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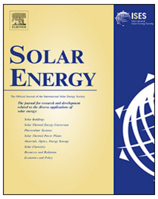

The performance enhancement of HTM-free ZnO nanowire-based perovskite solar cells via low-temperature $TiCl_4$ treatment

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ABSTRACT

Charge carrier transport layer made of aligned ZnO nanowires (NW) coated with TiO_2 layer via low-temperature hydrolysis process for perovskite solar cells (PSC) applications. Aligned ZnO NWs were grown by solution approach onto transparent conducting oxide substrates and treated with 25 mM of titanium tetrachloride ($TiCl_4$). TiO_2 layered ZnO NWs were composed of single crystalline, uniformly covered with amorphous TiO_2 nanoparticles was characterized by scanning and transmission electron microscopy. Such TiO_2 layered ZnO NW architecture, with the unique combination of high surface-area and infiltration of perovskite more into the electrode and a maximum photocurrent density (J_{SC}) of 14.30 mA cm^{-2} and a power conversion efficiency (η) of 7.05% are demonstrated, which is higher than the ZnO NWs. Dark current density is decreased for TiO_2 layered ZnO NW-based PSCs, due to the good interface formation between the electrode/sensitizer and it has higher energy barrier to overcome required high onset potential. TiO_2 layered ZnO NWs architecture opens up a novel configuration for high-performance optoelectronic devices.

1. Introduction

Organometal halide perovskites materials are one of the promising sensitizers for next-generation solar cells and it can be prepared at the ambient atmospheric condition, along with high charge carrier mobility, long carrier diffusion length, and large absorption coefficient (Mitzi et al., 1994; De Wolf et al., 2014; Park, 2015; Dong et al., 2015; Stranks et al., 2014). The perovskite-based solar cells have reached 22.1% efficiency and ease to fabricated at room temperature condition and low-cost compared with p-n junction photovoltaic devices (Shin et al., 2017; Brenner et al., 2016). The first report of perovskite solar cells was demonstrated by Miyasaka and co-workers in 2009. They employed $CH_3NH_3PbI_3$ and the analogue $CH_3NH_3PbBr_3$ as sensitizers in liquid-electrolyte-based dye-sensitized solar cells, achieving a power conversion efficiency (PCE) up to 3.81% (Kojima et al., 2009). Kim and co-workers later reported a solid-state perovskite solar cell with a PCE of 9.7% (Kim et al., 2012). Up to now, these devices not only show relatively high efficiencies newcomer to the solar cell family. Conventionally, metal-oxide nanoparticles are usually employed as a charge carrier transport layer in dye-sensitized and perovskite solar cells (Thakur et al., 2017). Although nanoparticles offer a large specific surface-area for mooring the absorber materials (sensitizers). But nanoparticle has the poor networking and interparticle connectivity limiting the efficient transport of photo-generation charge carriers (e−) (Lu et al., 2015). By replacing the conventional nanoparticulate of the metal-oxide film by aligned metal-oxide nanostructures may improve the electron transport and infiltration of sensitizer (Jiang et al., 2014). Furthermore, the absence of interparticle continuity grain boundaries is expected to minimize the carrier recombination. However, such efforts always accompanying the reduction in the specific surface-area of the photoanode materials and faster electron transport. Realizing such effoerds by low-temperature solution base approach may surplus enhance the technical viability of PSCs (Kim et al., 2013; Qiu et al., 2013; Sun et al., 2015). In response to this problem, the article intends a zinc oxide (ZnO)-based PSC technology as an alternate for TiO_2 in solar cells (Son et al., 2014). Furthermore, ZnO has higher electron mobility than that of TiO_2 by two-to-three orders of magnitude (Law et al., 2005; Dong et al., 2014). So, ZnO is expected to reveal faster charge carrier transport as well as reduce the recombination rate as likened to TiO_2. However, TiO_2 based photovoltaic device has higher efficiency than that of ZnO (Kumar et al., 2013; Islavath et al., 2017a). The main drawback of ZnO is chemically unstable and easily oxidized at normal condition. Subsequently, O'Regan et al. first reported the $TiCl_4$ treated NW-based solar cells have an efficiency of 0.07% which is significantly higher than the ZnO NWs (Atienzar et al., 2010). The advantage of titanium tetrachloride ($TiCl_4$) treatment is a downward movement of titania conduction band edge and a decrease recombination at the interface of ZnO/sensitizer (Manthina et al., 2016; Sommeling et al., 2006). Thin TiO_2 layer willing by numerous routes, such as atomic layer and chemical vapor deposition, sputtering and hydrolysis (low-

