

## Supporting information

### Construction of Al-ZnO/CdS Photoanodes Modified with Distinctive Alumina Passivation Layer for Improvement of Photoelectrochemical Efficiency and Stability

Ruyi Wang,<sup>a,b</sup> Xiaodong Li,<sup>e</sup> Lu Wang,<sup>a,b</sup> Xirui Zhao,<sup>c</sup> Guangcheng Yang,<sup>e</sup> Aidong Li,<sup>c</sup> Congping Wu,<sup>a,d</sup>

Qing Shen,<sup>f</sup> Yong Zhou,<sup>\*a,b,d</sup> and Zhigang Zou<sup>a,b,c,d</sup>

<sup>a</sup>National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures, Department of Physics, Eco-materials and Renewable Energy Research Center (ERERC), Nanjing University, Nanjing 210093, P. R. China.

E-mail: zhouyong1999@nju.edu.cn.

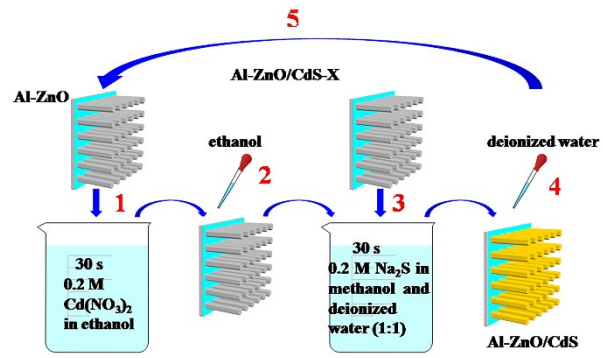
<sup>b</sup> Jiangsu Provincial Key Laboratory of Nanotechnology

<sup>c</sup> College of Engineering and Applied Science, Nanjing University, Nanjing 210093, P. R. China.

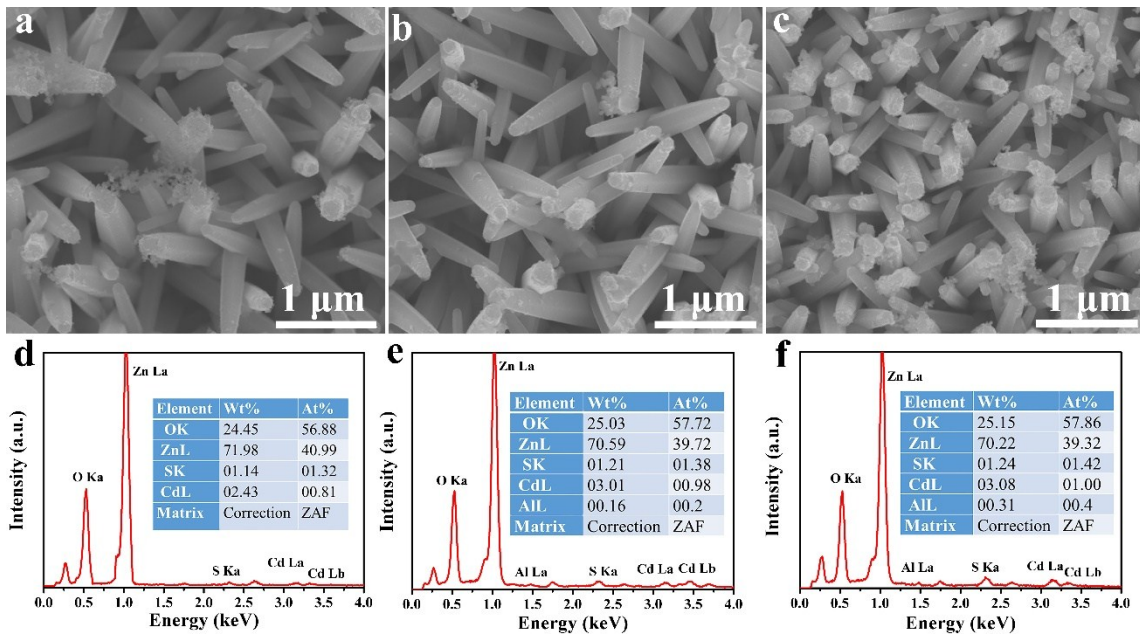
<sup>d</sup> Kunshan Sunlaite New Energy Co. Ltd., Kunshan Innovation Institute of Nanjing University, Kunshan, No. 1666, South Zuchongzhi Road, Jiangsu 215347, P. R.China.

<sup>e</sup> Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, P. R. China.

