Electronic Supplementary Information (ESI)

ZnO nanoparticle based highly efficient CdS/CdSe quantum dot-sensitized solar cells

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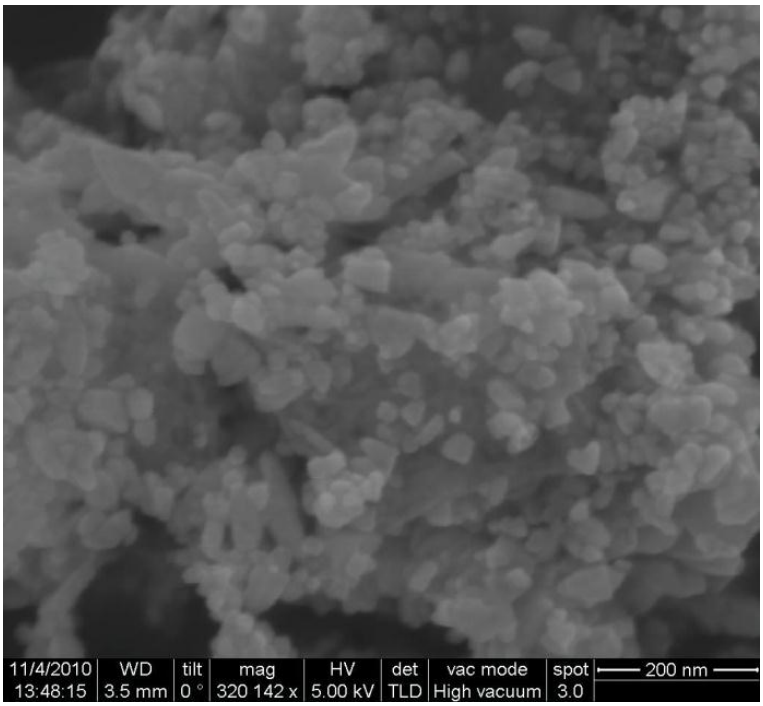

Fig. S1 SEM image of the as-synthesized ZnO nanoparticles in a continuous flow supercritical reactor recorded using a Nova 600 Nano SEM from FEI. The size of ZnO particle is about 20 nm.

