



Hybrid solar cells based on blends of poly(3-hexylthiophene) and surface dye-modified, ultrathin linear- and branched-TiO₂ nanorods

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ABSTRACT

We report on a comparative study of hybrid solar cells based on blends of poly(3-hexylthiophene) (P3HT) and TiO₂ nanorods. Two types of ultrathin TiO₂ nanorods, linear and branched, have been synthesized for the first time, and surface modified with different dyes before blending with P3HT. Using pristine P3HT as a reference, the short-circuit current and energy conversion efficiency of poly(3-hexylthiophene)/pyridine-HgBrRed-modified branched-TiO₂ solar cells were increased by over an order of magnitude, which were also 2–3 times those of the corresponding linear-TiO₂ cells. Our results indicate that the branching and the surface dye modification of TiO₂ nanorods could effectively facilitate charge transport in the nanostructured network and exciton dissociation at the inorganic/organic interfaces. Thermal treatment of the blend films was found to further increase the efficiency up to 0.16%.

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1. Introduction

Since the discovery of fast photoinduced electron transfer at the interface between a semiconductor polymer and fullerene [1], organic photovoltaic cells (PVCs) have been widely investigated due to their advantages of low-cost, light weight, easy fabrication, and possibility to fabricate flexible devices not feasible with inorganic materials [2–10]. Energy conversion efficiencies up to 5% have been obtained for improved polymer/fullerene blends [11]. However, the efficiency of organic PVCs is still limited by the low charge carrier mobility of polymer donors and organic acceptors as compared to inorganic semiconductors. In this context, hybrid inorganic–polymer solar cells using inorganic nanocrystals as electron acceptors to replace the PCBM are a promising alternative. The hybrid PVCs combine the favorable electrical and optical characteristics of the semiconductor organic polymer inorganic nanocrystal constituents. In particular, inorganic nanocrystals are well known for their large surface-to-volume ratios, high electron affinities and large electron mobilities. Therefore, it is commonly believed that hybrid inorganic–polymer PVC devices can partially overcome charge-

transport limitation. Moreover, a compensated light harvest of nanocrystal-polymer composites could enlarge the absorption range, leading to an efficient utilization of sunlight.

Till date, inorganic nanocrystals of ZnO [12], CdSe [13,14], CdS [15,16], and CuInS₂ [17] have been extensively studied for hybrid inorganic–polymer PVC devices. And nanoporous metal oxide electrodes [18–20] have also been used to investigate hybrid solar cells by several groups. TiO₂ is an environmentally friendly material, and nanocrystals of TiO₂ have been used for the fabrication of PVC devices together with conjugated polymer, but mostly in the form of bilayer or multilayer due to the polarity difference between the hydrophobic polymer and hydrophilic TiO₂ commonly synthesized in aqueous solutions [21,22]. Recently, several studies have been carried out to improve the performance of hybrid TiO₂ nanorods-polymer devices by surface ligand-modifications of the TiO₂ nanorods [23–26]. By choosing an appropriate ligand, the charge dissociation and charge transfer in the hybrid TiO₂-polymer PVC devices were significantly enhanced.

In this paper, we study the photovoltaic performance of hybrid solar cells based on P3HT and TiO₂ nanorods by focusing on three main questions. First, how does branching of the TiO₂ nanorods influence the PV performance? This study is enabled by our recent success in controlling the linear and branched morphologies of the ultrathin TiO₂ nanorods. Second, how is the PV performance affected by the surface dye-modifications of the TiO₂ nanorods?

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Porphyrin, N719 and HgBrRed were used in this study motivated to enhance both the interfacial charge separation and light harvest. Finally, what is the effect of heat treatment of the blend films on the PV performance? This is of particular relevance for the nanorod-polymer hybrids because the interface and morphology are essential to the overall PV characteristics. Our systematic studies here have resulted in some interesting results and shall be a useful guide for the development of cost-efficient hybrid inorganic-polymer solar cells.

2. Experiment

2.1. Materials and reagents

Titanium butoxide (Alfa Aesar, 98%), oleic acid (OA, pract., 95% International Laboratory USA), oleylamine (OLA, Aldrich, tech., 70%), stearic acid (SA, 95%, Sigma-Aldrich), triethylamine (TEA, 99%, Riedel-deHaën), cyclohexane (Acros, for analysis), octadecene (ODE, Sigma-Aldrich, 90%), protoporphyrin disodium salt (PPR, 98%, TCI, NACALAI, TESQUE, INC. KYOTO, JAPAN), Mercury dibromofluorescein disodium salt (HgBrRed, Practical grade, Sigma), N719 dye (95%, Sigma), and regioregular poly(3-hexylthiophene) (P3HT) were used as received without further purification. Other chemicals were of analytical grade and also used as received without further purification.

2.2. Synthesis and surface dye-modification of TiO₂ nanorods

2.2.1. Synthesis of linear TiO₂ nanorods [27].

An appropriate amount of oleic acid (3 mL) and cyclohexane (10 mL) were mixed. Into the mixture solution, Ti(OBu)₄ (0.5 mL) was slowly added dropwise. The resulting solution was sealed in a teflon-lined stainless autoclave, heated to 150 °C, and kept for 25 h. A light yellow sticky titanium complex precursor (viscous but transparent) was obtained, which was then extracted by precipitation with an excess of ethanol at room temperature. The titanium complex precursor was re-dispersed in a mixture consisting of 5 mL octadecene (ODE), 0.6 mL of oleic acid (OA) and 0.8 mL of oleylamine (OLA). The solution was heated to and maintained at 300 °C in a three-neck-flask under stirring for 1 h under an inert gas of N₂.

