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The effect of TiO_2 nanocrystal shape on the electrical properties of poly (styrene-*b*-methyl methacrylate) block copolymer based nanocomposites for solar cell application

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ABSTRACT

Titanium dioxide (TiO_2) nanocrystals were synthesized into two shapes, namely spherical and rod-like and used for the fabrication of polystyrene-*block*-poly(methyl methacrylate) (PSMMA) block copolymer based nanocomposites, which were employed as the active top layer of electro-devices for solar cell application. Electro-devices were designed using nanocomposites with high TiO_2 nanocrystal contents (50-70 wt%) and for comparison as-synthesized TiO_2 nanospheres (TiO_2NSs) and TiO_2 nanorods (TiO_2NRs) were also used. The morphology of the electro-devices was studied by atomic force microscopy showing good nanocrystal dispersion. The electrical properties of the devices were investigated by PeakForce tunneling atomic force microscopy and Keithley semiconductor analyzer, which showed higher electrical current values for devices containing TiO_2NRs in comparison to TiO_2NSs. Remarkably, the influence of the PSMMA block copolymer on the improvement of the conductivity of the electro-devices was also assessed, demonstrating that the self-assembling ability of block copolymer can be beneficial to improve charge transfer in the fabricated electro-devices, thus representing relevant systems to be potentially developed for photovoltaic applications. Moreover, the absorbance of the prepared electro-devices in solar irradiation range was confirmed by UV–vis spectroscopy characterization.

1. Introduction

Organic photovoltaic devices are an attractive alternative to achieve a low cost, light weight and environmentally friendly solar energy source [1–5]. Organic solar cells based on polymers, in particular, have been widely investigated owing to their ease of fabrication in comparison to conventional solar cell devices. However, the main drawback of polymer based photovoltaic devices is their lower solar power efficiencies generally up to 10% [3,5,6] as a consequence of the absence of components with high electron mobility. Consequently, this point is being extensively studied in order to achieve organic photovoltaic devices with higher carrier transport. One of the ways to enhance the charge transfer in an organic solar cell is the combination of polymers with inorganic semiconductors, resulting in hybrid inorganic/organic optoelectronic devices, such as photovoltaic systems [3,7,8]. Among the different inorganic semiconductors, TiO_2 inorganic nanocrystals (NCs) are frequently used as semiconductor in solar cell devices [3,4,7–14] since they deliver the highest energy conversion efficiency comparing to other available semiconductors. Moreover, semiconductive inorganic NCs can also strengthen the optical properties of polymers in the energy conversion device, especially for photovoltaic applications, since that can extend the overall absorption range. In this perspective, the synthetic protocol for the fabrication of TiO_2NCs is particularly crucial, as it is required to enable a suitable control on the NC size, shape and surface properties, all characteristics that strongly affect the nanomaterial efficiency as active components of solar energy conversion systems. In addition, the device performances are strongly dependent on the hybrid active layer morphology on the nanometer scale.

Many research works have focused on nanostructured composites and hybrid layers, which are viable for a variety of technological applications, including energy conversion in organic solar cells [8,15,16]. In our previous work, nanostructured hybrid composites were developed, by using poly(styrene-*b*-methyl

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methacrylate) (PSMMA) block copolymer as a template for the dispersion of as-synthesized colloidal TiO_2 nanorods (TiO_2NRs), which were incorporated into the polymer matrix up to high contents resulting in conductive nanocomposites [17]. In this work, the objective is to characterize novel electro-devices fabricated with a layer of TiO_2-PSMMA nanocomposite as a first approach to consider their potential application in optoelectronic devices. The synthesis of TiO_2NCs has been carried out by two different colloidal routes based on the hydrolysis of titanium tetraisopropoxide in oleic acid as surfactant, which gave the possibility to manipulate the NC growth kinetics and achieve size and shape control over resulting NCs. Thus, this allowed to obtain NCs with different size and shape depending on the synthesis protocol and to investigate the influence of the NC size and shape on the characterization of electro-devices based on nanocomposites.

The two kinds of as-synthesized TiO_2NCs employed in this work, TiO_2 nanospheres (TiO_2NSs) and nanorods (TiO_2NRs), were compared as active components for the fabrication of electro-devices. First both NCs kinds were studied by atomic force microscopy (AFM). The fabricated electro-devices were also investigated by means of AFM in order to analyze the morphology of the nanocomposite layer on the top of the devices. The electrical properties of the fabricated electro-devices were studied by tunneling atomic force microscopy (TUNA) to measure the current at nanoscale passing through the electro-devices and by Keithley semiconductor analyzer to determine the surface conductivity at macroscale. Finally, UV–vis spectroscopy was employed to investigate the UV absorption of the fabricated electro-devices.

