Electronic Supplementary Information

Solid-State CdSe Quantum Dot Sensitized Solar Cells Based on a Quaterthiophene as Hole Transporting Material

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1. Fabrication of CdSe QD-sensitized solar cells

1.1 Photoanode preparation

*TiO*₂ *films*. Fluorine-doped tin oxide substrates (FTO; Owens Corning) were cleaned several times with acetone, ethanol, and water in an ultrasound bath. A TiO₂ blocking layer was grown on the substrates by thermal annealing at 500 °C after depositing a titanium isopropoxide layer by spin coating (1000 rpm) from a 0.1 M Ti(IV) isopropoxide solution in isopropanol. This procedure was repeated twice generating a TiO₂ compact layer of less than 1 μ m (as measured by SEM). Mesoporous TiO₂ layers of about 3 μ m thickness were prepared over these substrates by spreading an aqueous slurry of Degussa P25 using the doctor blading procedure. The suspension was prepared by grinding a mixture of 1 g of TiO₂ powder, 2 mL of H₂O, 30 μ L of acetylacetone, and 30 μ L of Triton X100. The samples were subsequently sintered at 450 °C for 1 hour.

CdSe Coating. CdSe QDs were directly grown on the mesoporous TiO_2 layer by the Successive Ionic Layer Adsorption-Reaction (SILAR) method, which involves the adsorption of a Cd^{2+} precursor and subsequently an anionic Se^{2-} precursor. In our case the method was performed in air, at room temperature using aqueous solutions. The substrates were immersed in a 0.5 M Cd(CH₃COO)₂ for 2 min. Subsequently, they were transferred to a 1 M sodium acetate for 1 min and finally they were immersed in a seleno-sulphate solution (prepared as described previously¹) of pH 8 for 4 min. To complete the cycle, the substrates were immersed again in the sodium acetate solution for 1 min to remove the excess of non-adsorbed/unreacted ions. This set of steps is called a SILAR cycle. It was repeated in order to increase both the size and number of QDs. Figure S1 shows the reflectance spectra prior and after sensitization with different number of SILAR cycles.



Figure S1. UV-Vis diffuse reflectance spectra obtained for FTO/TiO_2 samples before and after CdSe coating with 15 and 20 SILAR cycles. The wavelengths corresponding to bandgap absorption at the QDs are indicated in both cases by a dotted line. BaSO₄ was used as the background.

CdSe-sensitized TiO₂ samples were also prepared by direct adsorption of presynthesized QDs. The procedure relies on the immersion of the electrode in a CdSe QD dispersion in CH₂Cl₂ as described elsewhere.² Colloidal dispersions of CdSe QDs capped with trioctylphospine (TOP) were prepared following the solvothermal route proposed by Q. Wang et al.³ Although the original synthesis leads to a toluene TOP-capped CdSe colloidal solution, the QDs can be precipitated by centrifugation in the presence of ethanol and redissolved in CH₂Cl₂. The QD coverage degree of the TiO₂ surface can be tuned by controlling the adsorption time.

The TOP-capped QD were also adsorbed on the TiO_2 surface using molecular wires: L-Cysteine (Cys) or 3-Mercaptopropionic acid (MPA). Initially the linker was adsorbed on the TiO_2 surface by immersing the FTO/TiO_2 samples during 24 h in a saturated solution of Cys in toluene or in a 1:10 (v/v) MPA solution in acetonitrile. Then, the samples were washed and immersed in toluene for 12 h in both cases to eliminate the non-adsorbed molecules from the pores. Finally, the QDs were immobilized by immersion of the TiO_2 samples in the toluene based TOP-capped CdSe colloidal solution.³ In the case of the linker-mediated adsorption, the QD coverage degree is dependent, not only on the adsorption time, but also on the linker nature.

 SiO_2 surface coating. A SiO_2 thin layer was grown on FTO/TiO_2/CdSe samples by dipping the substrates in a 0.1 M tetraethyl orthosilicate (TEOS) solution in ethanol for 1 min, followed by natural hydrolysis in air for 30 min. The samples were subsequently dried by annealing at 60 °C for 2h. According to Liu et al.⁴, this treatment allows for the passivation of QDs.

1.2 Deposition of the hole transporting material

Deposition of the hole conducting material. Prior to the deposition of the hole conducting layer, the samples were pre-immersed in an 1 mg mL⁻¹ solution of 3,3^{'''}-didodecylquaterthiophene (QT12) in toluene containing 0.2 M 4-tert-butylpyridine (4-TBP) at least for 3 hours in the dark. This treatment seeks for the adsorption of QT12 oligomers in order to increase the hydrophobicity of the pores and facilitate the subsequent permeation of a concentrated QT12 solution (20 mg ml⁻¹ in toluene), which was spin coated at 1000 rpm. In light for the aforementioned, this treatment is particularly important in the case of SILAR sensitized samples. Figure S2 shows the absorption spectrum of a QT12 thin film deposited on FTO.



Figure S2. UV-Vis diffuse absorbance spectrum obtained for a FTO/QT12 sample prepared by spin coating a 20 mg mL⁻¹ solution of QT12 in toluene at 1000 rpm.

The QD-sensitized samples with the quaterthiophene layer (FTO/TiO₂/CdSe/SiO₂/QT12) were annealed in an oven at different temperatures (60, 80, 100, 120, 140, 160, and 180 °C) for 10-20 min in air. As shown in Figure S3 the best cell performance was obtained after the treatment at 80 °C. Longer thermal treatments (up to 2 hours) at 80 °C did not reveal any additional improvement. Therefore, the solar cells were annealed at 80 °C for 10 minutes.