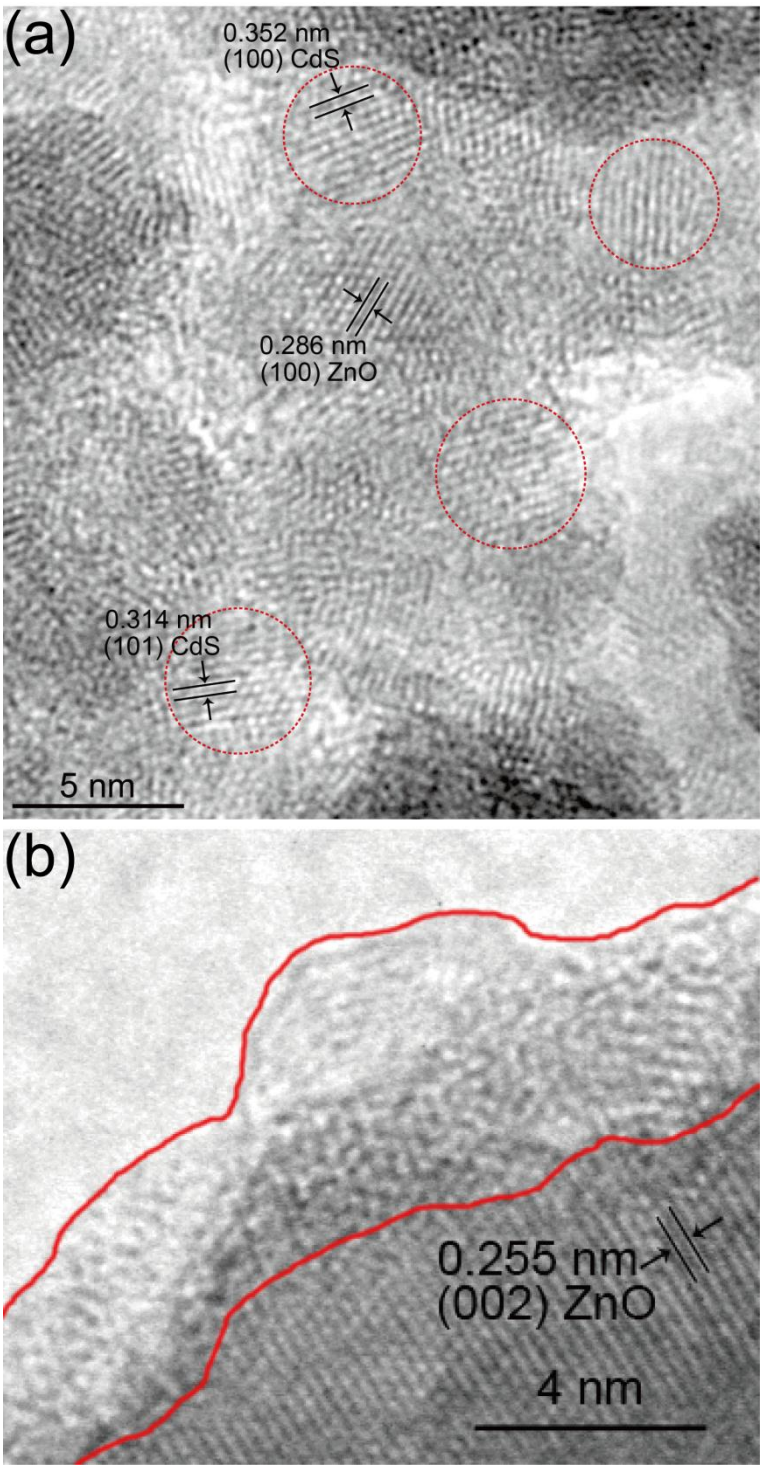

Fig. S2 HRTEM images of CdS QDs on ZnO film recorded using a JEM-2010 TEM from JEOL Ltd.. (a) shows that a hexagonal CdS is deposited on ZnO by the SILAR method and its crystal size is about 3.5 nm (marked out by red circles). (b) shows that the thickness of the CdS shell coated on ZnO is about 3-5 nm (marked out by red lines).

