



Luminescent cathode buffer layer for enhanced power conversion efficiency and stability of bulk-heterojunction solar cells



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ABSTRACT

We report high photovoltaic efficiency of over 9% in solution-processed, small-molecule (SPSM) 7,7'-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(6-fluoro-4(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[c]1,2,5]thiadiazole) *p*-DTS(FBTTh₂)₂: [6-6]-phenyl C70 butyric acid methyl ester (PC₇₀BM) blend based inverted BHJ solar cell by incorporating luminescent zinc oxide doped with sodium (ZnO:Na) quantum dots (QD) (ι-ZnO) as a cathode buffer layer (CBL) in inverted bulk-heterojunction (BHJ) solar cells for the first time. The ι-ZnO absorbs ultraviolet (UV) light and down-converts it to visible light. The ι-ZnO layer's emission overlaps significantly with the absorption of *p*-DTS(FBTTh₂)₂, leading to an enhanced absorption by *p*-DTS(FBTTh₂)₂. This resulted in a significant enhancement of photo-current from 15.4 to 17.27 mA/cm² and efficiency from 8% to 9.2% for ZnO and ι-ZnO based devices, respectively. This is among one of the highest efficiency values reported so far in the case of SPSM based single junction BHJ solar cells. The luminescent ZnO layer also protects the active layer from UV-induced degradation as solar cells show high stability under constant solar light illumination retaining more than 90% (~28 h) of its initial efficiency, whereas BHJ solar cells without the luminescent ZnO layer degraded to ~50% of its initial value under same conditions. Since ZnO is an essential part of inverted organic solar cells, the luminescent ι-ZnO CBL has great potential in inverted organic solar cells.

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1. Introduction

Bulk-heterojunction (BHJ) solar cells based on organic donors and fullerene derivatives have developed rapidly during the past decade because of their ease of fabrication, promising capability for low-cost, large-scale production of roll-to-roll coating technologies and rapid energy payback time [1–8]. Power conversion efficiency (PCE) of these devices has continued to increase through newly designed polymer materials and efficiency of more than 10% has been reported [9–12]. However, conjugated polymers have the batch to batch variations in molecular weight, polydispersity and

purity whereas solution processed small molecules (SPSM) are free from such variations and easy to synthesize [13–20]. Also, it is very important to balance between the morphology, interfacial layer and device fabrication to achieve higher PCEs. Our research program is focused on the development of improved interfacial layers to enhance the PCE of solar cells [15–17]. Highly efficient SPSM have been reported recently with PCE reaching nearly 9% in conventional structures with barium as cathode interlayer [15]. However, the conventional structure based BHJ solar cells degrade easily due to the use of low work function metal electrodes which are very sensitive to air [17]. On the other hand, inverted structures are more stable due to the use of less air-sensitive high work-function metals (Ag, Au) as the top hole collecting electrode (anode) and ZnO as the cathode buffer layer (CBL) between ITO and the active layer [21]. Recently polyethylenimine, 80% ethoxylated (PEIE) incorporated on the top of ZnO is used to enhance the efficiency of inverted SPSM solar cell to 7.9% [17].

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In inverted architecture, ZnO CBL plays an important role in electron collection and transport phenomenon. To improve the PCE of inverted BHJ solar cells, attempts have been made to enhance the conductivity of ZnO CBL by introducing various dopants such as Al, Ga, In etc [22–26]. However, there are no reports till date, on using rare-earth free luminescent ZnO exhibiting down conversion phenomenon as CBL, which can act as spectral convertors as well as UV shielding layer for inverted BHJ solar cells.

In this communication, we demonstrate highly efficient and stable inverted BHJ solar cells with rare earth free, Na doped ZnO (luminescent ZnO:Na quantum dots) (ι -ZnO QDs) as the CBL and p -DTS(FBTTh₂)₂:PC₇₀BM as the active layer. The ι -ZnO film absorbs UV light and down convert it to visible light (400–700 nm) with emission maxima at 545 nm. The corresponding emission of ι -ZnO layer overlaps significantly with the absorption of p -DTS(FBTTh₂)₂, leading to an additional light absorption by p -DTS(FBTTh₂)₂, and thus the overall absorption is enhanced, which is confirmed by UV–Vis and ultrafast transient absorption spectroscopy (TAS). This results in an increased PCE of 9.2% for ι -ZnO relative to 7.9% for intrinsic ZnO. Moreover due to its UV blocking characteristics, ι -ZnO increases the stability of the devices drastically as compared to intrinsic ZnO, under constant irradiation of light.

2. Experimental

Intrinsic undoped ZnO (ZnO) was synthesized by the sol-gel route in which, zinc acetate dihydrate [Zn(CH₃COO)₂H₂O] (Aldrich, 99.9%) with 0.1 M concentration was first dissolved in anhydrous ethanol [CH₃CH₂OH] (99.5+%, Aldrich) and rigorously stirred for 2–3 h at 80 °C. Subsequently, ethanolamine was added to the solution as sol stabilizer followed by thorough mixing process with magnetic stirrer for 12–15 h at 60 °C.

ι -ZnO was synthesized using sol-gel assisted wet chemical route, at ambient temperature. In which Equimolar concentrations of ethanolic solutions of zinc and sodium salts were used as precursors. Alkaline pH (~10) was maintained in order to facilitate the nucleation and growth of ι -ZnO QDs. To synthesize 0.1 M ι -ZnO QD solution, the precursors were stirred continuously for 2–5 h, at room temperature, resulting in a transparent colloidal solution. To restrict the size of QDs, ethanolamine was added as the capping agent. Both emission wavelength and integral intensity of emission in the yellow-green region of ι -ZnO QDs could be controlled by optimizing the concentration of the alkaline precursor, synthesis temperature, and pH conditions. Carrier concentration (hall effect) studies, were done using detailed AC transport measurements on a 14T physical property measurement system (PPMS) (Quantum design). IV measurements were done using Keithley source meter 2611.