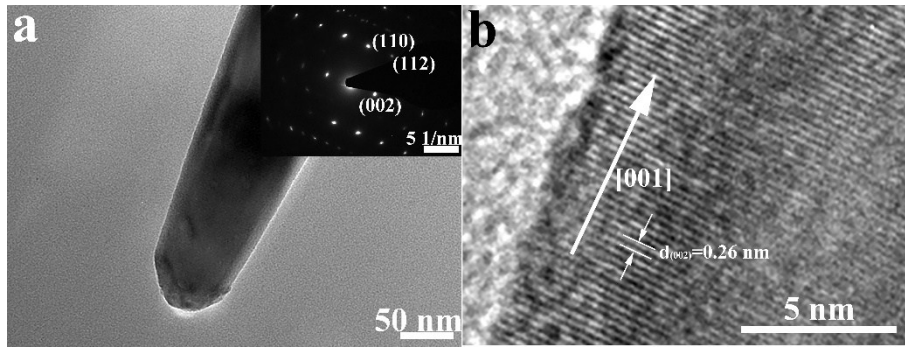
<sup>f</sup> Faculty of Informatics and Engineering, University of Electro-Communications, Tokyo 185-8585, Japan.



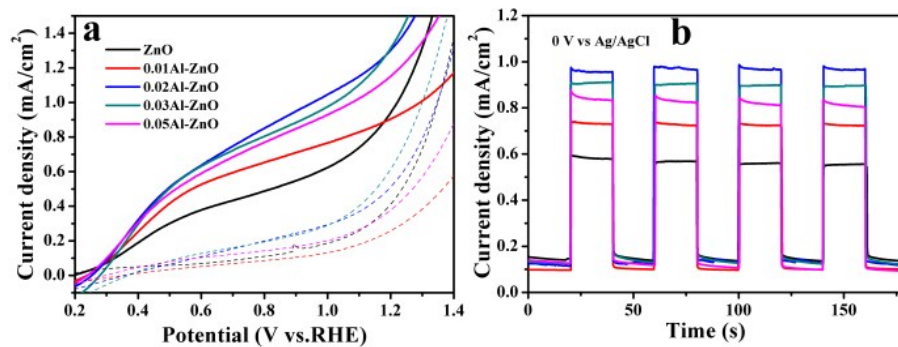
**Figure S1.** Schematic diagram of depositing CdS on Al-ZnO NRs by SILAR.



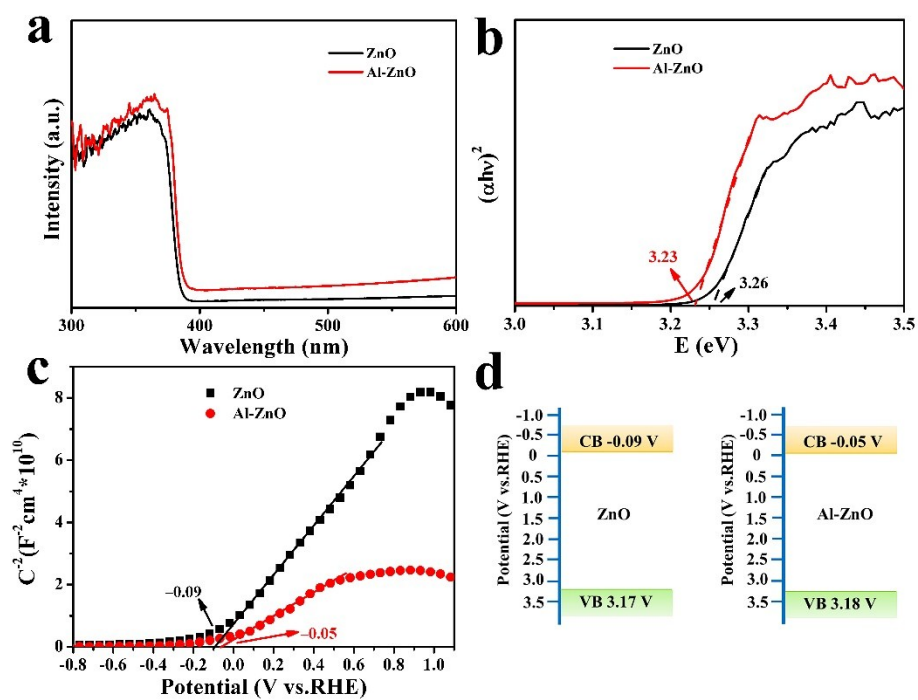
**Figure S2.** FE-SEM image and corresponding EDS, (a) and (d) for Al-ZnO, (b) and (e) for 0.01 Al-ZnO/CdS, (c) and (f) for 0.03 Al-ZnO/CdS.



