Architectured ZnO photoelectrode for high efficiency quantum dot sensitized solar cells

Electronic Supplementary Information (ESI)

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1. Experimental methods

Preparation and passivation of the photoelectrodes. ZnO nanoparticles with the size of 40-60 nm were prepared by a facile precipitation method. Zinc acetate aqueous solution of 0.03 M was gradually added into 0.06 M KOH aqueous solution at 60 °C for 60 min, and then were centrifuged and dried at 70 °C. ZnO nanoparticles, ethyl cellulose and α-terpineol were mixed to paste with weight proportion of 20%, 10% and 70%, respectively. The paste was then coated on a fluorine-doped tin oxide (FTO) glass substrate via doctor blading method to get mesoporous films with the thicknesses of 10-12 μm. The as-received ZnO substrates underwent a sintering process at 480 °C for 30 min. The area of the ZnO substrate was approximately 0.25 cm^2 (0.5 cm ×0.5 cm square). The ZnO substrate was immersed in the aqueous solution of 0.04 M H_3BO_3 and 0.1 M $(NH_4)_2TiF_6$ at room temperature for 30 min. The substrate was drained from the reaction solution and washed several times by deionized water. Then the passivated substrate was calcined at 400 °C for 30 min.

Quantum dots synthesis. For the growth of CdS quantum dots, first, the substrates were immersed into a 0.1M cadmium nitrate ($Cd(NO_3)_2$) methanol solution for 1 min. Then, the substrates were dipped into a 0.1M sodium sulfide (Na_2S) methanol solution for another 1 min to allow S^{2-} to react with the pre-adsorbed Cd^{2+}, which led to the formation of CdS. This procedure was called one SILAR cycle. In total, 5 cycles were employed to obtain suitable amount of CdS on the substrate. In the following step, CdSe deposited on the CdS coated substrates through a chemical bath deposition method. Briefly, 0.1M sodium selenosulphate (Na_2SeSO_3) aqueous, 0.1M cadmium acetate $Cd(CH_2COO)_2$ aqueous solution and 0.2M trisodium salt of nitrilotriacetic acid ($N(CH_2COONa)_3$) solution were mixed together with volume ratio of 1:1:1. Then the CdS coated substrates were vertically immersed into the solution for the deposition of CdSe layer under dark condition at 24 ^oC for 3 h. After the deposition of CdSe, a ZnS passivation layer was deposited by two SILAR cycles while being soaked in an aqueous solution containing 0.1M zinc nitrate and 0.1M sodium sulfide, which acted as Zn^{2+} and S^{2-} sources, respectively. Electrolyte employed in this study was composed of 1M S and 1M Na_2S in deionized water. Counter electrode is a Cu_2S film fabricated on brass foil. The preparation of Cu_2S electrode can be described as follows: brass foil was immersed into 37% HCl at 70 ^oC for 5 min, then rinsed with water and dried in air. After that, the etched brass foil was dipped into 1M S and 1M Na_2S aqueous solution, resulting in the formation of a black Cu_2S layer.

Characterization and measurement. The morphology was characterized by Scanning Electron Microscope (SEM, JSM-7000) and Transmission Electron Microscope (TEM, Tecnai G2 F20). Nitrogen sorption isotherms were measured using a Quantach-rome NOVA 4200e. Samples were degassed at 250 °C under vacuum for at least 6 hours prior to measurement. The multi-point Brunauer–Emmett–Teller (BET) method was used to determine the specific surface area. The Barrett–Joyner–Halenda (BJH) method was used for the pore diameter and distribution. The photovoltaic properties were measured using an HP 4155A programmable semiconductor parameter analyzer under AM 1.5 simulated sunlight with the power density of 100 mW/cm^2. Optical absorption (Perkin Elmer Lambda 900 UV/VIS/IR Spectrometer) was used to study the samples' light absorption properties. The PL spectra were measured by excitation wavelength of 320nm at room temperature using Shimadzu luminescence spectrometer RF-5301PC. The electrochemical impedance spectroscopy (EIS) was carried out through the Solartron 1287A coupling with the Solartron 1260 FRA/impedance analyzer to investigate electronic and ionic processes in the QDSCs.