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temperature solution process) on aligned nanostructure (Lee et al., 2010; Law et al., 2006; Muduli et al., 2011; Wang et al., 2010). Among these routes, the low-temperature solution process is simple and inexpensive. This process is widely used for preparing the thin TiO_2 layer on the aligned nanostructure (Wang et al., 2016; Kim et al., 2002).

In this paper, aligned ZnO NWs were grown by hydrothermal method and treated with the 25 mM $TiCl_4$ aqueous solution at different temperatures (3–50 °C). TiO_2 layered ZnO NWs offers higher surface-area, better infiltration of perovskite, and faster charge carrier transport thus improve the performance of PSC. It offers energy barrier for separation of drive charge carrier from perovskite, drop the dark current and increased the open-circuit voltage. Additionally, ZnO is physical and chemically stable in acidic solution at below 3 °C. Such TiO_2 layered ZnO NW electrodes were demonstrated to be favorable for fast charge carrier transport layer in optoelectronic devices.

2. Experimental details

2.1. Materials

Zinc acetate dihydrate Zn-$(O_2CCH_3)_2(H_2O)_2$ (> 98%), Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) (98%), Hexamethylenetetramine ($C_6H_{12}N_4$) (99%) and methanol (Fisher scientific), lead iodide (99%), Methylamine (TCI- 40% in Methanol, *ca.* 9.8 mol/L), hydroiodic acid (99.95%, TCI-57%), Dimethylformamide (DMF), isopropyl alcohol (Fisher scientific), were acquired from Sigma-Aldrich and used as received.

2.2. Seed layer preparation and ZnO nanowire growth

The aligned ZnO NWs were grown on ZnO seed layer coated fluorine-doped tin oxide (FTO) glass substrate by hydrothermal method. The seed layer precursor solution was prepared by dissolving 0.1 M zinc acetate dihydrate in methanol. The resultant solution was spin coated on the FTO glass substrate and annealed at 400 °C/10 min. Hydrothermal growth solution obtained by dissolving equal molar of zinc nitrate hexahydrate and hexamethylenetetramine in Di-water was filled in an autoclave. The seed layer coated substrates were loaded in an autoclave and heated at 95 °C for 2 h. After the reaction, substrates were removed from the solution and rinsed with deionized water and annealed at 400 °C for 30 min (Islavath et al., 2017a).

2.3. TiO_2 layered ZnO nanowire arrays

The stock 2M of $TiCl_4$ solution was prepared at 0 °C, by slowly adding the $TiCl_4$ into the 200 ml of Di-water and kept a longer duration to form transparent at room temperature. As prepared ZnO nanowire arrays were immersed in an aqueous 2 mM$TiCl_4$ solution at 0 to 50 °C for 30 min. After the reaction, substrates were removed from the solution and rinsed with deionized water and annealed at 400 °C for 30 min and TiO_2 layer is confirmed using the electron microscopy.

2.4. Perovskite solar cell fabrication

Fluorine-doped tin oxide (FTO) glass substrates (Rs: 12 Ω/□) were patterned using zinc dust and 2 M HCl. Aligned ZnO NWs were grown on seeded FTO glass substrate by hydrothermal method at 95 °C for 2 h. After the reaction, ZnO NWs were treated in 25 mM $TiCl_4$ solution for 30 min at 3–50 °C, rinsed in di-water and annealed at 350 °C/20 min (Islavath et al., 2017a; Sakai et al., 2013). The perovskite ($CH_3NH_3PbI_3$) layer was prepared using a spin coating on ZnO NWs. First, a 1 M lead iodide (PbI_2) solution was prepared by dissolving 462 mg PbI_2 in 1 ml of dimethylformamide (DMF) at 75 °C for 3 h. The PbI_2 layer was then deposited on NWs via spin coating at 4000 r.p.m. for 30 s and dried at 120 °C for 10 min. Then, 150 µl of 0.063 M CH_3NH_3I solution in 2-propanol was spin coated on the PbI_2 film and also dried at 120 °C for 10 min (Islavath et al., 2017a; Islavath et al., 2017b). Finally, cathode (Au) layer was deposited $CH_3NH_3PbI_3$ layer using sputtering and device active area is 0.16 cm^2. These devices mostly prepared in ambient condition (without glove box condition) and the performance of device was recorded in without light soaking bias; measured under simulated AM 1.5 100 mW cm^{-2} sunlight, forward bias to short circuit.

