Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Microwave assisted aqueous synthesis of core-shell $CdSe_xTe_{1-x}/CdS$ quantum dots for high performance sensitized solar cells

JianhengLuo, Huiyun Wei, Fan Li, Qingli Huang, Dongmei Li, Yanhong Luo* and Qingbo Meng*

Key Laboratory for Renewable Energy (CAS), Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condense Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, PR China. E-mail: qbmeng@iphy.ac.cn and yhluo@iphy.ac.cn; Fax: +86-10-8264-9242; Tel: +86-10-8264-9242

Synthesis of $CdSe_xTe_{1-x}/CdS$ quantum dots

In the present work, a two-step microwave assisted method is employed to realize the rapid and homogeneous growth of $CdSe_xTe_{1-x}/CdS$ QDs. First, the $CdSe_xTe_{1-x}$ core QDs were synthesized as below. $CdCl_2$ (1.25 mmol) was dissolved to 150 ml de-ionized water in 250 mL three necked flask. Then MPA (0.230 mL) and tri-sodium citrate dehydrate (50 mg) were added into the flask in sequence under vigorous magnetic stirring. After the pH of premixed solution was tuned to 9.0, Na_2TeO_3 (0.1 mmol), Na_2SeSO_3 (0.02 mmol) and $NaBH_4$ (100 mg) were added successively. The reaction vessel was transferred to the microwave oven equipped with a reflux condenser and heated to 95 ^oC for 10 min. $CdSe_xTe_{1-x}$ QDs was taken when the temperature cooled down to lower than 50 ^oC. Next, the $CdSe_xTe_{1-x}$ QDs with thin shell CdS ($CdSe_xTe_{1-x}$/CdS-I) were obtained by simply adding the 30 mL premixed precursor solution containing $CdCl_2$ (1.25 mmol) and MPA (0.185 ml) without prior purification. Specifically, the pH of solution was adjusted to 12.2 and then heated at 100 ^oC with microwave irradiation for another 20 min. For purification, alcohol was added, and then the suspension was centrifuged and the supernatant was removed.

Preparation of Na_2SeSO_3 solution

Anhydrous sodium sulfite (0.336 g) and selenium powder (0.0843 g) were added in 100 ml one-neck flask followed by 20 mL deionized water, which was heated to 80 ^oC in an oil bath for 4 h. After cooling down to room temeperature, the clear portion of the solution was filtered and stored in the refrigerator at 4 ^oC for use.

Fabrication of TiO_2 photoanodes

The double layered TiO_2 photoanodes were fabricated on well-cleaned FTO glass via doctor blade technique. A 11 μm-thickness transparent layer of 20 nm sized anatase TiO_2 particles was first deposited on FTO substrates, followed by sintering at 450 ^{o}C for 30 min. and 6 μm-thickness light scattering layer of 300 nm sized rutile TiO_2 particles was further coated, subsequently annealed at 450 ^{o}C for 30 min. Finally, the obtained TiO_2 electrodes were treated with an aqueous solution of 40 mM $TiCl_4$ at 70 ^{o}C for 40 min, followed by a sintering process at 500 ^{o}C for 30 min. The as-prepared TiO_2 electrodes were used for further sensitization with various QDs.

Fabrication of QDs sensitized TiO_2 photoanodes

To demonstrate the viability of $CdSe_xTe_{1-x}$/CdS-I QDs as sensitizer in QSCs, core-shell $CdSe_xTe_{1-x}$/CdS-I/CdS-II QDs sensitized TiO_2 was made to test their photoactivity. First, the bare TiO_2 electrodes were directly immersed into presynthesized $CdSe_xTe_{1-x}$/CdS-I QDs aqueous solution with pH~12 for 24 h to ensure maximized surface coverage. The overcoating of thick CdS-II shell had been achieved via in situ successive ionic layer adsorption and reaction (SILAR) method according to the literature procedure.[1] Briefly, the $CdSe_xTe_{1-x}$/CdS-I QDs modified TiO_2 electrodes were first dipped into a methanol solution containing $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.05 M) for 1 min, and then subject it into a $Na_2S \cdot 9H_2O$ (0.05 M) water/methanol solution (1:1 by volume) for 1 min in sequence. The electrodes were thoroughly rinsed with distilled water to remove the excess precursor after each dipping step. This procedure was repeated for 6 cycles to form core-shell $CdSe_xTe_{1-x}$/CdS-I/CdS-II sensitized electrodes. For comparison, $CdSe_xTe_{1-x}$/CdS-I and CdS-II QDs sensitized TiO_2 electrodes were also made.

