

Electronic Supplementary Information

Efficient CdSe Quantum Dot-Sensitized Solar Cells Prepared by Postsynthesis Assembly Approach

H. Zhang, K. Cheng, Y. M. Hou, Z. Fang, Z. X. Pan, W. J. Wu, J. L. Hua and X. H. Zhong*

Experimental Section

Preparation of Oil-Soluble CdSe QDs. Oil-soluble oleylamine (OAm) capped CdSe QDs with average size in the range of 3.2-5.4 nm and corresponding first excitonic absorption peak at $\lambda = 563 - 618$ nm were prepared according to a literature method.¹ Briefly, 10.0 mL of OAm and 0.5 mL of 2.1 M Se stock solution in trioctylphosphine (TOP) were heated to 300 °C under nitrogen atmosphere with stirring. 2.5 mL of 0.4 M Cd stock solution (prepared by dissolving CdO in oleic acid and ODE (v/v, 1:1) at 250 °C) was injected into the reaction flask. The temperature was then set at 280 °C for the subsequent growth and annealing of nanocrystals. After completion of particle growth, the obtained CdSe QDs were precipitated by adding methanol into the toluene solution and further isolated and purified by repeated centrifugation and decantation with addition of methanol and chloroform. The optical spectra (absorption and PL emission spectra) and the TEM images of the obtained CdSe QDs were shown in Fig. S1. The relative standard deviations of the obtained CdSe QDs are in the range of 4-6% based on the statistical analysis of more than 200 particles.

Preparation of Water-Soluble MPA-Capped CdSe QDs via Ligand Exchange. The water solubilization of the as-prepared oil-soluble OAm-capped CdSe QDs was achieved by replacing the initial hydrophobic surfactants (mainly OAm) with MPA according to literature method.² Typically, MPA (0.123 g, 0.4 mmol) was dissolved in 0.3 mL of deionized water together with 1.0 mL methanol, the solution was then adjusted to pH 12 with 40% NaOH. The MPA-methanol solution was then added into 5.0 mL CdSe QDs chloroform solution (containing 0.2 mmol CdSe) and stirred for 30 min to get the precipitation of the QDs. Then 10.0 mL water was added into the mixture and kept the stirring for another 20 min. The solution was separated into two phases finally and the CdSe QDs was transferred into the supernatant water from the underlying chloroform, the underlying organic phase was discarded and the aqueous phase containing the QDs was collected. The free MPA ligand in the QDs aqueous solution was isolated by precipitating the QDs with addition of acetone. The supernatant was discarded and the pellet was then re-dissolved in water for the next step use. The optical spectra of the water-soluble MPA-capped QDs obtained via water-soluble ligand exchange were shown in Fig. S1c.

Fabrication of QD-Sensitized Photoanodes and Solar Cells. TiO₂ Nanoparticulate electrodes were prepared by successive screen printing a 11.0- μm -thick transparent layer (home-made P25 paste) and a 4.0- μm -thick light scattering layer (200-400-nm TiO₂) over F:SnO₂-coated (FTO, 14 Ω /square) glass substrates, followed by sintered at 450 °C for 30 min in a muffle-type furnace. A post-treatment of the dried TiO₂ film with an aqueous solution of TiCl₄ were then carried out according to typical procedures for dye cells.³ The obtained TiO₂ mesoporous films were then coated with QDs sensitizers by immersing the film in an MPA-QD aqueous dispersion (with absorbance of 3.0 and pH of 11.0) and staying for 2 h before rinsed sequentially with water and ethanol and then dried with nitrogen. After finishing deposition, the QD bound TiO₂ film was coated with ZnS by twice dipping alternately into 0.1 M Zn(OAc)₂ and 0.1 M Na₂S solutions for 1 min/dip. After coating ZnS layer, the TiO₂ electrode was then subjected for sintering treatment in a muffle-type furnace at a temperature range of 300 °C for 2.5 min.

The cells were prepared by assembling counter electrodes and QD-sensitized photoanodes using a 50- μm thickness scotch spacer and with a droplet (10 μL) of polysulfide electrolyte. The Cu₂S counter-electrodes were prepared by immersing brass in HCl solution at 70 °C for 5 min and subsequently dipping it into polysulfide solution for 10 min. The polysulfide electrolyte solution consists of 2.0 M Na₂S, 2.0 M S, and 0.2 M KCl in methanol/water (3:7, v/v) solution. For QDSCs prepared under each condition, 3 cells were prepared and tested in parallel, and the one with the medium value was chosen as the final data.

