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High-performance inverted planar perovskite solar cells based on efficient hole-transporting layers from well-crystalline NiO nanocrystals

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ABSTRACT

NiO is an important hole-transporting material for preparing inverted planar perovskite solar cells (PSCs). Apart from some complicated preparation methodologies such as doping routes, pulsed laser deposition, atomic layer deposition and high temperature spray pyrolysis, the simpler solution-processed method can also achieve high-quality NiO hole-transporting layers for efficient inverted planar PSCs. One of the prerequisites for solution-processed high-quality NiO hole-transporting layers is pre-synthesized highly crystalline NiO nanocrystals (NCs). Here, we use the sophisticated solvothermal method to synthesize highly crystalline NiO NCs. The oleylamine ligands are used to well control the nucleation and growth of NiO NCs and achieve good colloidal stability in toluene, which make for high-quality NiO hole-transporting layers by solution process. The related measurements and analysises reveal that the as-prepared NiO hole-transporting layer shows faster hole extraction, more effectively suppressed recombination and fewer surface trap states than the typical poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonic acid) hole-transporting layer, finally contributing to superior photovoltaic performance of the corresponding device. This work highlights the feasibility of colloidal chemical synthetic route for pre-synthesizing highly crystalline and well dispersed semiconductor NCs suitable for preparing efficient PSCs by the simple solution-processed protocol.

1. Introduction

Perovskite solar cells (PSCs) have attracted enormous attention in the photovoltaic community due to the demonstrated high efficiency exceeding 20% and low-cost fabrication (Shin et al., 2017; Ye et al., 2017; Boix et al., 2015). PSCs with different structures including meso-super structure, planar structure and inverted planar structure all can work efficiently if the photon-generated carriers can be successfully separated and collected by the charge (electron or hole)-transporting layers (Kim et al., 2012; Jiang et al., 2017; Wu et al., 2017; Wu et al., 2016a,b; Krishna et al., 2015). So the charge-transporting layers play key roles in determining the photovoltaic performance of PSCs. Scheme 1 shows the general structure of inverted planar PSCs. From front-side to back-side of the device, it consists of fluorine doped tin oxide conductive glass (FTO) substrate, hole-transporting layer (HTL), perovskite layer, electron-transporting layer and Au/Ag layer. (Heo et al., 2015) [6,6]-Phenyl C_{61} butyric acid methyl ester ($PC_{61}BM$) is usually used to fabricate electron-transporting layer and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) is used as interface modified layer. (Shao et al., 2016; Rao et al., 2016) Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonic acid) (PEDOT:PSS) is one of the most widely used materials for preparing HTL (Adam et al., 2016; Shahbazi et al., 2016; Wang et al., 2014). Yet due to the acidic and hygroscopic characteristics, PEDOT:PSS is not an ideal material for preparing long-term stable inverted planar PSCs (Choi et al., 2015). Therefore, many inorganic materials such as CuSCN (Ye et al., 2015; Xi et al., 2017), NiO (Yin et al., 2017; Liu et al., 2017c; Kwon et al., 2016), CuO_x (Sun et al., 2016) have been utilized as substitutes for PEDOT:PSS. Among them NiO is the most successful one because it has a wide band gap ($E_g > 3.50$ eV), good optical transparency, appropriate energy levels for efficient hole transporting and electron blocking and good chemical stability (Zhu et al., 2014; Chen et al., 2015a; Yin et al., 2016). However, due to the critical shortcoming of high resistivity of NiO, it usually needs to be doped with other elements such as copper (Kim et al., 2015), magnesium and lithium (Chen et al., 2015b). The thickness of NiO HTLs should also be strictly controlled, which further needs some complicated preparation methodologies like pulsed laser deposition, atomic layer deposition and high temperature spray pyrolysis (Park