The subsequent product extraction was performed in air at room temperature. Upon adding an excess of ethanol to the reaction mixture, the TiO₂ nanowires product was precipitated. The precipitate was further purified by centrifugation and washed three times with ethanol to remove residual surfactants. The final TiO₂ nanorods protected by OA-coordination were easily re-dispersed in solvents such as chloroform or hexane, without any sign of further growth or irreversible aggregation.

2.2.2. Synthesis of branched TiO₂ nanorods.

Appropriate amounts of stearic acid (3 g) and cyclohexane (10 mL) were mixed. Into the mixture solution, Ti(OBu)₄ (0.5 mL) was slowly added dropwise. The above mixture was stirred at room temperature for 1 h, and then triethylamine (2 mL) was added in drops. The resulting solution was sealed in a teflon-lined stainless autoclave, heated to 150 °C, and kept for 25 h. A white precipitate was obtained, which was then extracted by precipitation with an excess of ethanol at room temperature. The precipitate was further purified by centrifugation and washed three times with ethanol to remove residual surfactants.

2.2.3. Surface modification and dye loading of the nanorods.

The as-synthesized nanorods were capped with insulating surfactant of oleic acid (OA) or stearic acid (SA) consisting of long alkyl chain, which may act as a potential barrier for charge transfer. Therefore, we carried out the ligand exchange treatment to replace the original long alkyl chain ligand using pyridine (PYR), as reported previously [28]. The TiO₂ nanorods were dispersed in pyridine and left under stirring at 80 °C until the solution turned clear (around 1 h). The pyridine-modified nanorods were then precipitated by adding excess ethanol and isolated by centrifugation at 3000 rpm.

An appropriate amount (~80 mg) of pyridine modified nanorods was re-dispersed in 20 mL of PPR/ethanol (1 mM), HgBrRed/ethanol (1 mM), and N719/ethanol (1 mM) solution, respectively. The mixtures were ultrasonicated in dark for 1 h to allow thorough dye adsorption. Afterwards, the nanorods loaded with different dyes were isolated by centrifugation and washed 3 times with ethanol to remove residual dyes. Nanorods loaded with PPR (dark red), HgBrRed (jacinth), and N719 (amaranth) using this method were then ready for further processing and measurements.

2.3. PVC fabrication and characterization

The hybrid PVC devices studied in this work featured a sandwich structure, ITO/PEDOT:PSS (50 nm)/P3HT:TiO₂ nanorods (80 nm)/Al (150 nm). Indium-tin oxide (ITO; 15 Ω/square) substrates were cleaned by a routine procedure, which included sonication in detergent followed by repeated rinsing in distilled water, acetone, and isopropanol, in sequence. After treatment with oxygen plasma, 50 nm of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid):(PEDOT:PSS) (Baytron P 4083, Bayer AG) was spin-coated onto the ITO substrate followed by drying in a vacuum oven at 80 °C for 8 h. A thin film of P3HT and TiO₂ nanorods was coated from an 1,2-dichlorobenzene solution onto the PEDOT:PSS/ITO substrate by spin-casting inside a nitrogen-filled dry-box. The film thickness of the active layer was around 80 nm, as measured with an Alpha Step 500 surface profiler (Tencor). Aluminum cathode was then thermally evaporated on the top of the active layer under a vacuum of 3×10^{-4} Pa.

Transmission electron microscopy (TEM) was performed on a JEOL 2010 transmission electron microscope. X-ray diffraction (XRD) analyses were performed on a Philips PW-1830 X-ray diffractometer with Cu K α irradiation ($\lambda = 1.5406$ Å) at a scanning speed of 1°/min (for as-prepared samples) and 0.5°/min (for composite films). Electronic absorption spectra were measured by a HP 8453 UV-vis spectrophotometer. The photoluminescence spectra were recorded on a fluorometer (JY FL-3). The spectral response was measured with a commercial photomodulation spectroscopic setup including a xenon lamp, an optical chopper, a monochromator, and a lock-in amplifier operated by a PC computer (model Merlin, Oriol). A calibrated Si photodiode was used as a standard in the determination of photosensitivity. Solar energy conversion efficiencies were measured at an illumination intensity of 100 mW/cm² with an AM1.5 solar simulator (Oriol model 91192). The current-voltage (*I*-*V*) characteristics of the PV devices in the dark and under illumination were measured with a Keithley 236 source-measure unit. The energy conversion efficiency (*ECE*) and fill factor (*FF*) were calculated according to the following equations [4,5,29]:

$$ECE = FF \times I_{sc} \times V_{oc} / P_{in}$$

$$FF = I_m V_m / I_{sc} V_{oc}$$

where P_{in} is the incident radiation flux, I_{sc} and V_{oc} are the short-circuit current and open-circuit voltage, respectively, and I_m and

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