2.5. Characterization

Morphology and cross-sectional images of aligned ZnO nanostructures were obtained by scanning electron microscopy (JEOL JSM-7610F). Transmission electron microscopy (TEM) ((Tecnai G2 F20 X-TWIN, FEI)) was used to characterize the microstructures of the ZnO nanostructure arrays. Current-voltage (I-V) characterization of DSSCs and PSCs were measured in the dark and under simulated solar light conditions (Newport, 94043A). The output power is calibrated to 1 sun condition (AM 1.5G) using NREL certified silicon reference cell. All the mentioned solar cell performance values are average of 8 cells. The quantum efficiency of solar cells was measured in a DC mode using Xe light source (Newport-70104, USA).

3. Results and discussion

It is well known that ZnO is a physical and chemically unstable in acidic solutions ($TiCl_4$ solution and strong acid), but very interesting to share the ZnO is physical and chemically stable in the aqueous acidic solution at below 3 °C. Near freezing temperature of water, the reaction takes place slowly, formation of $[H^+]$ ions less, and it will increase the potential of hydrogen (pH) value of the corresponding solution. Hence, the concentration of $[H^+]$ ions increases in solution with raising the temperature. Similarly, we followed and noticed pH value of 25 mM aqueous solution of $TiCl_4$ at the different reaction temperature (3–50 °C) and time (10–30 min) using the litmus papers as shown in Fig. 1(a, b). Before (Fig. 1(c)) and after treatment of ZnO NWs grown FTO glass substrate digital photograph as shown in Fig. 1(d). Fig. 1(d) shows the ZnO NWs treated with the 25 mM $TiCl_4$ solution at 3–50 °C for 30 min. ZnO NW arrays are physical and chemically stable at 3 °C for longer duration and arrays exhibited visible better transparent compare to as prepared NWs (Sakai et al., 2013). But ZnO NW arrays are physical and chemically unstable at above 10 °C, due to the increases $[H^+]$ ion concentration and thus leading to a reduction in the pH of the solution (Muduli et al., 2011; Ismagilov et al., 2012; Rig et al., 1998).

Before and after $TiCl_4$ treatment of ZnO NW arrays morphologies is investigated using SEM micrographs, it was observed the clear difference in surface and cross-sectional morphologies of ZnO NWs as shown in Fig. 2. As-prepared ZnO NWs have grown dense and with sharp tips, length around 1.7 µm. ZnO NWs sidewalls are smooth and well-defined (Fig. 2(a, d)). After $TiCl_4$ treatment at 3 °C for 30 min, the ZnO NWs have in the hexagonal shape with sharp tips, a diameter is marginally increased is shown in Fig. 2(b, e), which could upsurge the specific surface area of an electrode. After treatment, NW sidewalls become rougher due to the formation of TiO_2 nanoparticle on a surface of NWs and it is representing core-shell structure is formed. Correspondingly, similar set-up NWs were treated at 10, 30 and 50 °C for 30 min. After completion of the reaction time, clear substrates are observed visibly (Fig. 1(d)) and the surface and cross-sectional morphology of these substrates as shown in Fig. 2(c, f). NWs were dissolved in $TiCl_4$ solution and few of them detached from the FTO surface, due to the $[H^+]$ ions concentration increased and formed as hydrochloric acid in the solution. The hydrochloric acid effect the physical property of NWs (Muduli et al., 2011; Lan et al., 2013).

Influence of $TiCl_4$ treatment on morphology and microstructural of ZnO NWs were characterized using transmission electron microscopy (TEM). Before and after $TiCl_4$ treatment of ZnO NWs micrographs as shown in Fig. 3(a–c). The high-resolution TEM (inset in Fig. 3(a)) and selected-area electron diffraction (SAED) pattern reveals that [0 0 0 1]