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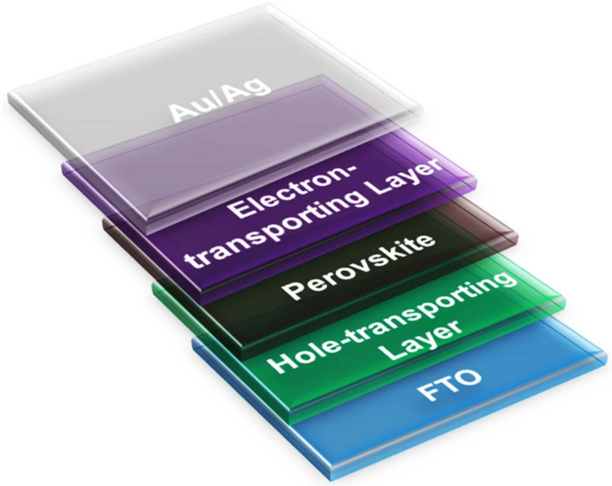

Scheme 1. Schematic illustration of the general structure of inverted planar PSCs.

et al., 2015; Seo et al., 2016; Wu et al., 2016a,b). Meanwhile, some researchers have been trying to use the simple solution-processed method to fabricate high-quality NiO HTLs, even at low temperature. (Lin et al., 2016; Bai et al., 2016) The typical examples reported by both Yin et al. and Zhang et al. confirmed that the pre-synthesized highly crystalline NiO_x nanocrystals (NCs) were suitable for solution-processed high-quality NiO_x HTLs for efficient inverted planar PSCs (Yin et al., 2016; Zhang et al., 2016a). They used a chemical precipitation method combining with high-temperature annealing process to synthesize crystalline NiO_x NCs. Namely, the nickel salts were firstly reacted with NaOH and then the precipitates were annealed at 270 °C to improve crystallinity. The drawbacks of the preparing method are obvious. It is hard to exactly control the composition, size and shape of the NiO_x precipitates by the chemical precipitation method. Furthermore, it is also difficult to avoid aggregation of NiO_x NCs during 270 °C annealing process.

Thanks to the great advancement of colloidal chemistry, NCs with highly crystalline, uniform shape, controlled size and composition can be synthesized through colloidal routes (Kwon and Hyeon, 2008; Zhang et al., 2016b; Zhou et al., 2016). One of the representative colloidal routes is solvothermal method, which stands among the most reliable, reproducible and simplest protocols available to form well-designed NCs (Lai et al., 2015). For example, Rajendran and Anandan used the simple solvothermal method for the preparation of large scale growth of spherical, hexagonal and rod-like NiO nanostructures, by using nickel acetate tetrahydrate and different ionic and non-ionic surfactants such as cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS) and poly ethylene glycol (PEG) in methanol (Rajendran and Anandan, 2015). Although the morphologies of NiO nanomaterials can be well controlled by the surfactants assisted solvothermal method, the sizes of NiO nanomaterials are too big to be suitable for preparing HTLs for inverted planar PSCs. Previously, we successfully synthesized well-crystalline TiO_2 quantum dots with size as small as 3.6 nm by using oleic acid assisted solvothermal method. The as-prepared TiO_2 quantum dots can be well dispersed in toluene for preparing high quality blocking layers for dye and quantum dot sensitized solar cells (Que et al., 2014; Zhang et al., 2016b). Inspired by these works and taking into account of the actual experimental results, here, we report the synthesis of highly crystalline NiO NCs by the facile oleylamine (OAm) assisted solvothermal method. The OAm molecules are used as co-ordinating ligands not only for well controlling the nucleation and growth of NCs but also for achieving good colloidal stability in toluene solvent, making for solution-processed fabrication of high-quality NiO HTLs. The device based on NiO HTL shows superior photovoltaic performance and stability to the one based on the typical PEDOT:PSS HTL because of the obvious advantages of NiO HTL in hole extraction, suppressing recombination and the intrinsic chemical and physical stability.

