

Supporting Information for

CdSe thin film: a versatile buffer layer for improving performance of TiO₂ nanorod

array:PbS QDs solar cells

Furui Tan,^{a,#} Zhijie Wang,^{b,#} Shengchun Qu,^b Dawei Cao,^d Kong Liu,^b Qiwei Jiang,^a Ying Yang,^d Shan Pang,^{*c} Weifeng Zhang,^{*a} Yong Lei^{*d} and Zhanguo Wang^b

^a Key Laboratory of Photovoltaic Materials, Department of Physics and Electronics, Henan University, Kaifeng 475004, PR China

^b Key Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, PR China

^c Key Laboratory for Special Functional Materials of Ministry of Education, Henan University, Kaifeng 475004, PR China

^d Institute of Physics & IMN MacroNano (ZIK), Ilmenau University of Technology, Ilmenau 98693, Germany

Corresponding Author

*E-mail: pangshan@henu.edu.cn. Tel: +86-371-23881358

*E-mail: wfzhang@henu.edu.cn. Tel: +86-371-23880659

*E-mail: yong.lei@tu-ilmenau.de. Tel: +49-3677693748

Experimental Section

Materials. Lead oxide (PbO, 99%), Cadmium oxide (CdO, 99%), 1-octadecene (ODE, 90%), oleic acid (OA, 98%) and Selenium (Se, 99.9%) were purchased from Sinopharm Group CO.LTD. Trioctylphosphine oxide (TOPO, 98%), tri-n-octylphosphine (TOP, 98%), bis(trimethylsilyl)sulfide (TMS, 99%) were obtained from Sigma-Aldrich. All chemicals were used as received without further processing. FTO coated glass substrates with a sheet resistance of 15 Ω·sq⁻¹ were supplied from Wesley Tech. Co., Ltd., China.

Synthesis of TiO₂ nanorod arrays. A compact TiO₂ layer was deposited on pre-cleaned FTO substrate by spin-coating a titanium-acetylacetonate precursor and then sintering at 450 °C for 90 min. This TiO₂ dense layer served as seed layer for growth of the subsequent TiO₂ nanorod arrays through hydrothermal reaction. Typically, the TiO₂/FTO substrates were sealed in 100 mL

Teflon line containing 1 mL tetrabutyl titanate, 30 mL hydrochloric acid and 30 mL deionized water. The hydrothermal deposition was performed at 160 °C for different reaction time ranging from 3 to 6 hours, thus yielding TiO₂ nanorod arrays with rod lengths ranging from 360 nm to 1.2 μm. The stainless steel was cooled to room temperature after reaction and the samples were thoroughly washed with deionized water and then annealed at 450 °C for 60 min.

Synthesis of PbS QDs. The PbS QDs with the first exciton peak at 1050 nm was synthesized as follows: PbO (2 mmol), oleic acid (OA, 7 mmol) and octadecene (ODE, 4 mmol) were degassed at 120 °C under N₂ flow for 60 min. After that, a clear solution containing 180 μL bis(trimethylsilyl)sulfide (TMS) and 5 mL 1-octadecene (ODE) was injected quickly and the heating mantle was removed after 1 min. When the reaction solution was cooled to room temperature, it was injected with 5 mL toluene and 10 mL ethanol to allow the precipitation of dark brown PbS QDs. The products were isolated by centrifugation at 4500 rpm and cleaned with toluene/ethanol solvent/antisolvent for at least three times. Finally, the QDs were dispersed in toluene to form a brown solution with a concentration of 40 mg/mL.

Synthesis of CdSe QDs. CdO (1 mmol), OA (10 mmol) and 3 g Trioctylphosphine oxide (TOPO) were dissolved in a four-neck round bottom flask and pumped at 140 °C under N₂ flow for 30 min. After that, the temperature was raised to about 280 °C during which the solution turned clear. A TOP-Se solution (containing 1 mmol Se in 3 mL tri-n-octylphosphine (TOP)) was injected into the flask quickly. The reaction was allowed at 260 °C for 4 min and then the heating mantle was removed. After the solution was cooled to room temperature, 10 mL acetone was injected to collect the red precipitation by centrifugation at 4500 rpm. The obtained CdSe QDs were cleaned with chlorobenzene/acetone solvent/antisolvent for at least three times and then dissolved in chlorobenzene to form a red solution with a concentration of 40 mg/mL.

