Ligand-exchange TiO₂ nanocrystals induced formation of high-quality electron transporting layers at low temperature for efficient planar perovskite solar cells

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ABSTRACT

Exploration of low-temperature solution-processed methodology for fabricating planar perovskite solar cells (PSCs) is meaningful for simplifying manufacturing, roll-to-roll industrial mass production on flexible substrates and designing perovskite tandem devices. However, some complicated, time consuming, or even high-cost methodologies such as atomic layer deposition, magnetron sputtering, and utilizing careful interface engineering are still needed for preparing efficient planar PSCs with TiO₂ electron transport layers (ETLs) at low temperature. Here, we report a simple ligand-exchange strategy to overcome the problems. We use oleic acid (OA) molecules as surface ligands for synthesis well crystalline and monodisperse TiO₂ nanocrystals. Subsequently, instead of high temperature decomposition, we find that the ligand-exchange strategy can also totally peel off these insulating ligands on the TiO₂ nanocrystal surfaces and form high-quality TiO₂ ETLs at low temperature. The OA-free TiO₂ ETLs prepared at 150 °C show high conductivity, fast electron extraction and transport speeds, low series resistance and high shunt resistance in the assembled PSCs, contributing to high performance devices with slight hysteresis and good reproducibility.

1. Introduction

Perovskite solar cells (PSCs) have attracted tremendous attention due to rapidly increased power conversion efficiency (PCE) from initial 3.8% to the highest values exceeding 20% in only a few years [1–6]. The outstanding properties of lead halide perovskites such as high extinction coefficient, broad light absorption range, low exciton-binding energy, long carrier lifetime and diffusion length, etc., make them superior materials for third generation solar cells [7–14]. The first pioneering work was done by Miyasaka et al. who used lead halide perovskites as photosensitizers to fabricate liquid-junction dye-sensitized solar cells with a PCE about 3.8% [1]. However, the devices exhibited poor stability because of the dissolution of lead halide perovskites by the liquid electrolyte. Park *et al.* utilized the famous hole conductor, *2,2′,7,7′*-Tetrakis *(N,N*-di-*p*-methoxyphenylamine)−9,9′-spirobifluorene (spiroOMeTAD), to substitute liquid electrolyte. The measure not only solved the problem but also obtained unexpected high PCE exceeding 9% [15]. Soon afterward, the mesoscopic PSCs, which have similar structure as that of dye-sensitized solar cells, underwent rapid progress and held the current world record PCE [16–22]. On the other hand, owing to the excellent semiconducting

properties of lead halide perovskites, especially the ambipolar nature [23], the planar device architecture can also work well. Without high temperature sintered mesoscopic layers in devices, these planar PSCs simplify the preparing process and can also be fabricated with low temperature process, which is compatible with roll-to-roll industrial mass production on flexible substrates in future and meaningful for fabricating tandem devices by avoiding damage of bottom cells with high temperature treatment [24–28].

Depending on the bottom transporting layers, the planar PSCs are mainly divided into regular n-i-p and inverted p-i-n architectures. Compared with the low temperature p-i-n devices which have achieved high performance with various kinds of efficient p-type transporting layers such as NiOₓ, CuSCN, CuOₓ, PEDOT: PSS, MoS₂, etc., [29–33] the n-i-p planar PSCs have not been so successful because of the scarce of n-type transporting materials suitable for low temperature process except of ZnO and SnO₂ which made great progress recently [34–39]. Generally, the efficient n-i-p planar PSCs with the most popular n-type TiO₂ electron transport layers (ETLs) are prepared with high temperature process because it is necessary for either sol-gel process TiO₂ or TiO₂ nanoparticles to enhance crystallinity and conductivity by thermal treatment [40]. Through careful interface engineering or utilizing

sophisticated equipment for atomic layer deposition or magnetron sputtering at low temperature, the efficient n-i-p planar PSCs with TiO$_2$ ETLs can be achieved [41–43]. However, they are either complicated, time consuming, or high cost. Therefore, it is still a big challenge to fabricate efficient low temperature n-i-p planar PSCs with TiO$_2$ ETLs.