Preparation of Cu_2S counter electrodes

Porous Cu_2S was prepared by immersing brass foil in 37% HCl solution at 70 °C for 5 min , followed by rinsing with deionized water and dring with nitrogen flow, and subsequently dipping it into polysulfide solution for 10 min for further use.

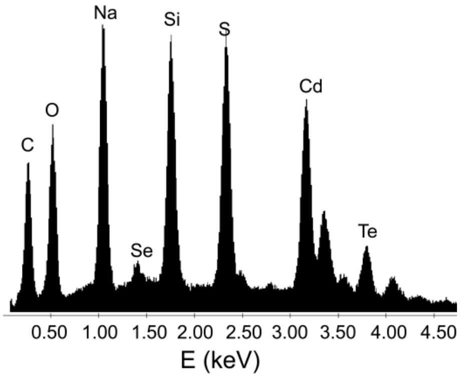

Fig. S1. EDX spectrum of $CdSe_xTe_{1-x}$, the corresponding atomic ratio of Te and Se is 1.03:0.18.

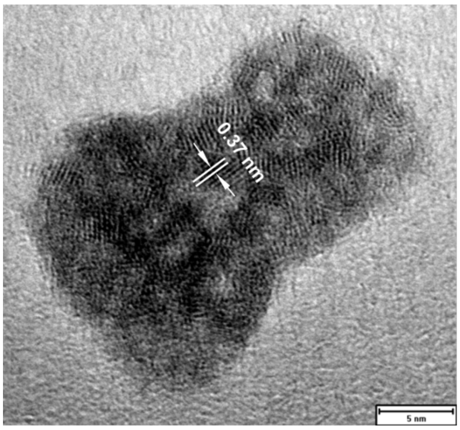

Fig. S2. HRTEM image of $CdSe_xTe_{1-x}$ QDs with an average size of 2.5 nm.

Stability of $CdSe_xTe_{1-x}$/CdS-I and $CdSe_xTe_{1-x}$/CdS-I/CdS-II based QSCs

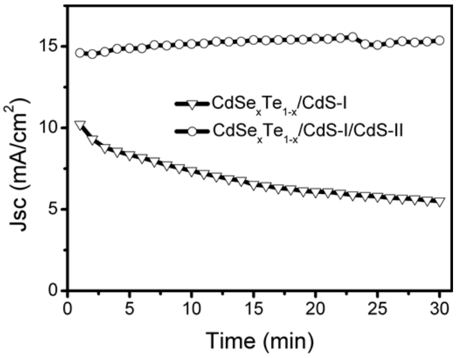

Fig. S3 Photocurrent stability of $CdSe_xTe_{1-x}$/CdS-I and $CdSe_xTe_{1-x}$/CdS-I/CdS-II under continuous illumination of 100 mW/cm^2.

Stability of the devices is evaluated by measuring *Jsc* with respect to time under continuous illumination of 100 mW/cm^2. As shown in Fig. S3, for $CdSe_xTe_{1-x}$/CdS-I/CdS-II based QSCs, a steady photocurrent is observed. While for the $CdSe_xTe_{1-x}$/CdS-I based QSCs, the photocurrent decreases quickly after 30 min irradiation. Strong corrosion of the polysulfide electrolyte on the $CdSe_xTe_{1-x}$/CdS-I likely leads to the reduction in photocurrent during long period operation. Therefore, it can be concluded that the in situ successive ionic layer adsorption and reaction growth of thick CdS shell on the $CdSe_xTe_{1-x}$/CdS-I is a promising strategy to enhance the photostability of $CdSe_xTe_{1-x}$/CdS-I QDs.

The influence of CdS-II cycles on the performance of $CdSe_xTe_{1-x}$/CdS-I based QSCs

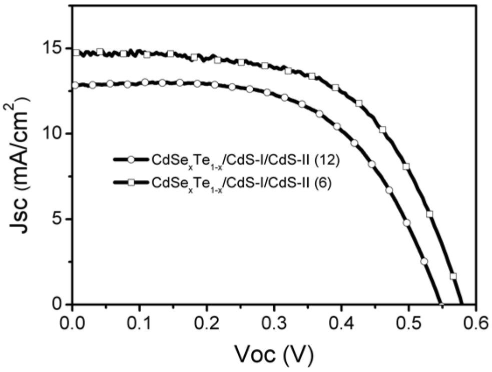

Fig. S4 The influence of CdS-II cycles on the performance of $CdSe_xTe_{1-x}$/CdS-I based QSCs