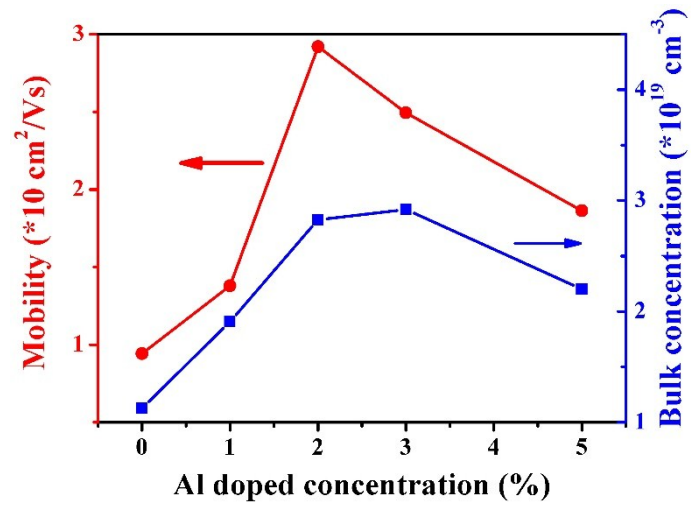
**Figure S3.** (a) TEM and (b) HRTEM images of ZnO. The inset of (a) shows selected area electron diffraction patterns.



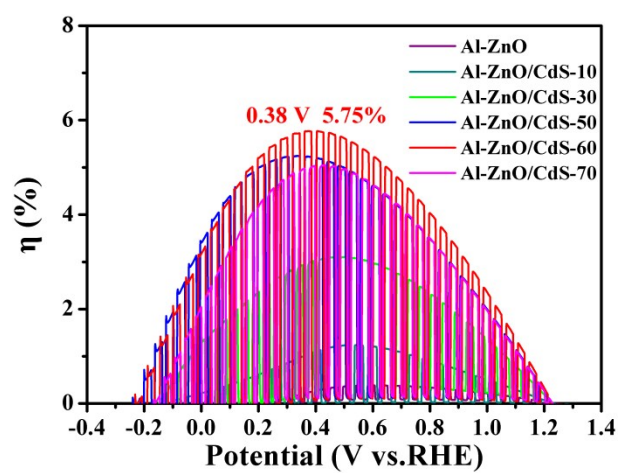
**Figure S4.** (a) Linear sweep voltammograms of Al-ZnO with different Al doping amount. The dotted line is the corresponding dark current curves), and (b) the corresponding amperometric I-t curves plotted at an external potential of 0 V versus Ag/AgCl, under chopped illumination.



**Figure S5.** (a) and (b) UV-vis absorption spectra of ZnO and Al-ZnO. (c) Mott-Schottky plots for ZnO and Al-ZnO, measured at 1 kHz. (d) Band positions of ZnO and Al-ZnO.

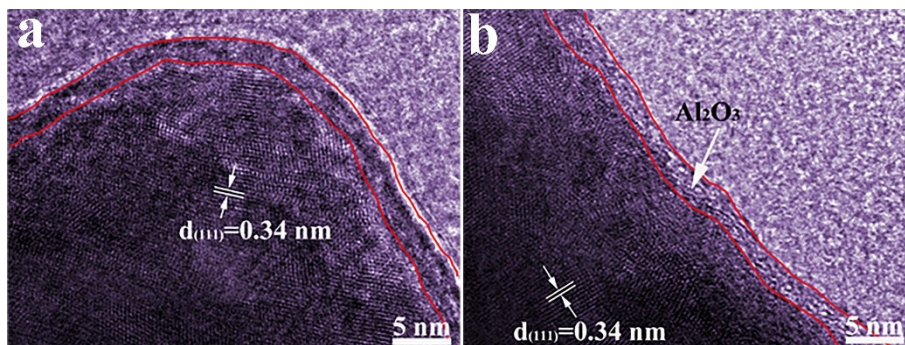


**Figure S6.** The mobility and charge carrier bulk concentration obtained from Hall Effect measurement of Al-ZnO with different Al doped concentration.

