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Nanostructured ZnO electron transporting materials for hysteresis-free perovskite solar cells

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ABSTRACT

ZnO and Indium-doped (In-doped) ZnO nanocrystals with four different morphologies including nanodisks, nanorods, nanotripods, and nanochips were synthesized via simple and low-temperature hydrothermal route. The associated morphologies and structures of the as-prepared nanocrystals were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The results showed that reaction temperature played a vital role in the formation of ZnO morphologies, and accordingly, zinc to indium molar ratio was proposed. The obtained In-doped ZnO morphologies were used as an electron transporting materials (ETMs) in perovskite solar cells (PSCs), and the photovoltaic results showed that the short-circuit-current-density (J_{SC}) and the average power conversion efficiency (PCE_{avg}) of the nanochips based PSCs were 21.9 mA cm^{-2} and 15.17%, respectively, which were largely enhanced compared with those of the nanodisks based PSCs (18.2 mA cm^{-2} and 11.18%). The substantial enhancement for the former was thanks to the sufficient perovskite absorber loading, better morphology and crystallinity. Furthermore, a conformal coating of PEI was applied on the surface of electron-rich In-doped ZnO nanochips, causing a favorable work function shift and overall leading to the significant boost in efficiency from < 15% up to > 18%.

1. Introduction

To date, the most efficient and viable way is the conversion of sunlight into electricity with the help of photovoltaic (PV) cells. It has attracted the attention of world energy field due to the growing demands of renewable energy and depletion of fossil fuels. In terms of low cost, superior light-harvesting ability, excellent carrier transport, broad light absorption range, good thermostability and relatively high photo-to-electric conversion efficiency, the perovskite solar cells (PSCs) provide economically and technically an alternative route for photovoltaic devices which will fulfill the future energy crises (Heo et al., 2013; Liu et al., 2013; McGehee, 2013; Burschka et al., 2013). A large number of research interests have been concentrating on developing the PSCs in recent few years (Noh et al., 2013; Mahmood et al., 2015c, 2017; Stranks and Snaith, 2015; Chen et al., 2015; Kim et al., 2015). Typically, PSCs are mainly composed of electron transporting layer (ETL), perovskite absorber, hole transporting layer (HTL) and Au as top electrode. Among them, ETL is considered to be a key element of PSCs, accommodating the high perovskite absorber loading, rapid electron transport without recombination, assures large interfacial area, and have great effects on the device efficiency (Mahmood et al., 2015b; Han et al., 2015; Wu et al., 2016). In the recent past, ETLs of TiO_2 has been widely investigated for PSCs owing to their wide-gap semiconductor characteristics and success have been achieved in terms of power conversion efficiencies (PCEs) of higher than 22.1% based on mesoporous TiO_2 ETL (Mahmood et al., 2015c; Yang et al., 2017). Meanwhile, other semiconducting oxide materials, including SnO_2, WO_3, ZnO and so on, have also been recognized as potential ETLs for PSCs (Mahmood et al., 2014a, 2015a, 2015d; Tavakoli et al., 2018). Among them, ZnO with distinct morphologies has been widely investigated due to its similar band-gap structure, ease of processing at low-temperature, viable growth schemes, and higher electron mobility compared to TiO_2 (Zheng et al., 2017; Song et al., 2017; Mahmood et al., 2014b).

Until now, nanostructured ZnO mainly in the form of nanoparticles, nanorods and nanosheets have been reported for moderately efficient PSCs which make it compulsory to find the effective ways to increase

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the efficiencies of ZnO in PSCs (Mahmood et al., 2014b, 2015b; Mahmood and Khalid, 2018). However, there are no systematic reports available on the growth of various morphologies of ZnO nanostructures and their impact on the performance of ZnO based PSCs synthesized via simple and inexpensive method. Over the past decades, ZnO nanostructures have been synthesized by different methods such as, precipitation method, chemical bath deposition, electrochemical deposition and hydrothermal method etc (Mahmood et al., 2014a, 2015b; Wu et al., 2016; Shi et al., 2012; Hosono et al., 2004; Guérin and Pauporté, 2011). Compared with these growth technologies, the hydrothermal route draws the considerable attention for several benefits, including environmental friendly, low cost and ease of processing with better control over the morphology (Mahmood et al., 2014a, 2015b; Wu et al., 2016). Thus, hydrothermal route is considered as a more effective method to grow ZnO nanostructures with high crystallinity and distinct shapes at low-temperature. However, so far, neither controllable synthesis of ZnO nanostructures with various morphologies via hydrothermal method nor detailed study on the corresponding ETLs' characteristics has been reported. To further enhance the functionality of the synthesized nanostructures, ZnO can be doped with various metallic elements namely gallium (Ga), Aluminium (Al), boron (B) and indium (In) in order to enhance the optical/electrical characteristics (Kong et al., 2003; Yang et al., 2002; Mahmood et al., 2013). In this respect, indium is the most suitable dopant for ZnO, owing to its less reactivity and strong resistance to oxidation environments relative to other metallic dopants. Moreover, it has been reported that In-doping can significantly enhance the carrier concentration, superior conductivity and thus, enhances the electron transport properties by reducing the work function (WF) of ZnO (Mahmood et al., 2013). Furthermore, a universal method to reduce the WF of ETLs and ITO is the use of conjugated polyelectrolytes such as polyethylenimine ethoxylated (PEIE) and polyethylenimine (PEI) by the formation of interfacial dipole, ensuring the highly efficient, hysteretic-less solar cells in a simple and efficient manner (Mahmood et al., 2015b).