Table S1 Device parameres of defferent CdS-II cycles on $CdSe_xTe_{1-x}$/CdS-I based QSCs

Sample	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	*η (%)*
$CdSe_xTe_{1-x}$/CdS-I/CdS-II (6)	14.79	0.578	0.59	5.04
$CdSe_xTe_{1-x}$/CdS-I/CdS-II (12)	12.83	0.548	0.59	4.15

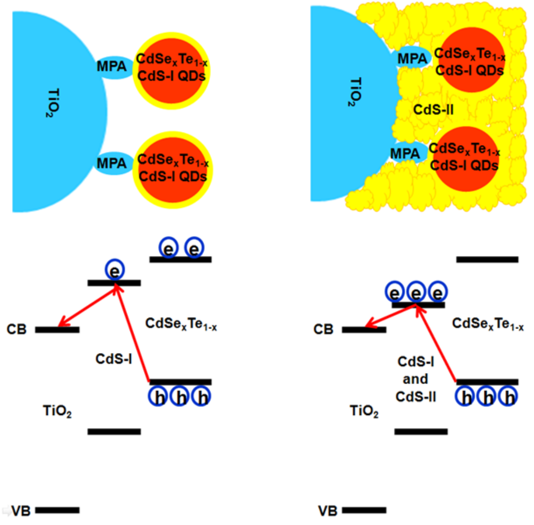

Fig. S5 Schematic illustrating of the energy level alignment for $CdSe_xTe_{1-x}$/CdS-I and $CdSe_xTe_{1-x}$/CdS-I/CdS-II quantum dot sensitized TiO_2 electrodes

As is well known, the effective bandgap of type II core-shell heterostructured QDs can be manipulated by selecting appropriate semiconductor materials and varying the core size and shell thickness. The effective bandgap determined by the valence band of core and conductive band of shell. To understand the physical processes underlying the broad light absorption, schematic illustrating of the energy level alignment for $CdSe_xTe_{1-x}$/CdS-I and $CdSe_xTe_{1-x}$/CdS-I/CdS-II quantum dot sensitized TiO_2 electrodes (Fig. S5) were added . Due to the quantum confinement effect, the conduction band of $CdSe_xTe_{1-x}$ (core) is up-shifted and a type-II structure with a staggered band offset is formed with the increasing shell thickness. The coupling of $CdSe_xTe_{1-x}$ with CdS shell results in stronger wave function interfacial interaction which leads to spatially indirect energy gap with the significant red-shift of the absorption edge of this core–shell QDs, in which the electronic alignment throughout the core-shell structure causes spatial separation of the electrons and holes between the $CdSe_xTe_{1-x}$ (holes) and CdS (electrons). This spatial separation of charge carriers enables fast electron transfer from the QD sensitizer to the TiO_2, which simultaneously suppresses the charge-recombination process because the shell acts as a tunneling barrier for the hole localized inside the core. Therefore, the obtained $CdSe_xTe_{1-x}$/CdS-I/CdS-II core/thick shell NCs has a narrower indirect band gap than both the direct bandgap of $CdSe_xTe_{1-x}$ and CdS. In our work, the resultant narrow bandgap can be easily controlled by varying the SILAR cycles of CdS shell to form thick shell with lower conductive band position, which caused the significant redshift of light absorption range. In addition, with the introduction of in situ SILAR deposition CdS-II layer, much surface state on aqueous QDs and TiO_2 can be passivated to retard the internal interface recombination.

Table S2 Reproducibility of solar cell performance

Sample	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	*η (%)*
$CdSe_xTe_{1-x}$/CdS-I	9.01	0.495	0.58	2.59
	10.23	0.502	0.53	2.72
	10.29	0.457	0.47	2.21
Average value	9.84	0.485	0.53	2.53
CdS-II(6)	7.57	0.515	0.55	2.14
	7.92	0.509	0.52	2.10
	8.37	0.501	0.47	1.97
Average value	7.95	0.508	0.51	2.06
$CdSe_xTe_{1-x}$/CdS-I/CdS-II(6)	14.49	0.575	0.58	4.83
	14.63	0.582	0.58	4.94
	14.79	0.578	0.59	5.04
Average value	14.64	0.578	0.58	4.91

Reference

(1) V. Gonzalez-Pedro, C. Sima, G. Marzari, P. P. Boix, S. Gimenez, Q. Shen, T. Dittrich and I. Mora-Sero, *Phys. Chem. Chem. Phys.*, 2013, **15**, 13835.