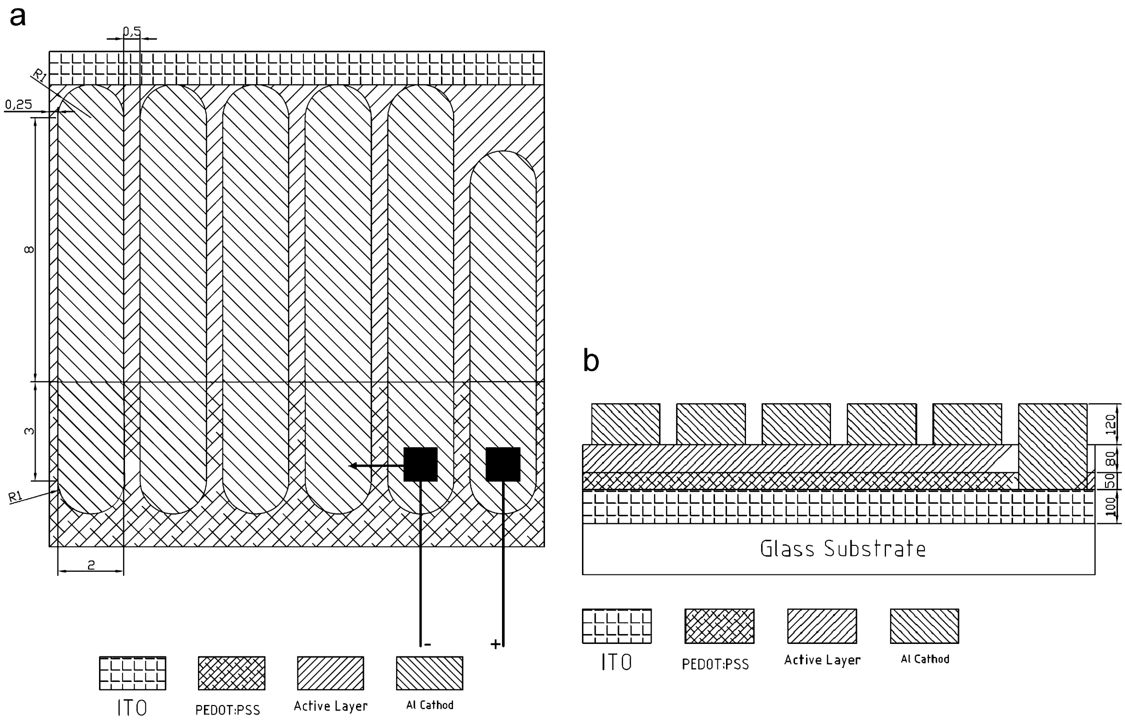

Fig. 1. Schematic illustration of solar cell structure: (a) device-front view diagram, (b) device-section diagram.