2. Experimental

2.1. Materials

The block copolymer used in this work was polystyrene-*block*-poly(methyl methacrylate) (PSMMA), from Polymer Source, with a polydispersity index (M_w/M_n) of 1.17 and number-average molecular weights of PS and PMMA blocks of 83,000 and 92,500 g/mol, respectively. For the synthesis of both TiO_2NSs and TiO_2NRs, titanium tetraisopropoxide (TTIP, 99.999%), trimethylamino-N-oxide dihydrate (TMAO, 98%), oleic acid (OLEA, 90%) and ethyleneglycol (EG, 99.8%) were purchased from Aldrich. Toluene, supplied by Labscan, acetone, supplied by Oppac, and 2-propanol and chlorobenzene, supplied by Panreac, were used as solvent. For the fabrication of electro-devices, indium tin oxide (ITO) coated glass (sheet resistivity 8-12 Ω/sq, Aldrich), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Clevios^{TM} AI 4083) and Poly(3-hexylthiophene-2,5-diyl) (P3HT, Aldrich) were used.

2.2. Synthesis of TiO_2 nanocrystals

Two different kinds of synthesized TiO_2NCs were employed for the preparation of TiO_2-PSMMA nanocomposites. The synthesis of TiO_2NSs was performed according to a reported procedure [18]. In a typical synthesis, a mixture of TMAO and OLEA was degassed. Then TTIP was added under nitrogen flow at 100 °C, followed by the EG injection. The slow hydrolysis of the titanium precursor resulted in OLEA-coated TiO_2NSs, with an average diameter of 5 nm.

On the other hand, TiO_2NRs were synthesized also following a previously reported method [17–19]. Briefly, TTIP was added to previously degassed OLEA under nitrogen flow at 100 °C. Subsequently, upon rapid injection of TMAO, a fast hydrolysis process started, leading to the formation of OLEA-coated anatase TiO_2NRs (average size of 3 nm in diameter and 18 nm in length). The obtained TiO_2NRs were precipitated from the reaction mixture upon the addition of methanol, isolated by centrifugation and re-dispersed in toluene.

2.3. Preparation of TiO_2-PSMMA nanocomposites

TiO_2-PSMMA nanocomposites were prepared following a protocol published elsewhere [17]. Firstly, PSMMA block copolymer solutions were prepared by dissolving a defined amount of block copolymer in toluene to reach a concentration of 5 mg/mL. The solution was left under magnetic stirring until a homogeneous mixture was obtained. Then, an adequate volume of TiO_2NS or TiO_2NR solution in toluene was added to the block copolymer solutions in order to obtain TiO_2-PSMMA nanocomposites at increasing TiO_2NC content, namely 50, 60 and 70 wt%. Nanocomposite solutions were stirred for a few hours.

2.4. Fabrication of ITO-glass/PEDOT:PSS/P3HT/TiO_2-PSMMA electro-devices

ITO coated glass substrate was firstly cleaned by sonication in deionized water for 15 min, followed by sonication in acetone for 30 min, sonication in 2-propanol for 30 min and finally sonication in deionized water again for 30 min. Electro-devices were fabricated as follows. Two PEDOT:PSS layers were spin-coated (Spin-coater model P6700 from Specialty Coating Systems, Inc.) onto previously cleaned ITO glass substrate and subsequently dried at 120 °C for 10 min under vacuum. Then, the P3HT layer was deposited by spin-coating a 15 mg/mL P3HT solution in chlorobenzene onto the PEDOT:PSS layer. The films were dried at 140 °C for 15 min. Finally, the TiO_2-PSMMA nanocomposite layer was spin-coated. For comparison, electro-devices based on pristine TiO_2NSs and TiO_2NRs, respectively, as last active layer of electro-device, were also fabricated. All layers were deposited at 2000 rpm for 120 s.

2.5. Techniques

The morphology of as-synthesized TiO_2NSs and TiO_2NRs onto silicon wafer substrate as well as onto conductive electrodes was studied by atomic force microscopy (AFM) under ambient conditions. AFM images were obtained with a Nanoscope IIIa scanning probe microscope (Multimode, Digital Instruments). Tapping mode (TM) was employed in air using an integrated tip/cantilever (125 μm in length with ca. 300 kHz resonant frequency). Typical scan rates during recording were 0.7 to 1 line/s using a scan head with a maximum range of 15 × 15 μm. Several replicates were prepared per each electro-device and different zones per each sample were investigated by AFM, in order to assess the uniformity of the films. The TiO_2NS and TiO_2NR thin films onto silicon wafer were analyzed upon exposure to 254 nm UV light (XX-15S, UVP Inc.) for 24 hours in order to remove the organic coating of the NCs. AFM investigation was also carried out on purposely scratched samples to measure the thickness of various systems. Therefore the thickness of the prepared systems resulted in 175 ± 5 nm for those based on pristine TiO_2NCs, whereas it was 93 ± 5 nm for the TiO_2-PSMMA nanocomposite films. All measured films were deposited onto an ITO layer, which is 120-160 nm thick according to the supplier specifications.

The size and shape of as-synthesized TiO_2NSs and TiO_2NRs was analyzed by transmission electron microscopy (TEM). A Tecnai G2 20 Twin transmission electron microscope operated at 200 kV with a resolution of 2.5 Å was used. Both TiO_2NS and TiO_2NR were deposited by drop casting onto carbon-coated copper grids.