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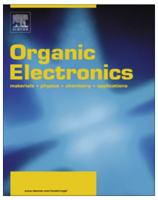

Solution-processed annealing-free ZnO nanoparticles for stable inverted organic solar cells

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ABSTRACT

We report the development and application of high-quality zinc oxide nanoparticles (ZnO NPs) processed in air for stable inverted bulk heterojunction solar cells as an electron extraction layer (EEL). The ZnO NPs (average size ~11 nm) were dispersed in chloroform and stabilized by propylamine (PA). We demonstrated that the ZnO NP dispersion with 4 vol.% of PA as stabilizer can be used in air directly and remains clear up to one month after preparation. Our inverted solar cells consisted of a blade-coated poly(*N*-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole (PCDTBT) and [6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) (1: 4 by weight) active layer sandwiched between a ZnO electron extraction layer and a MoO_3/Ag anode. All solar cells with ZnO films fabricated in air using PA-stabilized ZnO dispersions prepared within a time window of one month exhibited power conversion efficiencies (PCE) above 4%. In contrast, if the ZnO film was prepared in air using regular un-stabilized ZnO NP dispersion, the PCE would drop to 0.2% due to poor film quality. More interestingly, X-ray photoelectron spectroscopy and nuclear magnetic resonance measurements indicated that the PA ligands were not covalently bonded to ZnO NPs and did not exist in the deposited ZnO films. The spin-cast ZnO thin films (without any thermal treatment) are insoluble in organic solvents and can be directly used as an EEL in solar cells. This feature is beneficial for fabricating organic solar cells on flexible polymer substrates. More importantly, our non-encapsulated inverted solar cells are highly stable with their PCEs remaining unchanged after being stored in air for 50 days.

1. Introduction

Due to the high scientific and economic interest in organic photovoltaic research, the power conversion efficiency of organic solar cells has been pushed up steadily in the last decade, currently reaching 10% [1]. This progress was achieved through tremendous efforts in the development of low band gap materials [2], the control of fabrication process to optimize the active layer morphology [3], and the improvement of interface engineering [4].

One of the approaches of interface engineering focuses on the incorporation of electron and hole extraction layers between the active layer and the metal cathode/anode, to align the energy levels at the interface, and consequently to allow an efficient extraction of electrons and holes, respectively. In both conventional and inverted organic solar cells, various materials such as polyelectrolytes [4a],

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inorganic salts [5], and metal oxides (TiOx, ZnO, MoO_3, V_2O_5, WO_3) have been investigated and used as n-type or p-type interlayers to enhance the performance and/or the stability of the devices [6].

Among n-type materials, ZnO NP films, formed by sol–gel process, have been widely used in inverted organic solar cells. However, to form crystalline ZnO networks with good electron mobility, an annealing temperature over 200 °C is usually required, which is incompatible with the flexible polymer substrates used in the fabrication of solar cells. The solution-dispersed ZnO NPs have been shown as a good alternative to reduce the annealing temperature, and can be easily processed into films via various coating methods [7]. However, the ZnO NP dispersions in organic solvents are not stable in air and tend to form aggregates and quickly precipitate out, especially in the presence of moisture [8]. Therefore, organic ligands such as alkyl amine [9], alkyl thiol [10], carboxylic acid [11], and alkoxyacetic acid have been used to protect ZnO NPs and prevent their aggregation [8]. However, most ligands reported in the literature have high boiling points, which again require a high temperature annealing (>150 °C) to ensure complete removal of the ligands from the fabricated ZnO NP films in order to get good electron-transport properties.