Thanks to the advanced colloidal syntheses, high-quality metallic, semiconductor, magnetic, etc., nanocrystals with exactly controlled compositions, shapes, sizes, and crystal structures can be produced [44]. By coordinated with long hydrocarbon molecule ligands such as oleic acid (OA) and oleylamine (OAm), these nanocrystals are well dispersed in nonpolar, hydrophobic solvents and enable as building blocks to assemble electronic and optoelectronic devices [45–47]. And yet, such insulating ligands ultimately limit the functionality achievable by separating inorganic cores, restricting electronic coupling and confining interparticle interaction [48]. Fortunately, apart from the high temperature decomposition routes, the low temperature ligand exchange or stripping methods can also peel off insulating ligands to achieve functional utilization [49–51]. Therefore, it means that we can use these methods to fabricate high-quality TiO$_2$ ETLs for efficient low temperature n-i-p planar PSCs.

In previous studies, we reported the synthesis of OA-capped, well crystalline and monodisperse TiO$_2$ nanocrystals (TiO$_2$ NCs) with size about 3.6 nm, which could form thickness-controlled compact films on fluorine-doped tin oxide conductive glasses (FTOs) after high temperature sintering [52]. These compact TiO$_2$ films can play as efficient electron transporting and hole blocking layers in dye-sensitized solar cells, quantum dot-sensitized solar cells and mesoporous PSCs [52–58]. Here, we demonstrate that high-quality TiO$_2$ ETLs on FTOs can also be fabricated with ligand-exchange induced OA-free TiO$_2$ NCs at low temperature. Owing to the advantages of OA-free TiO$_2$ ETLs including higher conductivity, faster electron extraction and transport property, lower series resistance (R$_s$) and higher shunt resistance (R$_{sh}$) in the assembled PSCs, the devices with OA-free TiO$_2$ ETLs show superior photovoltaic performance to the one with OA-capped TiO$_2$ ETL. The devices show slight hysteresis and good reproducibility, moreover, the best one can achieve the highest PCEs of 19.03% and 19.07% by forward and reverse scan, respectively, and a steady-state PCE of 18.82%.

2. Experimental section

2.1. Materials

All used reagents were analytical grade (AR.) and purchased from Sigma-Aldrich Corp, unless specifically mentioned. Formamidinium iodide (FAI) and methylammonium bromide (MABr) salts were supplied by Xi'an Polymer Light Technology Corp, China. The spiroOMeTAD was supplied by Luminescence Technology Corp, Taiwan, China. TiO$_2$ NCs with size about 3.6 ± 0.4 nm were synthesized as previously reported [52]. FTOs with sheet resistance of 15 Ω □$^{-1}$ were purchased from Nippon Glass Corp. JP.

2.2. Synthesis of TiO$_2$ nanocrystals and ligand-exchange treatment

The details of the synthesis of TiO$_2$ nanocrystals are as follows: A mixture containing 0.5 g sodium hydroxide, 5 mL deionized water, 30 mL oleic acid, 5 mL ethanol, and 1 mL tetra-n-butyl titanate was added to a 50 mL autoclave and reacted at 180 °C for 24 h. After cooled to room temperature, the products at the bottom of the autoclave were collected and dispersed in 20 mL cyclonexane. Then 20 mL ethanol was used to precipitate the products, which were further centrifuged at a rate of 12000 rpm for 10 min. Finally, the products were re-dispersed in toluene with concentration of 07 g mL^{-1}.

The native OA ligands on TiO$_2$ NCs surfaces were peeled off and exchanged with BF$_4^-$ anions by NOBF$_4$ reagent and as reported in the literature [49]. In a typical process, 0.3 g TiO$_2$ NCs were dispersed in 10 mL hexane and 0.02 g NOBF$_4$ was dissolved in 10 mL *N,N*-

dimethylformamide (DMF), later the two solutions were mixed together under vigorously stirring. After 5 min, OA-free TiO$_2$ NCs were transferred into DMF phase due to the changed surface modification. The OA-free TiO$_2$ NCs were further purified by precipitation with the addition of toluene, whereafter redispersed in DMF with concentration of 20 mg mL^{-1}.

