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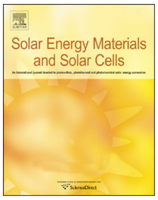

Effect of ZnO nanoparticles on the photochemical and electronic stability of P3HT used in polymer solar cells

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ABSTRACT

ZnO nanoparticles are widely used as electron acceptors in hybrid polymer blend solar cells as well as electron extraction materials in organic solar cells. Here, a study of the photochemical and electronic stability of poly(3-hexyl thiophene)/zinc oxide nanoparticle (P3HT/ZnO) interfaces is presented. Photostability is compared with device stability of hybrid bulk heterojunction solar cells under light soaking and dark storage. We first investigate the photocatalytic properties of ZnO in P3HT:ZnO blend layers. The results indicated that the photocatalytic activity of ZnO nanoparticles drastically increases the photooxidation rate of P3HT. Photostability of P3HT:ZnO active layers was significantly improved when irradiation was performed in absence of UV radiations and in absence of oxygen. Using optimal conditions to avoid photodegradation during light soaking still leads to rapid performance losses revealing device degradation is not related to photodegradation of the hybrid polymer blend but to electronic modification during illumination. Importantly, both dark storage in air as well as light soaking experiments show that the stability of interfaces between P3HT and ZnO nanorods is higher than that observed in devices using ZnO nanospheres. This points towards the importance of the shape of the ZnO nanoparticles for long time stability in polymer solar cells.

1. Introduction

With the increasing demand for energy, and the limited availability of fossil fuels, there is a need for a renewable, sustainable energy source. One source that always will be available is the energy of the sun, which can be converted directly into electricity. Organic solar cells (OSC) based on conjugated polymer: fullerene bulk heterojunctions are nowadays promising candidates for future low cost photovoltaic (PV) [1]. An alternative approach to OSC are hybrid polymer heterojunction solar cells (HSC) that use inorganic acceptors based on metal oxides instead of fullerenes leading to better control of morphology and higher blend stability [2]. Indeed morphological instability of OSC is currently one of the issues that hinders commercialization [3,4]. Furthermore device stability upon air storage represents another advantage of hybrid solar cells compared to their organic counterparts [5]. It is important to highlight that metal oxides such as ZnO and TiO_2 are not only amongst the most studied electron acceptors in hybrid solar cells based on polymer blends and organometal halide perovskite active layers [6], respectively, but these materials are nowadays also commonly used as materials for electron extraction layer (EEL) in solution processed OSC [7,8]. This makes polymer/ZnO interfaces very important for HSC and OSC.

Besides morphological and storage stability, operating stability under light exposure, called photostability, is another main challenge of polymer solar cells. Solar light with oxygen is one of the main triggers for polymer degradation [9,10]. Photochemical degradation of the conjugated polymer and its relation to the overall cell performance has received much attention [11–13]. It is worth recalling that almost all organic polymers are unstable under UV light irradiation at ambient air, photodegradation being strongly attenuated when irradiation is carried out in the absence of oxygen [14,15]. The impact of fullerene acceptors such as [6,6]-

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phenyl-C_{61}-butyric acid methyl ester (PCBM) on photostability of OSC was studied intensively. It was shown that fullerenes strongly decrease the photodegradation rate of the polymer in polymer: PCBM blends [16,17]. The radical scavenger properties of PCBM take part to the photostabilization of the blend due to the ability of fullerenes to terminate free radical reactions [18]. But in the case of HSCs using nanoparticle acceptors such as ZnO, photodegradation mechanism have not yet been studied in detail. This is particular important as for example ZnO is susceptible to have a photocatalytic activity and can lead to degradation of the conjugated polymer. Indeed, it has been demonstrated that the photocatalytic effect of semiconductors such as ZnO, which are useful for their antibacterial activity due to the formation of reactive species that act as oxidants, mainly results in the formation of radicals that are able to degrade the polymer matrix [19,20] (see Scheme S1 in SI). So far the ability of pigments to catalyze the photooxidation of polymers has received significant attention with regard to their mechanistic behavior [21], but to the best of our knowledge, degradation mechanism of conjugated polymer/ZnO interfaces have not yet be addressed although important for future applications as active layers in hybrid solar cells but also as interfacial layers in OSC. Therefore, it is highly interesting to study photocatalytic activity of ZnO in contact with donor polymer to identify potential impact on the lifetime of the HSC or OSC devices.