2. Experimental section

2.1. Materials

All used reagents were purchased from Sigma-Aldrich Corp, unless specifically mentioned. $PC_{61}BM$ (99.5%) was supplied by Luminescence Technology Corp, Taiwan, China. BCP and methylammonium iodide (MAI) were supplied by Xi'an Polymer Light Technology Corp, China. PEDOT:PSS (P VP AI 4083) was bought from Clevios Corp. FTO glasses with sheet resistance of $15\,\Omega\,\square^{-1}$ were purchased from Nippon Glass Corp (Japan) and used as substrates for preparing PSCs.

2.2. Preparation of NiO nanocrystals and inverted planar perovskite solar cells

NiO NCs were synthesized by a solvothermal method. Firstly, a solution containing 0.257 g nickel (II) acetylacetonate, 6 mL OAm and 10 mL toluene was prepared. Secondly, the solution was poured into a 50 mL autoclave and heated at 180 °C for 24 h. After natural cooling to room temperature, the solution was poured out and mixed with 20 mL ethanol to precipitate NiO NCs. The NiO NCs were collected after being centrifuged at a rate of 12,000 rpm for 10 min and then re-dispersed in toluene with concentration of $10\ mg\ mL^{-1}$.

FTOs ($1.5 \times 1.5\ cm^2$) were etched by Zn powder and 2 M HCl solution to form the designed pattern and then consecutively washed with isopropanol, acetone, distilled water and ethanol. Before preparing inverted planar PSCs, these FTOs were treated with UV-ozone for 30 min. The as-prepared NiO NCs dispersed in toluene ($10\ mg\ mL^{-1}$) was used for preparing NiO HTLs on the patterned FTOs by spin-coating the dispersion at 4000 rpm for 30 s, soon afterwards heated at 500 °C for 30 min. For comparison, the PEDOT:PSS HTL was also prepared on the patterned FTO. The PEDOT:PSS solution was spin-coated on the patterned FTO at 4000 rpm for 30 s and dried at 150 °C for 10 min to form 40 nm thick PEDOT:PSS HTL (Kim et al., 2017). The thickness of the NiO NCs and PEDOT:PSS films were identified by the cross-sectional SEM images.

$MAPbI_3$ perovskite layers were deposited on the NiO and PEDOT:PSS HTLs with the typical anti-solvent methodology (Ahn et al., 2015). A $1.2\ mol\ L^{-1}$ $MAPbI_3$ precursor solution made of 1.66 g PbI_2, 0.58 g MAI, 500 μL dimethylsulfoxide and 2500 μL *N*,*N*-dimethylformamide was prepared firstly. Then, 80 μL precursor solution was dripped on top of the NiO or PEDOT:PSS HTL and spin-coated at 1000 rpm for 10 s and then at 6500 rpm for 20 s. When the second-step spin-coating at 6500 rpm lasted for 5 s, the anti-solvent of chlorobenzene (500 μL) was dripped on the rotating substrate to rinse out residual DMSO and DMF in the precursor film. After thermal treatment at 100 °C for 10 min, the crystalline $MAPbI_3$ perovskite layer was formed. A thin layer of $PC_{61}BM$ was spin-coated onto the $MAPbI_3$ perovskite layer from a $20\ mg\ mL^{-1}$ chlorobenzene solution at 1500 rpm for 45 s and dried at 70 °C for 10 min. After that, 100 μL saturated methanol solution of BCP was dripped on top of the $PC_{61}BM$ layer during spin-coating at 6000 rmp and then dried at 70 °C for 10 min again. Finally, an Au electrode about 100 nm was thermally evaporated on the BCP layer under high vacuum through a shadow mask.

2.3. Characterization

The morphologies were observed by a JEM-2100 transmission electron microscopy (TEM) and a SU8000 field-emission scanning electron microscopy (SEM). The X-ray diffraction (XRD) patterns were recorded with a Bruker D8 Advance X-ray diffractometer using Cu Kα