2.3. Device fabrication

FTOs with size of 1.5×1.5 cm^2 were etched by Zn powder and 2 M HCl solution to form the designed pattern. They were consecutively washed with isopropanol, acetone, distilled water and ethanol; and finally treated with UV-ozone for 30 min.

For comparison, the OA-free TiO$_2$ NCs dispersed in DMF (20 mg mL^{-1}) and the OA-capped ones dispersed in toluene with the same concentration were both used for preparing TiO$_2$ ETLs. The TiO$_2$ ETLs were fabricated on the cleared and patterned FTOs by spin-coating the dispersions at 4000 rpm for 30 s, soon afterwards heated at 150 °C for 30 min. After cooled down to room temperature, the FTOs with TiO$_2$ ETLs were transferred to a nitrogen-filled glovebox for preparing PSCs.

Cs/FA/MA mixed triple cation perovskite layers were deposited on the TiO$_2$ ETLs with the typical one-step anti-solvent methodology. [55]. A precursor solution made of 0.507 g PbI$_2$, 0.172 g FAI, 0.02238 g MABr and 0.0807 g PbBr$_2$ in a mixture of anhydrous 760 μL DMF and 190 μL dimethylsulphoxide (DMSO) was prepared, subsequently 50 μL solution of CsI in DMSO (3.5 mol L^{-1}) was added. The precursor solution was spin coated at 1000 rpm for 10 s and then at 6500 rpm for 20 s. When the procedure at 6500 rpm lasted 5 s, 130 μL anti-solvent of chlorobenzene was poured on the spinning substrates to rinse out residual DMSO and DMF in the precursor films. The substrates were then heated at 100 °C for 10 min to form crystalline Cs/FA/MA mixed triple cation perovskite layers.

After preparation of Cs/FA/MA mixed triple cation perovskite layers on the TiO$_2$ ETLs, the hole transport layers were subsequently deposited by spin-coating 20 μL spiroOMeTAD solution containing 72.3 mg spiroOMeTAD, 28.8 μL 4-tert-butyl pyridine and 17.5 μL solution of lithium bis (trifluoromethane sulfonyl) imide (Li-TFSI) in acetonitrile (520 mg Li-TSFI dissolved in 1 mL acetonitrile) at 4000 rpm for 30 s. Finally, 80 nm Au electrodes were thermally evaporated under high vacuum (1×10^{-5} Pa) through a shadow mask. The distance between Au source and the substrate during deposition of Au electrode is 25 cm, the deposition rate of Au is 1.5 Å S^{-1}, and the substrate temperature is kept at 25 °C. For better understanding, the whole preparing processes from synthesis of TiO$_2$ NCs to fabrication of planar PSCs are illustrated in Scheme 1.

2.4. Characterization

The transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements were conducted using a JEM-2100 TEM, a SU8000 SEM and a Bruker Multimode 8, respectively. The X-ray diffraction (XRD) patterns were recorded with a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). The transmittance spectra were measured by a Lamda 950 UV–Vis–NIR spectrophotometer. The Fourier transform infrared (FTIR) spectra were obtained on a Nicolet Impact 410 FTIR spectrometer. The steady-state photoluminescence (PL) spectra were acquired using a fluorescence spectrophotometer (Thermo Scientific Lumina). The time-resolved photoluminescence (TRPL) spectra were acquired using an Omin-λ Monochromator/Spectrograph with the time-correlated single-photon counting method (Zolix).

The current density-voltage (J-V) characteristic curves of PSCs were recorded with a computer-controlled Keithley 2400 source meter under simulated AM 1.5 G solar illumination at 100 mW cm^{-2} with #94043 A solar simulator (PVIV-94043A, Newport, USA) in air. The voltage step and delay time were 20 mV and 10 ms, respectively. The forward scan