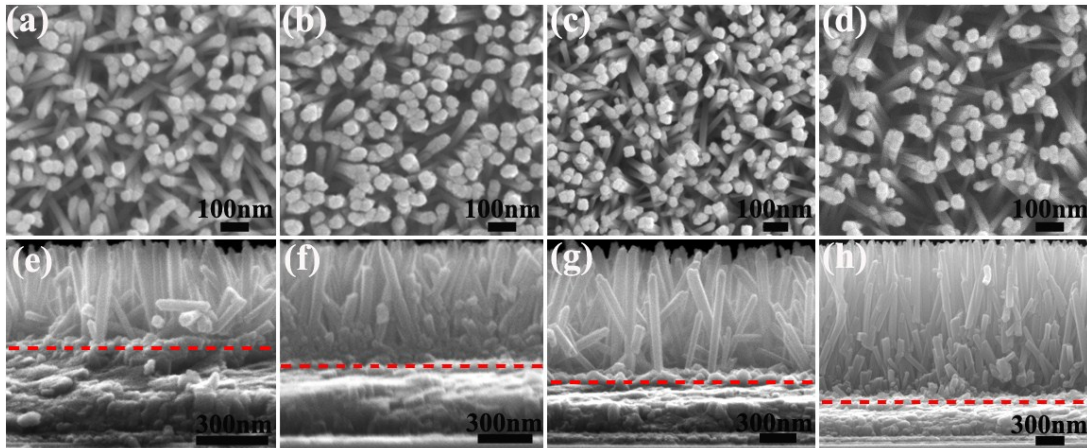


Figure S1. SEM images of the TiO_2 nanorod arrays with growing time of (a, e) 180 min, (b, f) 240 min, (c, g) 300 min, and (d, h) 360 min. The red line represents the location of TiO_2 seed layer on FTO glass.

The length of TiO_2 nanorod arrays could be easily tuned through controlling hydrothermal reaction time, so that the performance of our solar cells could be optimized by selecting a suitable TiO_2 nanorod array substrate. From Fig. S1, the length of the TiO_2 nanorod is about 360 nm, 480 nm, 700 nm and 1200 nm for the reaction time of 180 min, 240 min, 300 min and 360 min, respectively. The diameter of TiO_2 nanorod is almost unchanged. The variation on rod length makes it convenient to optimize the performance of solar cells.

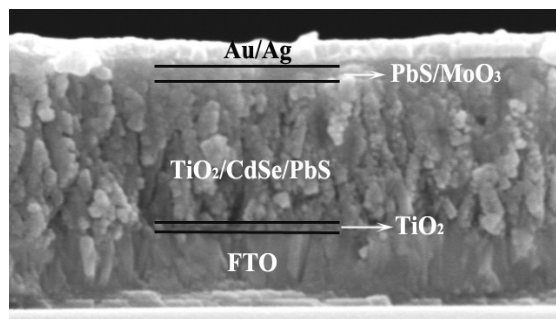


Figure S2. Cross-sectional SEM image of solar cell without pre-spincoating of diluted PbS QDs solution.

The complete infiltration of PbS QDs into the TiO_2 nanorod array is of great importance to the performance of solar cells. It is found that the QD thin film fabricated without several times of pre-spincoating of diluted QDs solution is not densely packed, and a number of pinholes and cracks could be present, due to which short circuit is often observed during the J-V measurements of these devices. Thus, our optimized procedure provides a feasible technic for the fabrication of compacted QD films on densely aligned nanoarray substrates.