It has been investigated that photovoltaic performance is mainly dependent on the crystallinity, morphology, dimensions and thickness of one-dimensional (1-D) nanostructures and play a crucial role in enhancing the overall PCE of the PSCs (Kim et al., 2015; Mahmood et al., 2015b, 2015c; Han et al., 2015; Wu et al., 2016). Because of the increasing demands of efficient and stable perovskite devices, herein, we explored controllable growth of ZnO nanostructures including nanodisks, nanorods, nanotripods, and nanochips using a viable, low-cost and low-temperature hydrothermal method. The morphologies and structures of these morphologies were also characterized in this study. In addition, the photovoltaic properties in PSCs were also investigated. The performances of the PSCs based on two-dimensional (2-D) ZnO nanochips ETLs were obviously enhanced, principally in crystallinity and high absorber infiltration owing to its large specific surface area and wide gaps between adjacent nanochips. The PCEs of PSCs based on In-doped ZnO nanodisks, nanorods, nanotripods, and nanochips ETLs were 11.3%, 12.71%, 12.9% and 15.24%, respectively. The PEI-coated In-doped ZnO nanochips, leading to significant enhancement of the PCE from nearly 15.24% up to over 18.2% with negligible hysteresis, thanks to a combination of complete perovskite infiltration, the interfacial PEI dipole layer, and the electron-rich nanochips ETM. To the best of our knowledge, no report has been published to date that is relevant to various In-doped ZnO nanostructured ETMs for perovskite solar cells in a systematic manner.

2. Materials and methods

2.1. Synthesis of pure and In-doped ZnO nanostructures and fabrication of solar cells

ZnO and In-doped ZnO nanostructures with four different morphologies (nanodisks, nanorods, nanotripods, and nanochips) were synthesized via simple two-step process: (i) seed layer formation using electrospray and (ii) hydrothermal growth of various nanostructures, respectively (Mahmood et al., 2013). For ZnO seed layer, 0.05 M precursor solution was prepared by dissolving zinc acetate di-hydrate in ethanol:water (30:70 v/v) mixture. An electrospraying setup was used to directly deposit the ZnO seed layer on fluorine-doped tin oxide (FTO) glass substrates as reported previously by us (Mahmood et al., 2014b). The feeding rate, applied high voltage, needle to substrate distance, and substrate temperature were kept at 0.003 mL/min, 5.7 kV, 4 cm, and 210 °C, respectively. The precursor solution was transferred to the needle tip via a syringe pump (KD200, KD Scientific Inc., USA). A stable cone-jet mode was achieved by applying high voltage with the help of a DC power supply (Korea switching, Inc., Republic of Korea) between the needle tip and the substrate surface.

In the second step, a modified hydrothermal method was to grow the four distinct morphologies by the decomposition of zinc nitrate hexahydrate and hexamethylenetetramine (HMT) stored in a sealed reaction vessel (Mahmood et al., 2013). Indium doping was achieved by adding indium chloride ($InCl_3$) with a concentration of 5 at.% into the hydrothermal solution. The FTO substrates with ZnO seed layer were kept inclined into the hydrothermal reaction vessel according to the reaction conditions (growth temperature, growth time and Zn:In molar ratio) mentioned in Table S1. After that, FTO substrates with ZnO and In-doped ZnO nanostructures were taken out from the reaction vessel and washed with distilled water several times to remove the residual zinc salts and dried with the gentle blow of nitrogen. Additionally, a thin layer of polymer, PEI was spin-coated (by preparing 2.5 mg/ml branched-PEI solution in deionized water) onto the surface of the ZnO and In-doped ZnO nanostructures at 5000 rpm for 1 min, followed by annealing at 100 °C for 5 min.

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For the fabrication of perovskite solar cells, firstly, a ZnO compact layer was deposited onto FTO glass substrates followed by sintering at 500 °C for 30 min (Mahmood et al., 2014b). A two-stage sequential deposition route was used to prepare the cells (Mahmood et al., 2014b). In a typical device fabrication process, 462 mg of lead iodide (PbI_2) were dissolved in 1 mL of dimethylformamide (DMF) using magnetic stirring under constant temperature of 70 °C overnight. Then, 25 µL of PbI_2 solution in DMF was spin-coated (for 20 s at 3000 rpm) onto the surface of pure and In-doped ZnO nanostructures and subsequent drying at 50 °C for 5 min and 100 °C for 5 min, respectively. After cooling down to room temperature, the substrates were further dipped into a methyl-ammonium iodide (MAI) solution prepared in 2-propanol with concentration of 10 mg/mL for 20 min. The substrates then washed with IPA and subsequently drying at 70 °C for 5 min. The hole-transporting layer (HTL) of spiro-MeOTAD was spin-coated (at 3000 rpm for 30 s) over the perovskite layer. At last, for back contact a 60 nm-thick Au layer was thermally evaporated on top of HTL. Devices were stored in the nitrogen-filled glove box at least for 10 h in dark to complete the self-diffusion of ionic species in the devices.

2.2. Characterizations

Scanning electron microscopy (SEM) was performed using a Magellan 400 microscope to reveal the plane-view and cross-sectional micrographs of pure and In-doped ZnO nanostructures and complete perovskite solar cells. The crystal phase of the nanostructures was obtained using an X-ray diffractometer (D/MAX-2500 Rigaku Co.) The X-ray photoelectron spectra of nanostructures were conducted with the help of X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific, Sigma Probe). Transmission electron microscopy (TEM; FEI Company, Tecnai G2 F30 S-TWIN) was used to confirm the microstructure of corresponding samples. The current-density versus voltage (*J-V*) curves of the devices was collected using a solar simulator (Newport) under steady illumination AM1.5 spectral filter, by masking the active area