Fig S3. Effect of annealing the FTO/TiO₂/CdSe/SiO₂/QT12 photoanodes for 20 minutes at different temperatures. All the curves were obtained at 20 mVs⁻¹ and under illumination with simulated solar light of 100 mW cm⁻² (1 sun, AM 1.5G). The inset presents the corresponding UV-Vis diffuse reflectance spectra.

IL casting. A solution of 0.2 M bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) and 0.2 M 4-tert-butylpyridine (4-TBP) in 1-ethyl-3-methylimidazolium bis(trisfluormethylsulfonyl) imide ionic liquid (EMimTFSI) was drop casted onto the corresponding FTO/TiO/CdSe/SiO₂/QT12 samples which were subsequently stored for 24 h in the dark. Before measurements the ionic liquid was wiped off carefully using a laboratory paper, being the photo-anodes ready to be clamped with the corresponding counter-electrode.

1.3 Counter-electrode and solar cell fabrication

Counterelectrode fabrication. A thin triphenylamine (TPA) layer was spread on FTO substrates by spin coating at 1000 rpm a 20 mg mL⁻¹ solution in CH_2Cl_2 . The thin films were then electropolymerized in the solid state at 1 V (vs Ag/AgCl/ KCl sat.) in a conventional three-electrode cell containing 0.5 M LiClO₄ aqueous electrolyte. The FTO/TPA working electrodes were removed from the electrochemical cell at controlled potential (1 V) when the charge passed was 20-25 mC/cm². Removal at +1 V guarantees that the film is extensively doped as indicated by the blue coloration exhibited by the samples.

Solar cell preparation. CdSe QD-sensitized photoanodes fabricated according to the procedures described in sections 1.1 and 1.2 were clamped to freshly prepared FTO/pTPA counterelectrodes and covered with a 0.1 cm^2 mask. Illumination with simulated solar light (100 mW cm⁻²) was performed from the photoanode side.

The solar cell performance was dependent on the doping level of pTPA. As pTPA was dedoped during illumination, a significant drop in the cell efficiency was noticed, even from the first to the second I-V curve measurement (Figure S4). New and freshly prepared counterelectrodes were employed for every single solar cell measurement reported in the manuscript. It is important to mention, that the drop in the cell efficiency should be ascribed to the counterelectrode because, when it was replaced by a new one, the cell performance was recovered.

All the cells showed important dark currents at reverse bias (leakage currents). Fig. S5 shows a typical dark I-V curve. The existence of these shunt currents likely indicates that the blocking layer at the FTO conducting glass supporting the TiO_2 nanoparticles contains pinholes that allow for the direct electron transfer from the QT12 to the glass. The leakage currents are clearly non-ohmic, which is probably linked to a partial dedoping of the counterelectrode. This is an electrochemical reaction in which the current grows exponentially with the applied potential (Tafel law).

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Figure S4. Changes occurred in the output parameters of the best performing photovoltaic cell obtained in this work between the first (straight line) and the second measurement (dashed line) under solar illumination and using the same FTO/pTPA counterelectrode. The corresponding power conversion efficiencies and those parameters necessary to calculate them (i.e. the short circuit current, j_{SC} ; the open circuit voltage, V_{oc} ; and the current density and the voltage at the point of maximum power, j_m and V_m) are presented in the figure.



Figure S5. Typical I-V curve recorded in the dark for the solid-state QDSC.

2. Experimental techniques

Absorption spectra were obtained for colloidal dispersions and sensitized electrodes. UV-Vis absorption spectra were recorded with a Shimadzu UV-2401PC spectrophotometer. For the modified TiO_2 photoanodes, the diffuse reflectance spectra were measured by means of an integrating sphere using $BaSO_4$ (Wako) as background. In some experiments a Kubelka–Munk

transformation was undertaken to facilitate the analysis of the reflectance data. Emission spectra were measured by means of a FluoroMax-A spectrofluorometer equipment using an excitation wavelength of 500 nm for QT12 solutions, while for CdSe QD colloidal solution the wavelength employed was 400 nm.

The electropolymerization of TPA was conducted at room temperature by potential step chronoamperometry using an Autolab PGSTAT30 Potentiostat controlled by the software GPES v.4.9 (both from EcoChemie B. V.). An Ag/AgCl/KCl (sat.) electrode and a Pt wire were used as reference and counter electrodes, respectively. For the complete solar cell I-V curves a μ Autolab III (EcoChemie B. V.) was used to perform a linear sweep voltammetry between 0 and +1 V at 20 mV s⁻¹ in combination with a solar simulator (Sun 2000-11018 from Abet Technologies, Inc.). The illumination intensity employed was 100 mW cm⁻² (AM 1.5G).

3. Table of output parameters of the optimized solar cells

QD attachment	$j_{sc}/\mu A \text{ cm}^{-2}$	V _{oc} /V	FF (%)	η (%)
SILAR	325	0.95	0.34	0.11
DirectAds	917	0.98	0.38	0.34
MPA-mediated	493	0.99	0.43	0.21
Cyst-mediated	682	0.95	0.35	0.23

Table S1. Photovoltaic performance of QDSCs with different modes of attachement of the CdSe QDs.

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