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Effects of ultraviolet–ozone treatment on organic-stabilized ZnO nanoparticle-based electron transporting layers in inverted polymer solar cells

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ABSTRACT

Electron transporting layers (ETLs) in inverted polymer solar cells (I-PSCs) were fabricated by spin coating a colloidal dispersion of ZnO nanoparticles (NPs), and the effects of ultraviolet–ozone (UVO) treatment on the ZnO NP ETLs were investigated. The brief UVO treatment (<5 min) could considerably improve the performance of the resulting I-PSCs (~30% increase in power conversion efficiency); whereas, excessive UVO treatment (>10 min) caused significant degradation. The characterization of the ZnO ETLs as a function of the UVO treatment duration revealed that brief treatment can remove the residual organic stabilizer molecules on the surface of the ZnO films by UV induced decomposition mechanism. However, excessive treatment can generate additional defects on/within the ZnO films, which can induce charge recombination. This effect was further confirmed by the thermal treatment of the ZnO ETLs at a high temperature (280 °C) at which the organic surfactants could be removed. Flexible I-PSCs were also fabricated using indium doped tin oxide coated plastic substrates and the usefulness of the room temperature UVO treatment was further confirmed in view of its potential applicability in flexible devices.

1. Introduction

Polymer solar cells (PSCs) have been recognized as promising candidates for the development of next-generation solar cells [1,2]. The inherent advantages of polymers, such as ultra-low cost, high processability, and light weight have enabled the exploration of new niches, specifically in large-area flexible energy devices [3]. One important challenge has been to enhance the power conversion efficiency (PCE) through the development of organic semiconducting active materials [4–6]. However, as the PCE of PSCs has been continuously improved to higher than 8%, the long-term air stability of the PSCs has emerged as another major challenge in the way of commercializing PSCs [7]. Inverting the cell structure is a simple and reliable strategy to improve the environmental stability of PSCs. Inverted PSCs (I-PSCs) have effectively enhanced the stability by using low work-function metals, while avoiding direct contact between a popular, yet acidic, hole transporting buffer layer (HTL), poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) and indium doped tin

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oxide (ITO), a regular transparent conducting electrode [8,9].

In conventional PSCs, holes are collected into ITO through HTLs, such as PEDOT:PSS, and electrons are collected through low work function metals, such as Al. However, in I-PSCs, the electrons are collected through an electron-transporting layer (ETL) deposited on ITO and holes are collected through high work-function metals, such as Au and Ag [10,11]. The key parameters to achieve efficient ETLs include selective hole-blocking capability, low resistivity for electron conduction, and transparency in the visible spectral region. Various wide band-gap n-type metal oxides possessing work functions lower than ITO with respectable electron-transporting properties, such as TiO_2 [12], ZnO [3,13,14], and Cs_2CO_3 [15], have often been used as ETLs. Among these, ZnO has popularly been used because of its high electron mobility, reduced light-absorption ability, and high environmental stability [16]. Atomic layer deposition (ALD) [10,17], electrodeposition [16], sol–gel technique [3,18], and spin coating from colloidal nanoparticles [8] have been used to prepare ZnO based thin film ETLs. While ALD requires high vacuum and electrodeposition use electrolytes, which can lead to inclusion of potential impurities, coating preformed colloidal nanoparticles or forming thin films by in situ sol gel reaction of precursors are more practical solution-based methods. Bearing in mind that an important potential use of PSCs is in the construction of flexible power generation devices, the importance of using low-temperature and vacuum-free processes to fabricate ETLs have been much sought after.