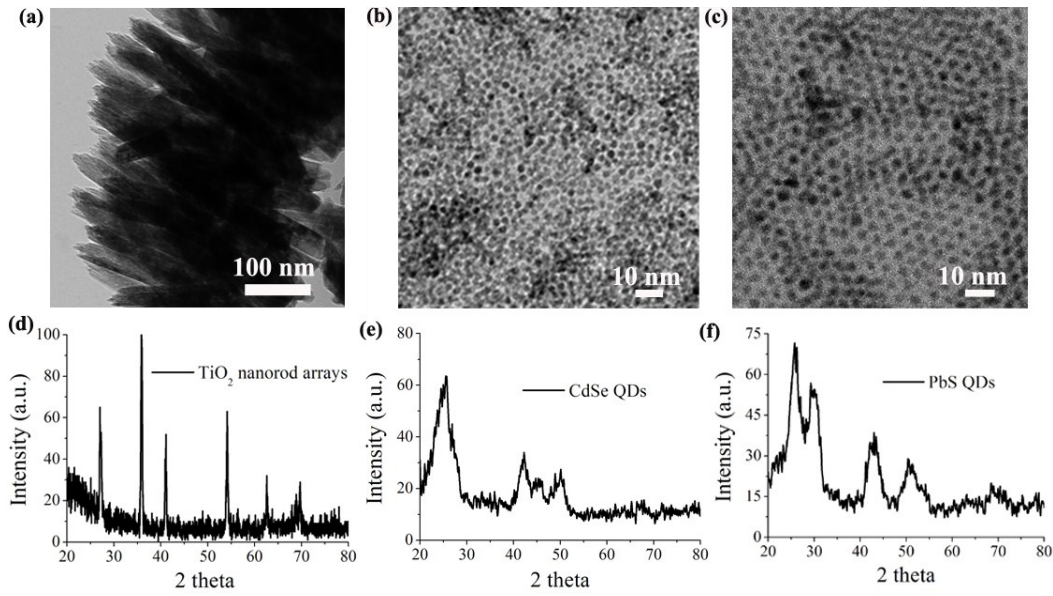


Figure S3. TEM images of (a) synthesized TiO_2 nanorods, (b) CdSe QDs, and (c) PbS QDs. (d-f) The XRD patterns corresponding to the materials in (a), (b) and (c), respectively.

TiO_2 nanorod arrays were scratched off from the FTO substrate and tested by TEM. Thus, a bundle of nanorods could be observed, as shown in Fig. S3a. The observed rod length in the TEM view is, however, smaller than the original length on the substrate due to the scratch-induced breaking up. The TEM images of CdSe and PbS QDs in Fig. S3b and c show excellent mono-dispersion, which is good for precisely controlling the electrophoretic deposition and complete infiltration. XRD patterns (Fig. S3d-f) demonstrate the formation of TiO_2 nanorod, CdSe and PbS QDs with Rutile (PDF No. 71-650), Cadmoselite (PDF No. 77-21) and Galena (PDF No. 65-135) phase, respectively.

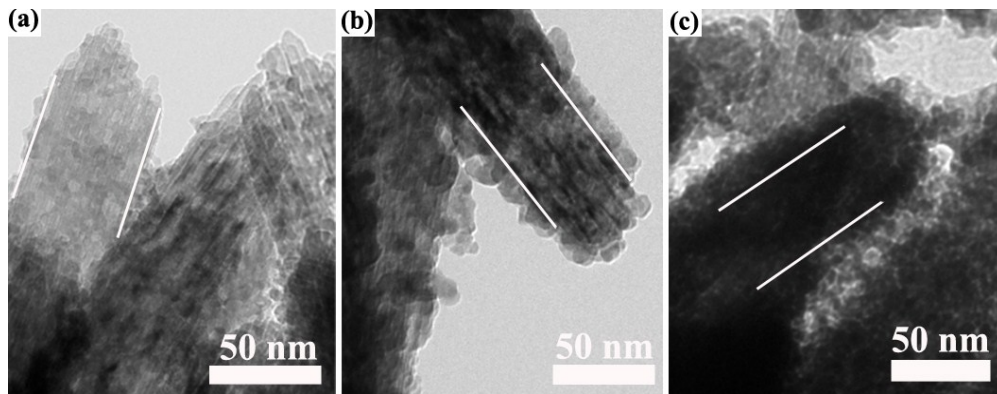


Figure S4. TEM images of CdSe QDs deposited on TiO₂ nanorods with CdSe EPD time of (a) 5 min, (b) 10 min, and (c) 20 min, respectively.

In order to investigate the dependence of solar cell performance on different thicknesses of CdSe capping layer, we have carried out experiments on EPD of CdSe QDs with different reaction time. With short EPD time such as 5 min, the amount of CdSe QDs on the TiO₂ rod is found to be very small (Fig. S4a). Increasing the EPD time will increase the QDs thickness (about 15 nm for 10 min's deposition in Fig. S4b) while deposition for too long time causes a large aggregation of CdSe QDs between TiO₂ nanorods (Fig. S4c), which may influence the infiltration of PbS QDs.

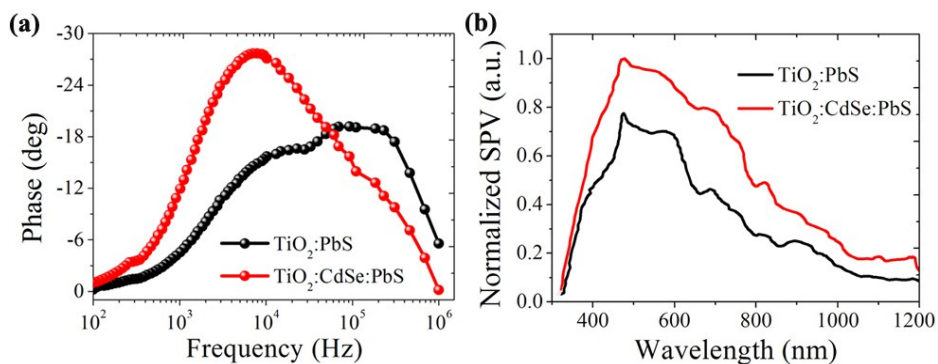


Figure S5. (a) EIS phase plots and (b) SPV spectra of the two sets of solar cells.