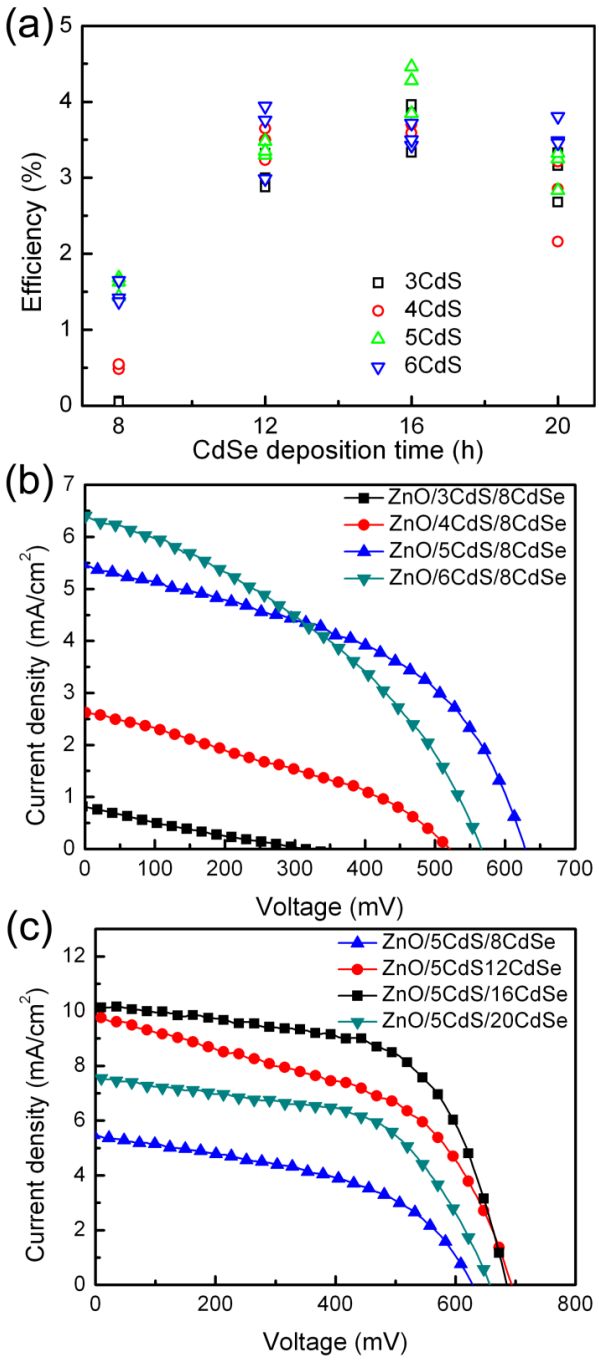

Fig. S3 (a) Efficiencies of the tested QDSCs. The typical *J*-*V* curves for QDSCs fabricated with (b) different CdS SILAR cycles and the same CdSe CBD deposition time (8 h), (c) the same CdS SILAR cycle (5 cycles) and different CdSe CBD deposition time.

As shown in Fig. S3, not only *J*sc but also *V*oc change a lot with different deposition cycles of CdS and CdSe. According to previous works [1-3], *V*oc can be expressed by the following equation,

$$V_{oc} = \left[\frac{kT}{q}\right] \ln\left\{\frac{J_{inj}}{n_{cb} k_r [S_2^{2-}]}\right\}$$

where k is the Boltzmann constant, T is the absolute temperature, q is the electronic elementary charge, J_{inj} is the flux of electron injection from the QDs, n_{cb} is the surface electron concentration of ZnO in the dark equilibrium, k_r is the rate constant of recombination reaction occurred at the ZnO/electrolyte interface, and $[S_2^{2-}]$ is the concentration of S_2^{2-} in the electrolyte.

In our QDSC systems, the $[S_2^{2-}]$ and n_{cb} are assumed to be constant since the ZnO substrates and the electrolyte are the same. Thus, *V*oc is positively correlated to J_{inj} and negatively correlated to k_r. More deposition cycles of CdS and CdSe indicate a larger absorbance of incident photons, and are apparently able to increase the J_{inj}. Furthermore, the evolution of QDs deposition leads to a better coating on the ZnO surface, which significantly decreases the bare ZnO surface and the possibility of its exposure to the polysulfide electrolyte, thus reducing the recombination rate (k_r) at the ZnO/electrolyte interface.

Therefore, the change of *V*oc could be attributed to different deposition cycles of CdS and CdSe. The same phenomenon has been observed in our previous work [3]. As the CdSe growth time increasing from 6 h to 14 h, the Voc of the TiO_2 nanotube based CdS/CdSe QDSCs increased from 602 mV to 689 mV, nearly 100 mV improved. Further, how the CdS and CdSe deposition affecting the electron injection and recombination reaction, respectively, needs more investigations in detail.

[1] A. Hagfeldt and M. Grätzel, *Chem. Rev.*, 1995, **95**, 49-68.
[2] S. Q. Fan, D. Kim, J. J. Kim, D. W. Jung, S. O. Kang and J. Ko, *Electrochem. Commun.*, 2009, **11**, 1337-1339.
[3] Q. Zhang, G. Chen, Y. Yang, X. Shen, Y. Zhang, C. Li, R. Yu, Y. Luo, D. Li and Q. Meng, *Phys. Chem. Chem. Phys.*, 2012, **14**, 6479-6486.

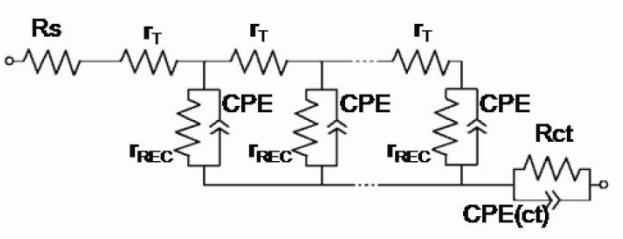

Fig. S4 Equivalent circuit used to fit the electrochemical impedance spectroscopy. *R*s is the ohmic serial resistance of the cell. r_T is the charge transport resistance in the photoanode film; r_{REC} is the charge recombination resistance at the photoanode/electrolyte interface; CPE is the constant phase element of the photoanode film; and *R*ct and CPE(ct) are the charge transfer resistance and the constant phase element at the counter electrode/electrolyte interface. The impendence of CPE is described as $Z_{CPE} = Q(j\omega)^{-n}$ ($0 \leq n \leq 1$). Q and n are frequency-independent parameters of the CPE.