To fabricate the device ITO-coated glass substrates were cleaned with soap, water, acetone and isopropanol under ultra-sonication for 1 h followed by UV ozone treatment for 15 min. The prepared colloidal solution of ι -ZnO and ZnO were spin-coated on ITO coated glass substrate (20 Ω /sq) at 3000 rpm. The ι -ZnO and ZnO films were annealed at 200 °C for 1 h in the air. The thickness of films was ~30 nm, determined by a profilometer. PEIE (Mw = 70,000 g/mol) with a concentration of 35–40 wt% in H₂O when received from Aldrich, was further diluted with 2-methoxyethanol to a weight concentration of 0.4%. The solution was spin-coated on the ι -ZnO as well as ZnO films) at 5000 rpm for 1 min. The approximate thickness of the film was 10 nm. Spin-coated PEIE films were annealed at 100 °C for 10 min in ambient air atmosphere. The BHJ active layers (ca. ~120 nm) were spin-casted in a N₂ filled glove box from the solution of p -DTS(FBTTh₂)₂:PC₇₀BM (60:40 wt ratio) in chlorobenzene with 0.4 v/v% DIO, with the overall concentration of 35 mg/mL. The prepared solutions were annealed at 90 °C for 15 min before

film casting. The coated films were annealed at 70 °C for 10 min to evaporate residual solvent and additional annealing at 80 °C for 5 min to obtain the optimum result. Finally 10 nm MoO_x and 100 nm Ag were deposited sequentially under ~10⁻⁶ Torr by thermal evaporation through a shadow mask to form an active area of ~4.5 mm².

3. Results and discussion

We prepared ι -ZnO with different Na⁺doping ratios (Table S1 and Fig. S1, Supplementary Information). Incorporation of Na in ZnO nanocrystals was confirmed by atomic absorption spectroscopy (AAS) using AAS Vario 6 system from Analytikjena. We have found that 3% Na⁺ doping ratio gives optimum emission in the visible region and it retains n-type character (Table S2, Supplementary Information). So, we have used 3% Na⁺ doped ZnO (denoted as ι -ZnO) for further characterization. Fig. 1a shows atomic force microscopy (AFM) image of a ~30 nm-thick ι -ZnO film, obtained via spin coating of a sol-gel derived solution (see Experimental section) on the indium tin oxide (ITO) substrate. The film has a continuous and smooth surface with a roughness of ~1.9 nm and particle size of <10 nm. The uniform distribution of the ι -ZnO is evident from the transmission electron microscopy (TEM) image as shown in Fig. 1b. The high resolution TEM image shows that the ι -ZnO exhibit uniform size (Fig. 1c) with particle sizes of 5 ± 2 nm. The d values of electron diffraction pattern (Fig. S2, Supplementary Information) matches well with that of JCPDS file (no. 36-1451).

Fig. 2a shows the transmittance spectra of ITO, intrinsic ZnO and ι -ZnO films. Both intrinsic ZnO and ι -ZnO show high transmittance in the 370–900 nm range whereas ι -ZnO shows negligible transmittance below 370 nm range. ITO also shows high transmittance above 300 nm and hence ITO does not absorb significant UV light above 300 nm i. e. it is transparent for wavelengths >300 nm. The UV–Vis absorption spectra of ι -ZnO and intrinsic ZnO are shown in Fig. 2b. Intrinsic ZnO shows very low absorption in UV region whereas ι -ZnO shows broad absorption around 370 nm. The ι -ZnO absorbs UV light and downconverts U to visible light. The corresponding Photoluminescence (PL) emission spectrum of ι -ZnO is in the 400–700 nm range with maxima at 545 nm. ι -ZnO gives yellow-green (~545 nm) broad-band photoluminescence (Fig. S3, Supplementary Information) under UV (370 nm) excitation. This strong emission is attributed to substitutional incorporation of Na⁺ in the Zn⁺² site [27,28]. The calculated Quantum yield (QY) of ι -ZnO is nearly 0.7 (Table S3, Supplementary Information). This high QY is also supported by the PL decay curve (Fig. S4, Supplementary Information).

The UV–Vis absorption of p -DTS(FBTTh₂)₂ overlaps strongly with the PL emission spectrum of ι -ZnO (Fig. 2b). It results in an enhancement in the absorption spectrum of p -DTS(FBTTh₂)₂:PC₇₀BM (Fig. 2c). The ι -ZnO film absorbs UV light and down convert it to visible light (emission) which overlaps with the absorption of p -DTS(FBTTh₂)₂. This leads to an additional light absorption by p -DTS(FBTTh₂)₂ and hence enhancement in its absorption. The corresponding integrated photon counts for ZnO and ι -ZnO are 1.460 × 10²¹ and 1.673 × 10²¹, respectively. Due to this, an increase in the PL emission of p -DTS(FBTTh₂)₂ is observed (Fig. 2d). We further established the downconversion assisted enhancement in the absorption and hence emission intensity, using ultrafast (sub-80 fs) pump-probe transient absorption (TA) spectroscopy. The films of ι -ZnO/ p -DTS(FBTTh₂)₂:PC₇₀BM and ZnO/ p -DTS(FBTTh₂)₂:PC₇₀BM, were pumped at 320 nm (0.6 W, laser fluence 40 μ J/cm²) followed by a white light probe. The results are shown in the form of 3D sets of wavelength-time- Δ OD TA spectra in Figs. 3 and 4. The transient spectra (Fig. 3) contain two main features: ground state

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