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Supporting information

Impressive Enhancement on the Cell Performance of ZnO Nanorods-Based Perovskite Solar Cells with Al-doped ZnO Interfacial Modification

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1. Experimental section

Materials:

PbI_2 and N, N-dimethylformide (DMF) were purchased from Sigma-Aldrich and Alfa Aesar, respectively. All the chemicals were directly used without further purification. Substrates of the cells are fluorine-doped tin oxide conducting glass (FTO) (Pilkington; thickness 2.2 mm, sheet resistance 14 Ω/square). Before use, FTO glass was first washed with mild detergent, rinsed with distilled water for several times and subsequently with ethanol in an ultrasonic bath, finally dried under air stream. CH_3NH_3I was synthesized by the literature method.[1]

Fabrication of ZnO NRs modified with AZO:

To make the surface of seed layer more even, the 80 nm thick dense ZnO layer which also acted as the hole blocking layer was first deposited on FTO substrates by spin-coating zinc acetate dihydrate in methanol ($Zn(CH_3COO)_2·2H_2O$, 0.5M) and heating at 350 °C for 30 min in air. Then began to grow nanorods, FTO substrates coated with ZnO seed layer were suspended facedown in an aqueous bath which contained zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$, 25mM), hexamethylenetetramine (HMTA, 12.5mM), polyethyleneimine (PEI, 5mM) and ammonium hydroxide ($NH_3·H_2O$, 350mM) in deionized (DI) water at 90 °C.[2-3] After a growth period, the substrates were thoroughly rinsed with DI water, dried, and annealed at 200 ° C for 30 min. As the growth time changed from 55min to 80min with interval of 5min, the range of the length of NRs was from 280nm to 1050nm. For assembling AZO shell over the surface of ZnO NRs, a certain amount of aluminum nitrate was added in the 20 mM zinc acetate in ethanol and stirred for 30min to prepare five different AZO precursor solutions and the Al/(Al+Zn) (molar ratio) were 0%; 2%; 5%; 10% and 15%. Afterwards, the dried bare ZnO NRs were spin-coated with the clear and homogeneous precursors (3000 rpm, 30 s) for once and heated to 550 °C slowly for 1 hour.

The XRD patterns of ZnO NRs interfacially modified with different concentrations of AZO is shown in Figure S1. The (0 0 2) peak of the wurtzite structure of ZnO NRs is observed, which indicates excellent orientation in the c-axis direction of these NRs and there is no significant peak of Al_2O_3. EDX analysis has been employed to semi-quantitatively investigate the chemical composition of the AZO shell on the ZnO NRs, as shown in Figure S2. Accordingly, the molar ratios of aluminum and zinc are 2.15: 97.87 for the ZnO NRs modified with AZO shell of Al doping 5% on FTO glass. Because of the presence of ZnO dense layer and NRs on FTO glass, the molar ratio of atoms measured are slightly below 5%.

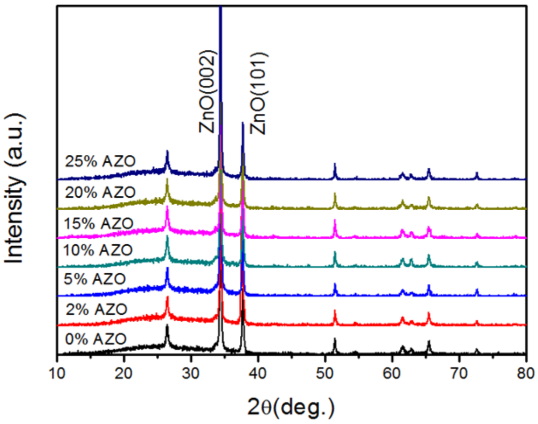

Figure S1. X-ray diffraction pattern of the ZnO NRs interfacial modified with different concentrations of AZO.

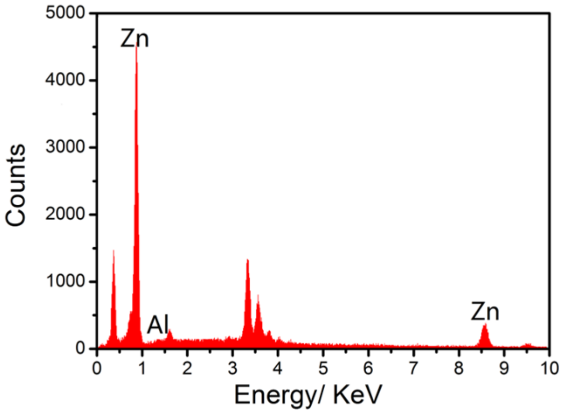

Figure S2. EDX analysis of ZnO NRs modified with 5% AZO.