Photovoltaic performances (J - V curves) of cell devices were recorded on a Keithley 2400 source meter under illumination by an AM 1.5 G solar simulator (Oriel, Model No. 91160, equipped with a 300 W xenon lamp). The power of the simulated light was calibrated to 100 mW/cm² by a NREL standard Si solar cell. Photoactive area was 0.237 cm². Incident photon-to-current conversion efficiency (IPCE) signal was recorded on a Keithley 2000 multimeter under the illumination of a 150 W tungsten lamp with a Spectral Product DK240 monochromator. Electrochemical impedance spectroscopy (EIS) measurements were conducted with an impedance analyzer (Zahner, Germany) at -0.5V bias potential and 10 mV of amplitude over the frequency range of 0.1 Hz to 100 kHz under dark condition.

TEM Images and Optical Spectra. Transition electron microscopy (TEM) were obtained using a JEOL JEM-2100 instrument with accelerating voltage of 200 kV. The TiO₂ films with CdSe QDs sensitizers (~5.0 μm thick without scattering layers) were scratched off the FTO glass and dispersed in ethanol with the help of ultrasonic, from which a few drops were taken over a TEM grid and dried for TEM images. Scanning electron microscopy (SEM)

was performed using an FEI Sirion high resolution SEM system equipped with an energy dispersive spectroscopy (EDS). The absorption spectra of CdSe QDs sensitized electrodes composed of 11.0- μm thick TiO_2 films with dimension of 2.0×1.0 cm (without scattering layers) were recorded on a UV-visible spectrophotometer (Shimadzu UV-2450). The steady state photoluminescence (PL) emission spectra were recorded on a Cary Eclipse (Varian) fluorescence spectrophotometer.

Calculation of QD coverage on TiO_2 surface

The QDs density on the film of 1.55×10^{15} particle/ cm^2 of projected area can be calculated from the measured absorbance (1.42) integrated with the extinction coefficient of 5.4 nm CdSe QDs (taken as $5.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).⁴ Taking the particle as spherical and monodisperse with a diameter of 5.4 nm, the total surface area covered by the QDs would be of 355 cm^2 on the basis of a closed packed QD monolayer. On the other hand, the Brunauer-Emmett-Teller surface area of $49.1 \text{ m}^2/\text{g}$ was measured for TiO_2 paste after sintering treatment, which is in agreement with literature values.⁵ The density of $2.14 \text{ mg}/\text{cm}^2$ of projected area was measured for our $11.0 \mu\text{m}$ - TiO_2 film without scattering layer. Therefore, the total inner surface area of the film is as large as $1051 \text{ cm}^2/\text{cm}^2$ of projected area. Finally, by dividing the surface area that may be covered by the QDs by the total surface area of the film, we get a value for the QD fractional coverage equal to 34%

References:

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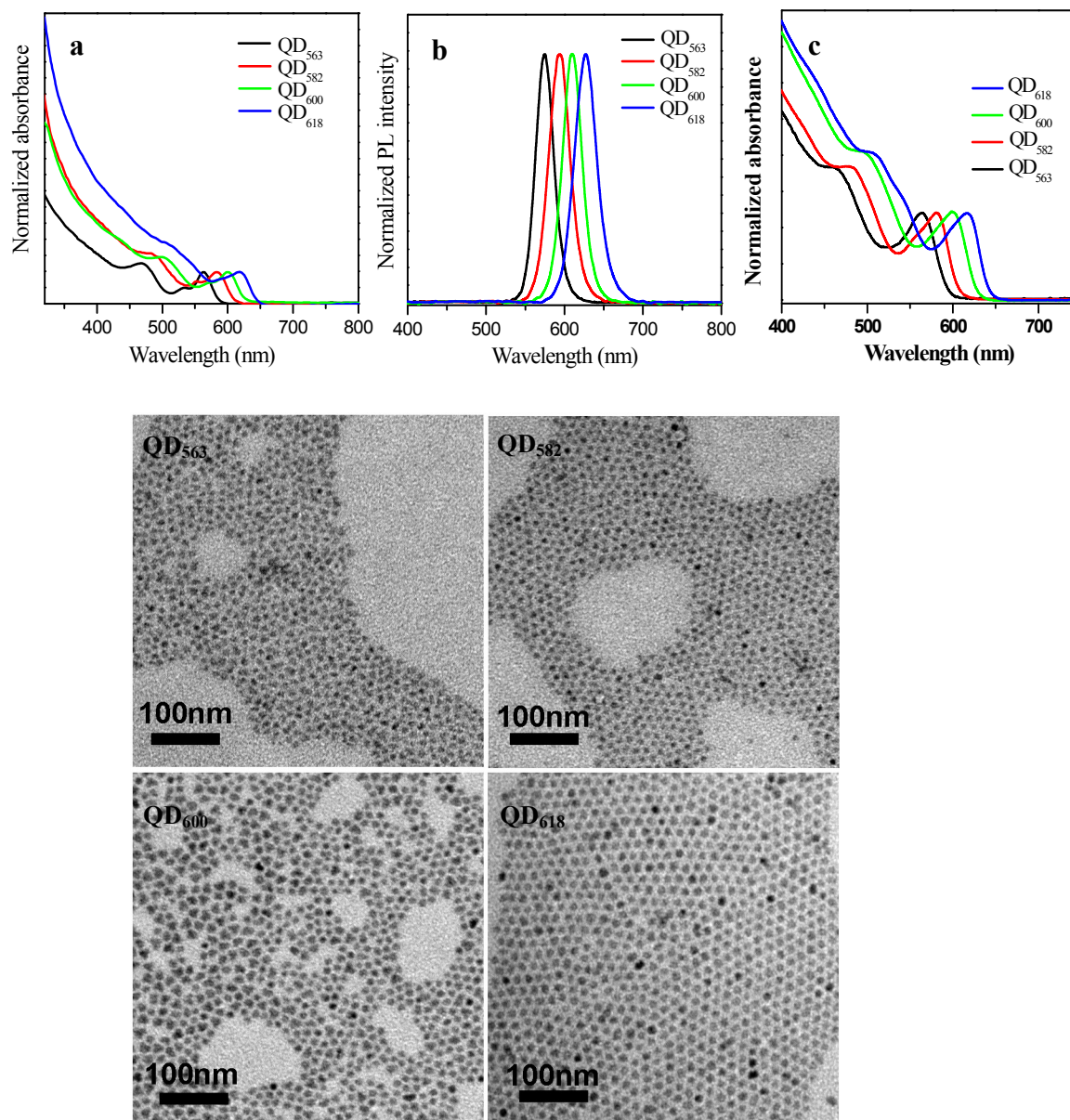


Fig. S1 UV-vis absorption (a) and PL emission (b, $\lambda_{\text{ex}} = 400$ nm) spectra of as-prepared CdSe QDs dispersions in toluene with corresponding wide-field TEM images shown below. (c) UV-vis absorption spectra of MPA-capped CdSe QDs dispersions in water derived from initial hydrophobic QDs.

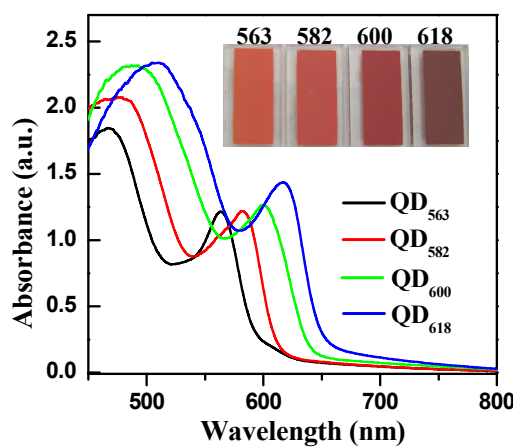


Fig. S2 UV-vis absorption spectra of different sized CdSe QD sensitized TiO₂ films after deposition for 2 h. Inset: photographs of the corresponding films.