Direct deposition of preformed colloidal ZnO nanoparticles (ZnO NPs) on the ITO substrate is a simple and scalable approach to fabricate ETLs because of their appropriate work function and ease of synthesis [4,5] in addition to the potential for low-temperature uses [8,19]. The major challenges in this method have been in achieving even spatial distribution of individual nanoparticles using a simple coating method and high electron transfer within ZnO ETLs without high-temperature post-treatments [20–22]. Recently, the improved spatial distribution of ZnO NPs as a thin form factor has been reported in a few groups by using polymeric or organic molecules as a matrix/surfactant [19,21,22]. Preventing the aggregation of ZnO NPs with a smooth film surface morphology enabled the enhanced performance of the I-PSCs with various polymer active materials. However, the removal of surfactant materials, which contributed to the improved dispersion of ZnO NPs, while aggravating the electron transfer/transport by providing additional resistance, was often a crucial issue in the optimization of the performance of ZnO ETLs. The research studies by So et al. indicate that UVO treatment could effectively remove the polymeric surfactant, while achieving reliable electronic coupling between the ZnO ETLs and the active layers [21].

Herein, we fabricated I-PSCs using ZnO ETLs by spin coating of a colloidal ZnO NP dispersion containing an organic stabilizer and the effects of UVO post-treatment on the performance of ZnO ETLs were investigated. I-PSCs with the structure of ITO/ZnO NP/active layer/PEDOT:PSS/Ag (Fig. 1) were fabricated and a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester) (PCBM) was used as the active material. For ZnO ETLs, a colloidal ZnO NP dispersion stabilized by an organic surfactant, 2-(2-methoxyethoxy) acetic acid (MEA), was spin coated on ITO substrates to yield thin films and the UVO post-treatment was performed at room temperature. The effects of the UVO treatment on the surface properties of the ZnO ETLs and the cell performance of the corresponding I-PSCs were investigated as a function of the UVO treatment time. Brief UVO treatment of the ETLs considerably improved the performance of the I-PSCs (by ~30%) by effective removal of the residual organic surfactant by which the electronic coupling with the active layers and/or among ZnO NPs increased. Excessive UVO treatment degraded the performance of the ZnO NP ETLs because of the generation of surface defect sites. Similar effects caused by the removal of organic surfactants were further confirmed using thermal annealing treatments. The usefulness of this room temperature UVO treatment was further confirmed by fabricating flexible I-PSCs using plastic ITO substrates.

2. Experimental

2.1. Materials

Zinc acetate dihydrate, KOH, 2-(2-methoxyethoxy) acetic acid (MEA), and 1,2-Dichlorobenzene (*o*-DCB) were obtained from Aldrich. 1-Butanol and methanol were purchased from Avantor Performance Materials. P3HT, PCBM, and PEDOT:PSS aqueous solutions (Clevios HTL solar) were provided by Rieke metal Inc., Nano-C Inc., Heraeus, Clevios, and GmbH respectively. All the chemicals were used without further purification.

2.2. Synthesis of ZnO NPs

The ZnO NPs were synthesized according to the previously reported sol–gel reaction with some modifications [23,24]. In general, 2.95 g of $Zn(CH_3CO_2)_2{\cdot}2H_2O$ (99%) was dissolved in 125 mL of methanol under vigorous stirring at 60 °C. A solution of KOH (1.48 g) dissolved in 65 mL of methanol was slowly added drop-wise to the $Zn(CH_3CO_2)_2{\cdot}2H_2O$ solution. The reaction mixture was stirred for 2 h at 60 °C. After 2 h, the reaction was halted and the final product was collected by centrifugation, washed several times using methanol, and methanol was removed. 1-Butanol was immediately added to the white precipitate. Finally, this solution was used to enhance the dispersion of the ZnO nanoparticles in 2-(2-methoxyethoxy)acetic acid (MEA).

2.3. UVO treatments of the ZnO NP-based ETLs

UVO treatment was performed using a commercial UV-ozone cleaning system with a 185/254 nm mercury lamp (Jelight Co. Inc.). To investigate the effect of the UVO treatment as a function of time, the surface of the ZnO film on the ITO glass substrates was treated by UVO for 0 (as-prepared), 2, 4, 6, 10, and 15 min. Fig. 1 shows the schematic of the UVO treatment.