Deposition of $CH_3NH_3PbI_3$ layer:

$CH_3NH_3PbI_3$ layer was deposited among the ZnO NRs through means of conventional two step method in air. Firstly, 1.2 M PbI_2 dissolved in DMF was filled in the gap of ZnO NRs by spin-coating at 3000 rpm for 60 s and then heated at 90 °C for 2 min to remove DMF solvent. After it cooled down to room temperature, the film was spin-coated again to get a relatively thick and smooth film, which were subsequently heated at 90 °C for 10 min. Secondly, the $CH_3NH_3PbI_3$ absorber layers were obtained by immersing the PbI_2 films prepared in the previous step into the solution of CH_3NH_3I in isopropanol (10mg/ml) for about 20 min and heat treated at 90℃ for about 5 min. The above process was repeated several times. Then, the $CH_3NH_3PbI_3$/ZnO NRs films were heated at 90 °C for 30 min in air. Finally, hole-transport material layer was formed by spin-coating *spiro*-MeOTAD solution at 3000 rpm for 30 s. Au electrodes of 80 nm-thickness were deposited onto the prepared film by thermal evaporation (Kurt J. Lesker) at an atmospheric pressure of 10^{-7} Torr to complete the solar cells.

2. Results

The current density-voltage (I−V) characteristics of the cells were recorded on Princeton Applied Research, Model 263 under AM 1.5 100 mW/cm^2 irradiation obtained from Oriel Solar Simulator 91192. The surface morphology and composition of samples was characterized by a scanning electron microscope (SEM, FEI XL30 S-FEG). The incident photon to current efficiency (IPCE) was measured by home-made IPCE setup. The thickness of NRs layers was measured by a surface profiler (KLA-TencorP-6). Impedance spectroscopy (IS) measurements were performed with an IM6ex electrochemical workstation (ZAHNER).

Table S1. Photovoltaic parameters of cells based on 450nm ZnO NRs modified with AZO on different Al doping levels.

Al/(Al+Zn)	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF	PCE (%)
0%	19.50	772	0.57	8.6
2%	19.11	845	0.61	9.9
5%	19.84	900	0.60	10.7
10%	19.21	867	0.57	9.5
15%	17.23	858	0.60	8.9

In order to exclude the influence of other factors, $Al(NO_3)_3$ and $Zn(Ac)_2$ were respectively added in ethanol. The two precursor solutions were spin-coated on the surface of ZnO NRs (450 nm) to form ZnO or Al_2O_3 shells. These interfacial modifications are not key factors for the enhanced efficiencies of the cells, which is obtained from Table S2.

Table S2. Parameters of cells based on 450nm ZnO NRs modified with ZnO and Al_2O_3.

Sample	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF	PCE (%)
bare ZnO NRs	19.50	772	0.57	8.6
ZnO NRs-ZnO	19.84	791	0.56	8.8
ZnO NRs-Al_2O_3	19.16	806	0.57	8.8

After treating the nanorods of different lengths with 5% AZO via the same two step means, the contents of PbI_2 filled in nanorods voids were substantially the same. This results show that photovoltaic performance is better for the shorter ZnO NRs in the range from 280 nm to 450 nm, which is consistent with results of previous studies.[4] Then Figure S3 demonstrated the reduced cells performance with increasing length of the nanorods, which was summarized in Table S3. Associated study is underway.

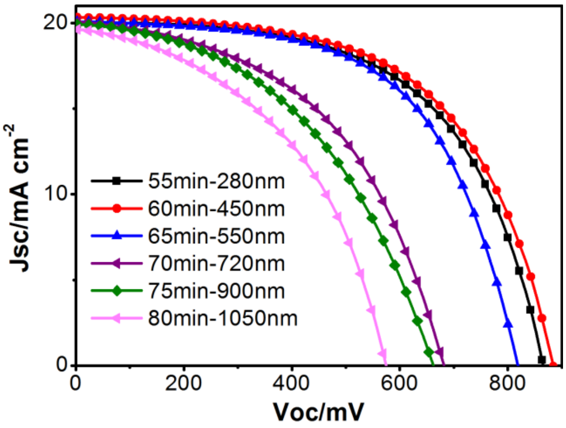

Figure S3. I-V curves of cells based different lengths of ZnO NRs modified with 5% AZO.

Table S3. Parameters of cells based on different lengths of ZnO NRs modified with 5% AZO.

NRs length(nm)	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF	PCE (%)
280	20.1	869	0.58	10.1
450	20.3	890	0.58	10.5
550	20.1	816	0.59	9.7
720	20.1	680	0.49	6.7
900	20.0	659	0.46	6.1
1050	19.6	575	0.46	5.2

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