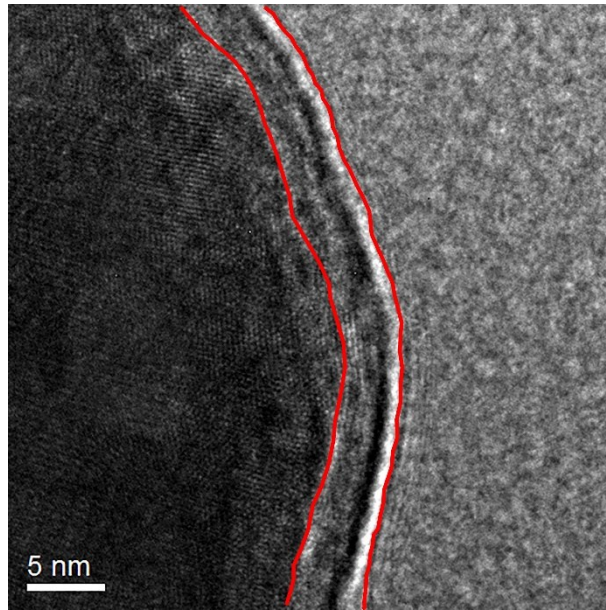


**Figure S7.** Photoconversion efficiencies of Al-ZnO and Al-ZnO/CdS with different SILAR cycles.

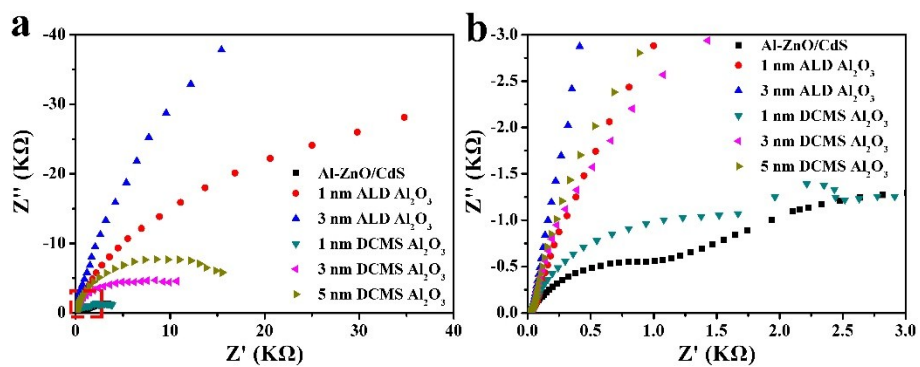




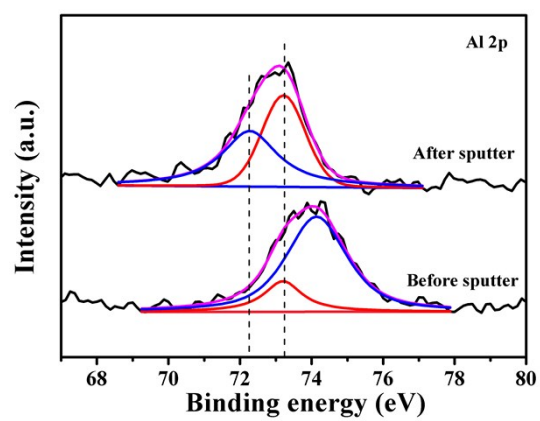
**Figure S8.** The HRTEM images of the Al-ZnO/CdS photoanode coating with  $\sim 3$  nm  $\text{Al}_2\text{O}_3$  by (a) DCMS and (b) ALD.



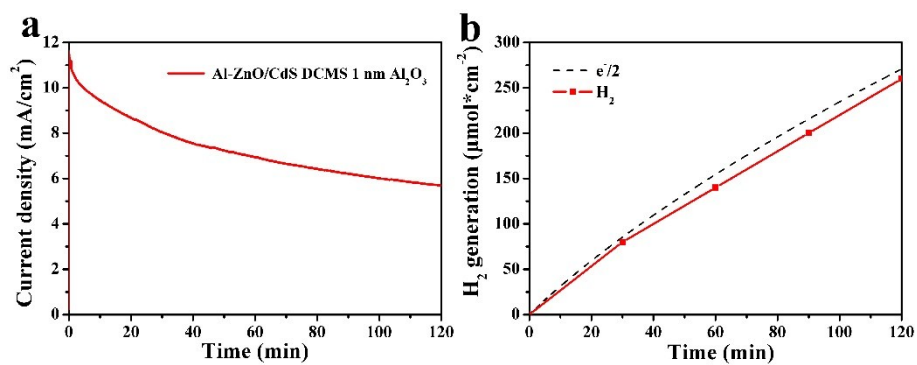
**Figure S9.** The HRTEM images of the Al-ZnO/CdS photoanode coating with  $\sim 5$  nm Al<sub>2</sub>O<sub>3</sub> by DCMS.