In this paper, we report the use of a short and low boiling point compound, propylamine (PA, bp 48 °C) as an effective stabilizing ligand for the ZnO NPs. The addition of PA at a concentration of 4% (v/v) keeps the ZnO NP dispersion in chloroform, chlorobenzene or dichlorobenzene stable over one month, even after exposure to ambient air. More importantly, the spin-cast ZnO NP films do not require any thermal annealing or plasma treatment and can be directly used as an electron extraction layer in inverted solar cells. In this work, pyridine and triethylamine have also been tested as the ZnO NP stabilizers. However, they are not as effective as propylamine although triethylamine is a stronger base than propylamine. In order to understand the mechanism involved in the stabilization of ZnO NPs by propylamine, the ZnO NP dispersion and the spin-cast films were characterized by nuclear magnetic resonance (NMR) and X-ray photo-electron spectroscopy (XPS), respectively. It was found that the PA ligands were not chemically bonded to ZnO NPs and did not exist in the deposited ZnO films. The concentration of the PA has been optimized. It is interesting to point out that our non-encapsulated inverted solar cells based on the PCDTBT:$PC_{71}BM$ blend and PA stabilized ZnO NPs are quite stable with their PCEs remaining unchanged after being stored in air for 50 days. Therefore, these air-processed and annealing-free ZnO nanoparticles are very valuable for the technology transfer of organic solar cells from the lab to the industry.

2. Experimental

2.1. Instrumentation and materials

NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrometer. The samples were prepared in deuterated $CHCl_3$. Chemical shifts were reported as δ values (ppm) relative to internal chloroform residue (7.25 ppm). The XPS spectra were recorded on a Phi 5500 system, using a monochromatic Al X-ray source with beam energy of 1486 eV and a take-off angle of 45°. PCDTBT was provided by St-Jean Photochemicals Inc. and $PC_{71}BM$ was purchased from Nano-C, and they were used without further purification. The ZnO nanoparticles were synthesized according to our previous procedure [7a]. The ZnO nanoparticles were dispersed in anhydrous chloroform. After filtration through a 0.2 μm filter, a clear colorless dispersion was obtained and stored in a nitrogen-purged glovebox. Prior to device fabrication, it was diluted with anhydrous chloroform in order to obtain an optimal ZnO film thickness by spin-casting, and propylamine was added via a micropipette.

2.2. Device fabrication and characterization

The bulk heterojunction solar cells were fabricated on pre-patterned indium tin oxide (ITO) coated glass substrates. The sheet resistance and thickness of the ITO are 12 Ω/sq and 150 nm, respectively. The ITO substrates were thoroughly cleaned in detergent and DI water, ultrasonicated in acetone and isopropyl alcohol for 15 min, and dried in an oven at 120 °C. UV–ozone treatment was then performed for 15 min. A ZnO NP film (~20 nm-thick) was spin-cast on top of the ITO substrates from a freshly prepared ZnO dispersion at 700 rpm. Afterward, an active layer was blade-coated onto the ZnO film from a dichlorobenzene solution of PCDTBT:$PC_{71}BM$ with a weight ratio of 1:4 and dried overnight at room temperature in a nitrogen-filled glovebox. The PCDTBT:$PC_{71}BM$ solution with a PCDTBT concentration of 3 mg/mL was prepared three days before deposition and heated at 100 °C over night.

The blade speed was set at 35 mm/s to get 70 nm thick active layers. Finally, to complete the solar cell architecture, a bilayer anode consisting of 100 nm Ag on top of 10 nm molybdenum oxide was thermally evaporated through a shadow mask on the active layer to form cells with an active area of 1 cm^2. The thicknesses of the films were measured by a Dektak profilometer.

The photovoltaic parameters were extracted from the current–voltage (*J*–*V*) characteristics measured in air with a Keithley 2400 Digital SourceMeter and the photocurrent was generated under air mass 1.5 global (AM 1.5G) irradiation of 100 mW/cm^2 from a ScienceTech SS 500W solar simulator. The light intensity was adjusted using a calibrated Si photodiode with a KG-5 filter purchased from PV Measurements, Inc. The external quantum efficiency (EQE) was performed using a Jobin-Yvon Triax spectrometer, a Jobin-Yvon xenon light source, a Merlin lock-in amplifier, a calibrated Si UV detector, and an SR570 low noise current amplifier. It is worth pointing out that the short-circuited photocurrent reported in this paper was always calculated from the wavelength integration of the product of the EQE curve and the standard AM 1.5G solar spectrum.

3. Results and discussion

Fig. 1 shows the evolution of the ZnO NP dispersion with time before and after exposure to air. Within 5 min