EIS measurements were performed with the frequency varied from 1 MHz to 100 Hz. The Bode mode plots in Fig. S5a show that the peak frequency of the CdSe QDs incorporated device (near 7000 Hz) is smaller than that without CdSe, which indicates that the effective recombination rate in $\text{TiO}_2:\text{CdSe}:\text{PbS}$ solar cell is lower than that in the reference cell. Besides, across the entire light region from 350 nm to 1200 nm, the modified device generates a larger steady-state surface photovoltage than the reference (Fig. S5b), suggesting an enlarged number of charge carriers that can be transported to the surface of PbS QD film.

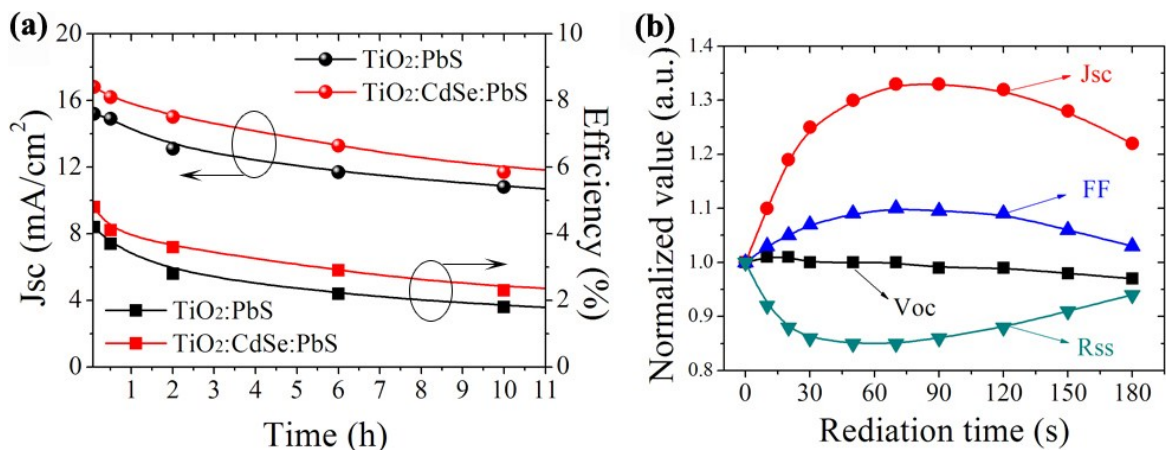


Figure S6. Stability of the solar cells stored and tested in normal atmosphere. (a) J_{sc} and PCE variation in 10 hours. (b) Normalized values of V_{oc} , J_{sc} , FF, and R_{ss} at the early stage of light illumination.

Like conventional QDs based photovoltaic devices, these two devices also show somewhat performance decay. As shown in Fig. S6, the J_{sc} and PCE of the $\text{TiO}_2:\text{CdSe}:\text{PbSe}$ device present a decrease from $16.9 \text{ mA}/\text{cm}^2$ to $11.8 \text{ mA}/\text{cm}^2$ and 4.8% to 2.3% , respectively, when the device is placed in atmosphere for 10 h. The $\text{TiO}_2:\text{PbS}$ device shows a similar decaying tendency, indicating that an encapsulating procedure is needed for the long-term usage of QDs based devices. To get more useful information, normalized performance parameters of the two devices at the early stage of light illumination for the $\text{TiO}_2:\text{CdSe}:\text{PbSe}$ device are given in Fig. S6b. J_{sc} and FF show an increase and a following decrease feature, while the V_{oc} delivers a gradual decrease feature. R_{ss} decreases first and then increases obviously. This could be probably caused by the oxidation at the film interface that does harm to electrical contact.

Table S1. Photovoltaic performance of solar cells with different CdSe EPD time on the 360 nm TiO₂ nanorod arrays.

Time (min)	Voc (V)	Jsc (mA/cm ²)	FF (%)	Eff (%)	Rss (Ω)
0	0.48	18.8	47	4.2	235
5	0.50	19.0	48	4.6	228
10	0.52	19.8	50	5.2	240
20	0.49	17.7	45	3.9	405

As given in Fig. S4, different EPD time generates different amounts of CdSe QDs loading on TiO₂ rod surface. The performance of solar cells with CdSe QDs is thus greatly influenced by the thickness of CdSe layer, as shown in Table S1. Typically, the best performance was obtained when CdSe QDs was deposited for 10 min, corresponding to about 15 nm in CdSe layer thickness. Further increasing EPD time would cause a deterioration in series resistance (R_{ss}) due to the excessive amount of CdSe QDs, which would accordingly reduce the loading of PbS QDs. Thus, EPD time of 10 min has been selected for further optimizing the solar cells.