**Figure S10.** (a) EIS Nyquist plots of Al-ZnO/CdS coated with 1 and 3 nm Al<sub>2</sub>O<sub>3</sub> by ALD and DCMS. (b) Amplified section in (a).



**Figure S11.** Al 2p spectra of Al-ZnO/CdS DCMS 3nm Al<sub>2</sub>O<sub>3</sub> before and after Ar sputter.



**Figure S12.** (a) Photocurrent stability of the Al-ZnO/CdS DCMS 1 nm Al<sub>2</sub>O<sub>3</sub> obtained at 1.23 V vs. RHE. (b) H<sub>2</sub> evolution for the Al-ZnO/CdS DCMS 1 nm Al<sub>2</sub>O<sub>3</sub> sample derived from the potentiostatic photocurrent measurement. The dashed line correspond to a faradaic efficiency of 100%.

**Table S1.** A brief review of similar ZnO/CdS photoelectrodes and the corresponding photoresponses.

Photoanode	Electrolyte	Photocurrent density (mA/cm <sup>2</sup> )	Maximum Photoconversion efficiency (%)	Ref.
ZnO/CdS NAs	0.25 M Na <sub>2</sub> S and 0.35 M Na <sub>2</sub> SO <sub>3</sub>	6 (0 V <sub>Ag/AgCl</sub> , λ≥435 nm )	—	[1]
ZnO/Ag/CdS NAs	0.25 M Na <sub>2</sub> S and 0.35 M Na <sub>2</sub> SO <sub>3</sub>	4 (0V <sub>SCE</sub> , 100mW/cm <sup>2</sup> )	3.13 (0.34 V vs.RHE)	[2]
3D branched ZnO NWA/CdS	0.5 M Na <sub>2</sub> S	3.58 (0 V <sub>Ag/AgCl</sub> , 70 mW/cm <sup>2</sup> )	3.1 (not given)	[3]
ZnFe <sub>2</sub> O <sub>4</sub> /ZnO/CdS NAs	0.5 M Na <sub>2</sub> S	3.88 (0 V <sub>Ag/AgCl</sub> , 70 mW/cm <sup>2</sup> )	4.43 (0.2 V vs.RHE)	[4]
ZnO/CdS NAs	1 M Na <sub>2</sub> S	3.31 (0 V <sub>Ag/AgCl</sub> , 100 mW/cm <sup>2</sup> )	—	[5]
ZnO/CdS NTs	0.25 M Na <sub>2</sub> S and 0.35 M Na <sub>2</sub> SO <sub>3</sub>	~7.5 (0 V <sub>SEC</sub> , λ≥420 nm )	—	[6]
ZnO NRs/CdS	1 M Na <sub>2</sub> S	6 (0 V <sub>Ag/AgCl</sub> , 100 mW/cm <sup>2</sup> )	—	[7]
3D ZnO/Au/CdS sandwich	0.25 M Na <sub>2</sub> S and 0.35 M Na <sub>2</sub> SO <sub>3</sub>	5.7 (0 V <sub>Ag/AgCl</sub> , 100 mW/cm <sup>2</sup> )	—	[8]
ZnO NRs/CdS	0.25 M Na <sub>2</sub> S and 0.35 M Na <sub>2</sub> SO <sub>3</sub>	9.16 (0.4 V <sub>SCE</sub> , 100 mW/cm <sup>2</sup> )	4.03 (about -0.4 V <sub>SCE</sub> )	[9]
H-ZnO/CdS/Ni(OH) <sub>2</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub> (with pH buffered to ~7)	4.65 (0.4 V <sub>Ag/AgCl</sub> , 60 mW/cm <sup>2</sup> )	4.12 (0.68 V vsRHE)	[10]
Al-ZnO/CdS 60 SILAR cycles	0.25 M Na <sub>2</sub> S and 0.35 M Na <sub>2</sub> SO <sub>3</sub>	9.7 (0 V <sub>Ag/AgCl</sub> , 100 mW/cm <sup>2</sup> )	5.75 (0.38 V vs.RHE)	This work
Al-ZnO/CdS/Al <sub>2</sub> O <sub>3</sub> 5 s DCMS	0.25 M Na <sub>2</sub> S and 0.35 M Na <sub>2</sub> SO <sub>3</sub>	11.4 (0 V <sub>Ag/AgCl</sub> , 100 mW/cm <sup>2</sup> )	6.6 (0.41 V vs.RHE)	This work

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