The study of solar cells stability is quite complex as all the layers and interfaces are involved in the degradation process as oxidation of electrodes, delamination processes, morphological and photochemical changes within the active layer [22]. Therefore, the study of the photostability of the sole active layer deposited on inert substrate is a relevant way to elucidate its intrinsic degradation process. We have recently studied the electronic properties of ZnO nanoparticles as EEL in polymer solar cells using P3HT and PTB7 blended with fullerene as active layers in detail [23–25]. In order to evaluate the photo-catalytic activity of the used ZnO nanoparticles, we study here P3HT:ZnO blends leading to large areas of interfaces between both materials compared to P3HT/ZnO interfaces in polymer solar cells. In the past, P3HT:ZnO blend HSC as well as photostability of P3HT under different conditions have been investigated intensively making P3HT:ZnO polymer blends a good model system. The different tools used to monitor degradation processes in materials for OPV are described in previously reported works [26]. The main goal of the study was to affirm or confirm the degradation of P3HT induced by the photocatalytic activity of the ZnO nanoparticles, and then to determine its potential role in the degradation/stability of HSCs under illumination. The role of ZnO nanoparticles on the photo-oxidation mechanism and corresponding kinetics of P3HT under UV–visible light irradiation is studied in detail. The approach is based on the identification of many photoproducts formed during illumination, which are macromolecular and molecular nature potentially trapped in the film or released in the atmosphere. Moreover, the specific role played by the spectral distribution of the source (w and w/o UV radiations), the atmosphere (w or w/o oxygen) and the shape of the nanoparticles (nanorods or nanospheres) was investigated. Stability of HSCs upon light exposure and air storage was studied to correlate photo-induced and atmospheric degradation mechanism in HSC.

2. Experimental section

2.1. Materials and samples preparation

ZnO nanospheres were prepared as published elsewhere [23,25]. Solution of 0.4415 g of potassium hydroxide KOH (Aldrich Chemicals 99.99%) in 23 mL of methanol was added dropwise to a solution of 0.8202 g of zinc acetate $Zn(Ac)_2$ (Aldrich Chemicals 99.99%) in 42 mL of methanol (Acros 99.99%) and 0.25 mL of distilled water at 60 °C under magnetic stirring (mole ratio KOH/$Zn(Ac)_2=1.54$). After 2 h 15 min, the mixture was concentrated by using a rotary pump. Then, the solution was left at rest to decant and the white solid precipitate was washed with methanol. After washing, ZnO nanoparticles with 6 nm as average diameter were formed as determined by TEM analysis (Fig. S1 in SI). ZnO nanorods (NRs) were synthesized as published before [27,28]. First KOH was replaced by NaOH in this process under otherwise identical conditions. Then after 2 h 15 min at 60 °C, the growth solution was condensed to 10 mL under reduced pressure at 55 °C (until the solution became clear). This step, so-called condensation step, affords the seed solution, from which NRs are grown by further heating at 60 °C during a given reaction time. Pure NRs were obtained by repetitive precipitation and washing steps using methanol. Average dimension of the nanorods were determined by TEM analysis to 8 nm in diameter and 50 nm in length (Fig. S1 in SI). Both ZnO nanospheres and nanorods bear acetate ligand at their surface as shown before [25,28]. The strong photoluminescence with a maximum centered on 550 nm observed for both nanospheres and nanorods (see Fig. S2) indicates the presence of oxygen vacancies [29] as shown by XPS before [25]. The synthesized ZnO nanoparticles are thus non-stoichiometric ZnO.

2.2. Solar cells fabrication and characterization

Both ZnO nanospheres and nanorods were first transferred into chloroform by centrifugation of the initial solution, followed by removing the supernatant and adding pure chloroform to the residual solution. The ZnO concentration in chloroform was 30 mg/mL. Regioregular P3HT was purchased from Sigma-Aldrich (RR ≥ 90%). P3HT was solubilized in chloroform under mechanical stirring of 4 h. The P3HT concentration in chloroform was 15 mg/mL.

HSCs were prepared according to the following procedure: First ITO substrates were thoroughly cleaned by sonication in acetone and ethanol followed by rinsing with water and sonication in isopropanol and applying ultraviolet-ozone for 10 min A thin layer of poly(3,4-PEDOT: PSS) (CLEVIOSTM AI 4083) was spin-coated on the cleaned ITO pre-coated glass substrate at the speed of 4000 rpm for 60 s followed by heating on a hot-plate at 140 °C for 20 min The thickness of PEDOT:PSS was measured to 40–50 nm. The substrates were then transferred to a nitrogen-filled glove box. The active layer of P3HT:ZnO (nanospheres or nanorods) blend with a weight ratio of 1:2 was dissolved and then was spin-coated at 1500 rpm for 60 s without further annealing. The final active layer was measured to 100 nm. Subsequently the device was pumped down in vacuum at 1×10^{-6} Pa and a ~120 nm thick Al electrode was deposited on top. The deposited Al electrode area defined the active area of the devices as 0.24 cm^2.

The current density–voltage (*J*–*V*) characteristics of the devices were measured using a Keithley 238 Source Measure Unit inside the glove box. Solar cell performance was measured under Argon atmosphere by using a Newport class AAA 1.5 Global (AM 1.5G) full spectrum solar simulator with an irradiation intensity of 100 mW cm^{-2}. Light intensity was measured with a calibrated Si-diode from Newport Company. Shadow masks were used to well-define the illuminated area to 0.24×1.0 cm^2. Comparison of masked and unmasked solar cells gave consistent results with photocurrent increase by less 1% for unmasked devices.

2.3. Irradiation

The P3HT and P3HT:ZnO nanoparticles samples were irradiated under accelerated artificial conditions. The aging device was a