Bulk Intermixing-Typed Perovskite $CH_3NH_3PbI_3/TiO_2$ Nanorod Hybrid Solar Cells

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Supporting Information

1. Synthesis of TiO_2 nanorods

The controlled growth of high-aspect-ratio anatase titanium dioxide nanorods were synthesized by the hydrolysis of titanium tetraisopropoxide according to the literature [S1]. First, oleic acid (120 g) was stirred vigorously at 120 ◦C for 1 h in a three-neck flask under Ar flow, then allowed to cool to 90 ◦C and maintained at this temperature. Titanium isopropoxide (17 mmol) was then added into the flask. After stirring for 5 min, trimethylamine-N-oxide dihydrate (34 mmol) in 17 ml of water was injected rapidly. The trimethylamine-N-oxide dihydrate was used as a catalyst for polycondensation. The reaction was continued for several hours to have complete hydrolysis and crystallization. Finally, TiO_2 nanorods were obtained with a size of about 4-5 nm in diameter and 30–40 nm in length [S2].

2. Ligand exchange process.

To remove the insulating ligands, OA-capped TiO_2 NRs were first sonicated with methanol (20 ml as-synthesized OA-TiO_2 NRs in 20 ml methanol) and extracted using repeated centrifuge separation (first 2000 rpm for 5 mins, and the 2nd and 3rd centrifuge separation was carried in 40 ml methanol with speed of 1500rpm for 5mins). The extracted product (TiO_2 NRs powder) was dispersed into 20 ml of PYR or ACR solutions and sonicated for 30 mins for homogeneous dispersion. For TiO_2 NRs in the PYR solution after sonication, it was further stirred at 75 °C until the solution turned clear. Accordingly, the original ligand molecules of O.A. were removed, and the pyridine molecules of a weak bonded ligand that were on the surface of the TiO_2 NRs could be removed by heating. The ACR-capped TiO_2 NRs powder was extracted after sonication by centrifuge separation with 30 ml acetone with speed of 9000 rpm for 2 mins for 3 times and was re-dispersed into DMF solvent for device fabrications.

3. Fabrications of BI- typed perovskite solar cells

FTO glasses were cleaned and then spin-coated with the 0.15 M titanium diisopropoxide bis(acetylacetonate) (75%, Aldrich) in 1-butanol (Aldrich) solution at 4000 r.p.m. for 30 s, which was heated at 70^{o}C for 5 min. After cooled down to the room temperature, the same process was repeated twice with 0.3 M titanium diisopropoxide bis(acetylacetonate) solution in 1-butanol. The coated FTO glass was annealed at 600 °C for 30min to obtain the compact TiO_2 electron selective layer.

We modified the sequential deposition processes (also known as a two-step process) to deposit the iodine perovskite ($CH_3NH_3PbI_3$)/TiO_2 NRs hybrid films. TiO_2 NRs of various concentrations (without and with ligand exchange treatments) were mixed with the PbI_2 precursor dissolved in a dimethylformamide (DMF) solvent (0.7 M); the solution was mildly stirred at 90 °C overnight to obtain homogeneous nanocrystal dispersion. The stirred solution of PbI_2 and TiO_2 NRs was then deposited as a film of thickness approximately 250 nm on the substrate using spin coating. Subsequently, methylammonium iodine (MAI, CH_3NH_3I) solution (10 mg/mL in isopropyl alcohol) was deposited on the pre-coated

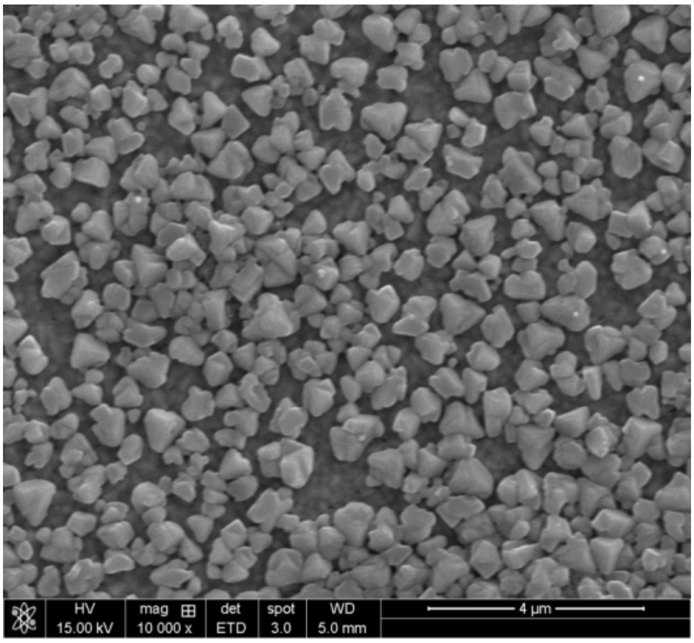
PbI_2/TiO_2 thin film for further reaction, resulting in the formation of the $CH_3NH_3PbI_3/TiO_2$ NRs hybrid layer. The $CH_3NH_3PbI_3/TiO_2$ hybrid thin film was annealed at 90 °C before depositing an organic hole transport layer spiro-OMeTAD. Top electrode of Ag was then thermally evaporated in vacuum of 10^{-6} torr.

4. Characterizations and measurements

High-resolution transmission electron microscopy (HRTEM) images were obtained using an FEI Tecnai G2 F20 200 kV field emission TEM. Mapping the elemental distribution in the samples was performed in a JEOL 2100F 200 kV TEM, equipped with a probe-type corrector for spherical aberration, in the scanning TEM (STEM) mode. Electron energy loss spectroscopy (EELS) spectra were collected, while the STEM probe was rasterizing an image. Energy loss signals of the $L_{2,3}$ edge of titanium at 456 eV and the $M_{4,5}$ edge of iodine at 619 eV were extracted respectively from the EELS spectra to form the compositional maps of Ti and I. The photocurrent-voltage (J-V) characteristics (Keithley 2410 source meter) were obtained by using a solar simulator (Newport Inc.) with the A.M. 1.5G filter under an irradiation intensity of 100 mW cm^{-2}. The external quantum efficiencies (EQEs) were measured by using a Xe lamp in combination with a monochromator (Newport Inc.). A field emission scanning electronic microscope (FE-SEM, FEI Nova Nano SEM 450) was used to examine the top- and cross-sectional morphologies of various perovskite films. Photoluminescence (PL) and Time-resolved photoluminescence (TRPL) spectroscopy was performed with a time-correlated single photo counting (TCSPC) module (Picoharp 300, PicoQuant). A pulsed laser (466 nm) with an average power of 30 μW operating at 20 MHz with duration of 70 ps at 300K was used for excitation. X-ray photoelectron spectroscopy (XPS) was obtained in VG Scientific ESCALAB 250 system. The X-ray source was generated from an aluminum target (photon energy of 1486.8 eV) with the pass energy of 20 eV. The take-off angle for photoelectron collection was 45° from surface normal. Argon plasma etching at a rate of 3 Å/sec was also used to sputter the surface for depth profiling. The FT-IR spectrum was recorded on a Perkin-Elmer spectrometer. The samples were prepared on KBr plates and measured over the range 800–4000 cm^{-1}.

5. Surface morphology of BI-typed perovskite films with 2.0 mg/ml of ACR-TiO_2

As the concentration of ACR-TiO_2 NRs was higher than 2.0 mg/ml, the aggregation of TiO_2 NRs resulted in a rough surface morphology of the perovskite thin film and consequently deteriorated device performance.



Reference

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