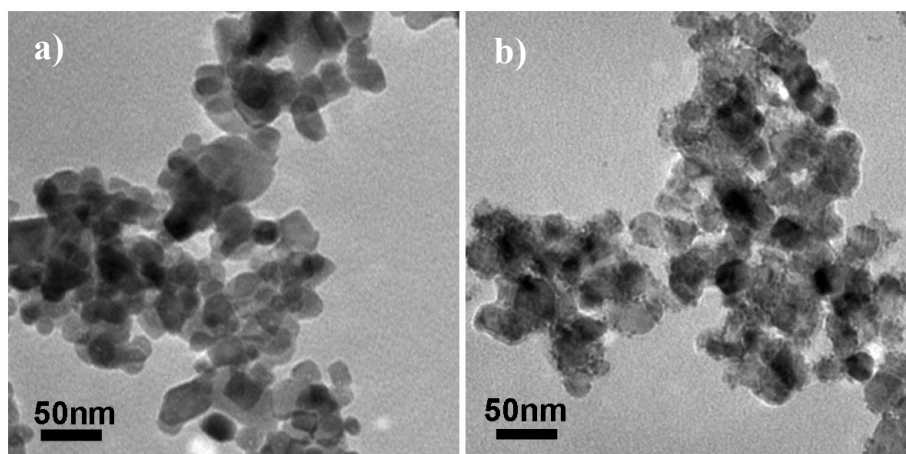


Fig. S3 Wide-field TEM image of: (a) bare TiO₂ film without the deposition of CdSe QDs, and (b) CdSe QDs bound TiO₂ film.

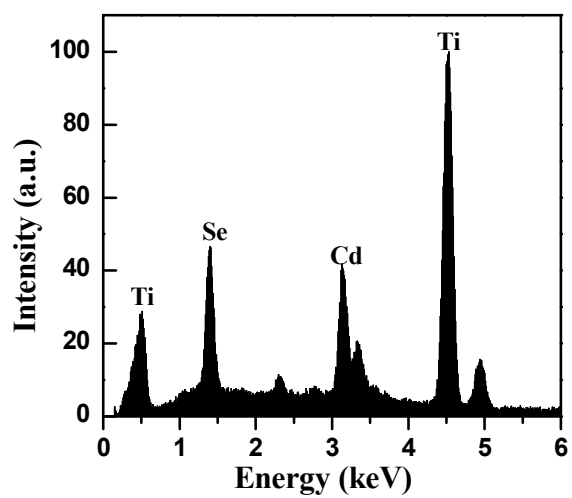


Fig. S4 Typical EDS spectra of CdSe QD sensitized TiO₂ film

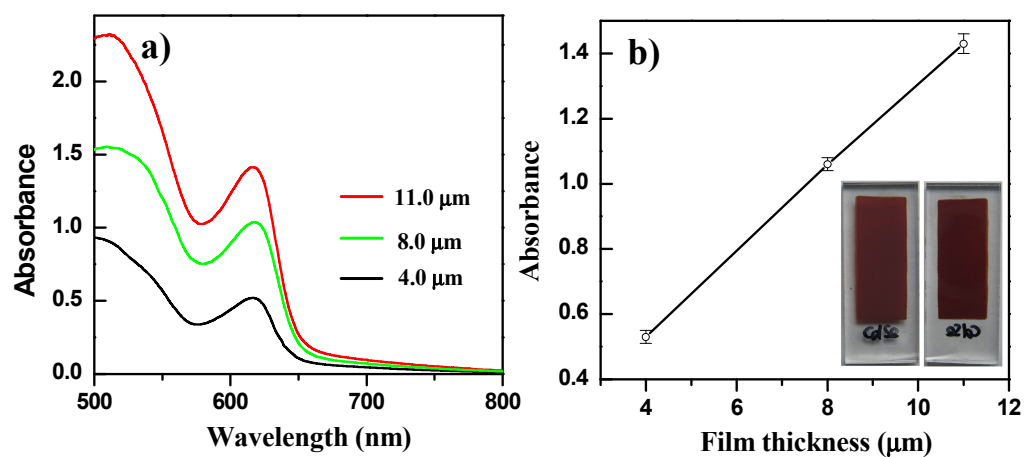


Fig. S5 (a) UV-vis absorption spectra of CdSe QDs sensitized TiO₂ film with different thickness. (b) Dependence of absorbance at the first excitonic absorption peak position on the thickness of TiO₂ film. Inset: photographs of the film taken from the front and back sides.