Supporting Information

Charge Transfer Kinetics in CdSe quantum dot sensitized solar cells.

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Experimental Section:

Preparation of colloidal CdSe QDs. CdSe QDs, capped with trioctylphosphine (TOP) and dispersed in toluene, were prepared by a solvothermal route that allows size control. Briefly, selenium reacts with cadmium myristate in toluene in the presence of oleic acid and TOP. The reaction takes place at 180 °C in a sealed autoclave. The QD size depends on reaction time; for the QDs used in this work the reaction time was 15 hours that corresponds around 3.3 ± 0.1 nm. For DA of QDs onto TiO₂ surface, solvent exchange is needed and a CH₂Cl₂ (99.6%, Sigma Aldrich) CdSe QDs dispersion was prepared by centrifugation of the toluene colloidal dispersion, and redissolution.

Preparation of QD sensitized electrodes. A compact layer of TiO₂ (thickness ~ 100-200 nm) was deposited by spray pyrolysis of an aerosol of titanium (IV) bis(acetoacetonato) di(isopropanoxylate) (Sigma Aldrich) onto the SnO₂:F (FTO) coated glass electrodes (Pilkington TEC15, 15W/sq resistance). The FTO electrodes were kept at 400 °C during spraying to burn off all the organics, thus leaving behind a compact layer of TiO₂. Subsequently, the coated substrate was fired at 450 °C for 30 min. A commercial 20-450 nm particle size TiO₂ paste (18NR-AO, Dyesol, Queanbeyan, Australia) was deposited on top of the TiO₂ compact layer. Around 0.24 cm² TiO₂ films were deposited by the doctor blade technique and subsequently sintered at 450 °C for 30 min in a muffle-type furnace. The thickness of the sintered TiO₂ films was approximately 10 mm measured by a profilometer Dektack 6 from Veeco. The TiO₂ photoanodes were sensitized with colloidal QDs in CH₂Cl₂ solution for 24 hours, without any particular linker. Additionally, in-situ growth of QDs on TiO₂ mesoporous films by chemical bath deposition (CBD) was also carried out following the procedure published by Gorer and Hodes. Firstly, as the Se source, an 80mM sodium selenosulphate (Na₂SeSO₃) solution was prepared by dissolving elemental Se powder in a 200mM Na₂SO₃ solution. Secondly, 80mM CdSO₄ and 120mM trisodium salt of nitrilotriacetic acid (N(CH₂COONa)₃) were mixed in a volume ratio 1:1. Finally, both solutions were mixed in a volume ratio 1:2. The TiO₂ electrodes were placed in darkness in a glass container filled with the final solution for 12 hours deposition time. All the electrodes were coated with ZnS by twice dipping alternately into 0.1M
Zn(CH₃COO)₂ and 0.1M Na₂S solutions for 1 min/dip, rinsing with Milli-Q ultrapure water between dips.

**Solar cell configuration.** The solar cells were prepared by assembling an Cu₂S counter electrode and a QDs sensitized FTO/TiO₂ electrode using a silicone spacer (thickness 50 mm) and with a droplet (10 ml) of polysulfide electrolyte prepared following the procedure described in by Giménez et al.²: 1 M Na₂S, 1 M S, and 0.1 M NaOH solution in Milli-Q ultrapure water.

**Optical and electrical characterization:**
The absorption in Kubelka-Munk units of the different TiO₂ electrodes sensitized with QDs has been extracted from their diffuse reflectance using the relation: \( F(R) = (1-R)^2/2R \), where \( R \) is the measured diffuse reflectance. This representation allows a direct comparison of the amount of QDs adsorbed on each sample. The approximate estimation of the concentration, \( C \), of the QDs adsorbed on the TiO₂ film can be found by the following linear dependence of the Kubelka Munk function vs. \( C \): \( F(R) = \varepsilon C / S \), where \( \varepsilon \) is the extinction coefficient, provided that the scattering coefficient \( S \) remains constant for the different TiO₂ films. The ZnS coating leads to a slight increase of absorption (~10% compared to uncoated specimens). The diffuse reflectance of spectra QD sensitized TiO₂ samples were recorded by a Varian Cary 500 Scan UV_VIS-NIR spectrophotometer with an integration sphere.

Current-Potential curves were obtained using a FRA equipped PGSTAT-30 from Autolab. The cells were illuminated using a solar simulator at AM 1.5 G, where the light intensity was adjusted with an NREL-calibrated Si solar cell with a KG-5 filter to 1 sun intensity (100 mWcm⁻²).

The photophysical characterization of the samples was carried out in QD-sensitized TiO₂ films of 4 µm. When specified, the electrolyte was added on the sensitised film and measured directly. The picosecond to microsecond emission lifetime measurements were carried out with a Lifespec picosecond fluorescence lifetime spectrometer from Edinburgh Instruments. As excitation source the diode laser with 405 nominal wavelength was used. The instrument response measure at the FWHM (full width at half maximum) was below 300 picoseconds. The transient absorbance experiments were recorded by excitation of the
sensitized films at 440 nm with pulses from a nitrogen pumped dye laser PTI GL-301 (<1 ns pulse duration, 1 Hz, intensity 0.09 mJ·cm⁻²). The resulting photoinduced changes in optical density were monitored at 620 nm by employing a 150 W tungsten lamp, with 1 nm bandwidth monochromators before and after the sample, a home-built photodiode based detection system and a TDS-200 Tecktronix oscilloscope.
Figures:

**Figure S1.** Steady-state luminescence emission spectra under normal conditions for both CdSe-ZnS sensitised TiO₂ films. $\lambda_{exc} = 405$ nm.
Figure S2. Emission decays under normal conditions for both CdSe-ZnS TiO$_2$ sensitised samples. The excitation wavelength was $\lambda_{\text{ex}}$=405 nm. The decays were monitored at $\lambda_{\text{m}}$=555 nm and $\lambda_{\text{m}}$=520 nm for the s-DAD and s-CBD samples respectively. IRF is the Instrument Response Function.
REFERENCES