2. BET results

Table S1 Surface areas, pore volumes, and pore diameters of ZnO and passivated ZnO films

Smaple	BET surface area /m^2.g^{-1}	Pore volume /cm^3.g^{-1}	Average pore diameter /nm
ZnO	57.7	0.342	31.3
Passivated ZnO	68.6	0.401	29.7

2. QD distribution

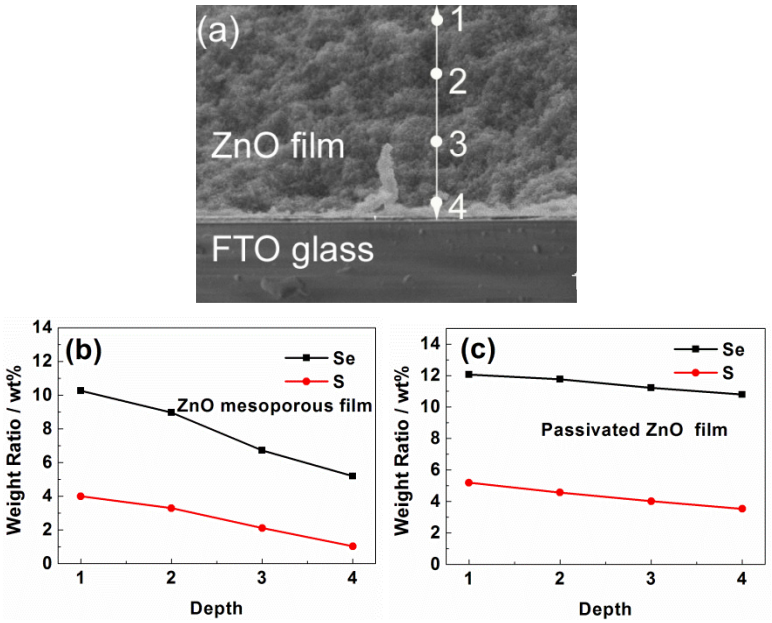

Figure S1 (a) SEM image of the cross section of the ZnO film, Se and S elements distribution from surface to bottom along the cross sections of the film (b) and passivated film (c).

Table S2 Se and S elements distribution in the film and passivated film.

Depth	Se/ wt%	S/ wt%

	ZnO film	Passivated film	ZnO film	Passivated film
1	10.26	12.06	3.99	5.19
2	8.96	11.76	3.29	4.57
3	6.72	11.22	2.11	4.01
4	5.19	10.79	1.03	3.53

4. Electrochemical impedance results

Table S3. Electrochemical impedance results of QDSCs

Samples	R_{ct} (Ω)	τ_n (mS)
ZnO	131.6	50.4
Passivated ZnO	470.3	317.9

5. J-V curves of QDSCs under dark condition

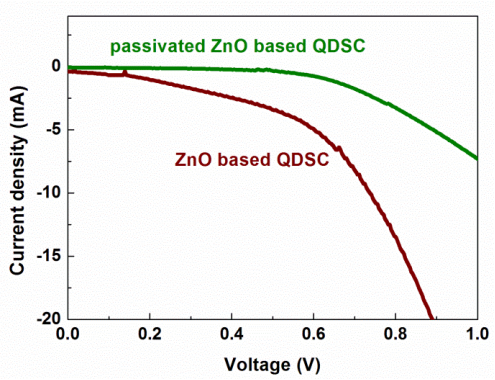

Figure S2. J-V curves of QDSCs with assembled of ZnO and passivated ZnO photoelectrodes under dark condition

6. Comparison with recent reports for ZnO based QDSC

Table S4. Performance of QDSCs with comparasion with recent reports for ZnO based film

Samples	Voc (V)	Jsc (mA)	FF	η (%)
Ref.21	0.63	17.3	0.38	4.15
Ref.22	0.69	12.6	0.42	3.60
Ref.23	0.58	5.42	0.34	1.07
Ref.24	0.76	3.68	0.44	1.24
Ref.25	0.72	13.9	0.42	4.24
This manuscript	0.62	15.4	**0.49**	**4.68**

7. The stability of the QDSCs.

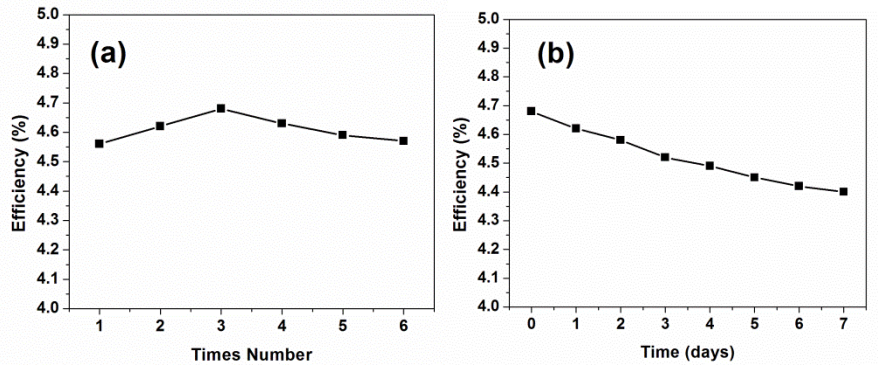

Figure S3. (a) efficiency of QDSC after different measure times and (b) after different days when the cells placed in air under 24 °C.