Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Unpredicted electron injection in CdS/CdSe quantum dot sensitized ZrO_2 solar cells

Shlomit Greenwald, Sven Rühle, Menny Shalom, Shay Yahav, and Arie Zaban

Experimental Methods:

In situ deposition of CdS and CdSe QDs:

Before the growth of the CdSe QDs an intermediate layer of CdS was deposited by SILAR on the mesoporous electrodes (ZrO_2 or TiO_2) while on the flat ZrO_2 electrodes the CdS layer was deposited by CBD.

SILAR CdS-QDs deposition: Mesoporous ZrO_2 or TiO_2 electrodes were successively dipped into a 0.1M $Cd(ClO_4)_2$ aqueous solution, de-ionized H_2O, 0.1M Na_2S aqueous solution, and H_2O again, each for 1minute, which is one SILAR cycle. Four SILAR cycles were applied to the samples before they were dried in air.

CBD CdS-QDs deposition: Compact ZrO_2 electrodes were immersed in a mixture of 2.35 mL of 0.5 M $CdSO_4$, 2.65mL of 0.7M NTA (Nitrilotriacetic acid trisodium salt), 4.25ml of 0.5M Thio-Urea 0.5M, and 7.55ml of H_2O, at pH11 (adjusted with 10% NaOH solution). The solution with the electrodes was heated to 80^{o}C for 2 hours, resulting in CdS coating of the electrodes.

CBD CdSe deposition: As the Se source 1.26g of Na_2SO_3 and 0.315g Selenium powder were dissolved in 90ml de-ionized H_2O, heated and stirred at 70^{o}C over night. The solution was then cooled down and the following solutions were mixed and added to it: 1.652gr Potassium Nitrilo-triacetate (NTA) in 30ml 3-D H_2O, and 0.833gr $CdSO_4$ in 30ml 3-D H_2O. The electrodes were immersed in the solution and kept at 10^{o}C in dark for 24-30 hours before they were washed with water and dried in air.

Incident Photon to Current Conversion Efficiency (IPCE)

Incident photon to current conversion efficiency measurements (IPCE) were performed with a flat and a porous CdSe sensitized ZrO_2 electrode using CdS as an intermediate layer (same electrodes as in Fig. 1). The measurements were performed in a home-built system using monochromatic light without white bias light. For both electrodes the IPCE onset is around 670 nm (1.85 eV), which is close to the bandgap of bulk CdSe (1.73 eV). We emphasize that the CBD grown QDs have a broad size distribution such that strong quantum confinement occurs only in a fraction of the QDs. Calculating the J_{sc} from the IPCE data results in 0.5 mA/cm^2 for the flat system, which is in reasonable agreement with the data from the *I-V* measurement. For the porous system a similar value is calculated, which is significantly smaller compared to the measured J_{sc} of 1.36 mA/cm^2. We attribute this to the difference in light intensity of both measurements (low monochromatic light intensity for IPCE, 1 sun for *I-V* measurements). We conclude from the IPCE data that the lowest excited QD levels can inject electrons into the ZrO_2 conduction band.

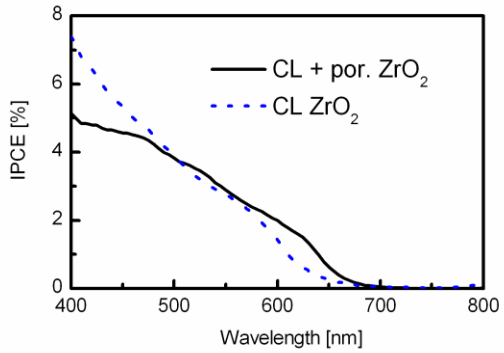

Figure S1: *The incident photon to current conversion efficiency shows an onset for the flat and porous QDSC around 670 nm, which corresponds roughly with the optical bandgap of bulk CdSe. We note that the CBD deposited CdSe QDs have a broad size distribution such that strong quantum confinement does only occur in a fraction of the QDs that are excited at shorter wavelengths*

Cyclic Voltammetry Characterization of Compact TiO_2 and ZrO_2 Layers

Cyclic voltammetry (CV) measurements are a powerful tool to investigate the quality of compact layers which are covering a FTO substrate. If the compact layer is of low quality with a large number of pinholes electrolyte can penetrate into these holes and make electrical contact with the underlying FTO substrate. If the electrolyte contains a redox couple with fast charge transfer kinetics at the interface with the FTO such as $Fe(CN)_6^{2+}$ / $Fe(CN)_6^{3+}$ a significant current density is measured. Figure S2a shows CV measurements of a compact TiO_2 and compact ZrO_2 layer deposited onto FTO compared to a bare FTO substrate. The aqueous electrolyte contained the $Fe(CN)_6^{2+}$ / $Fe(CN)_6^{3+}$ redox couple (0.001 M $K_4Fe(CN)_6$, 0.01 M $K_3Fe(CN)_6$, 0.5 M KCl, pH 10 using KOH) and the potential was measured with respect to a Pt wire that served as a pseudo reference electrode. Clear oxidation and reduction peaks are visible for the bare FTO substrate, which are fully suppressed in the presence of the compact TiO_2 or ZrO_2 layer. Such behavior is typical for high quality compact layers with a very low density of pinholes. Only the TiO_2 covered FTO substrate shows a current onset at potentials below -0.8 V, which is due to electron transfer into the electrolyte via trap states close to the CB edge or via the CB states. Figure S2b shows the same set of measurements with the polysulfide electrolyte that is typically used in QDSCs. As in the previous case we observe a strong blocking behavior of the compact layers, providing strong experimental evidence that in QDSC with a compact TiO_2 or ZrO_2 layer direct electron transport into the FTO via QDs can be excluded.

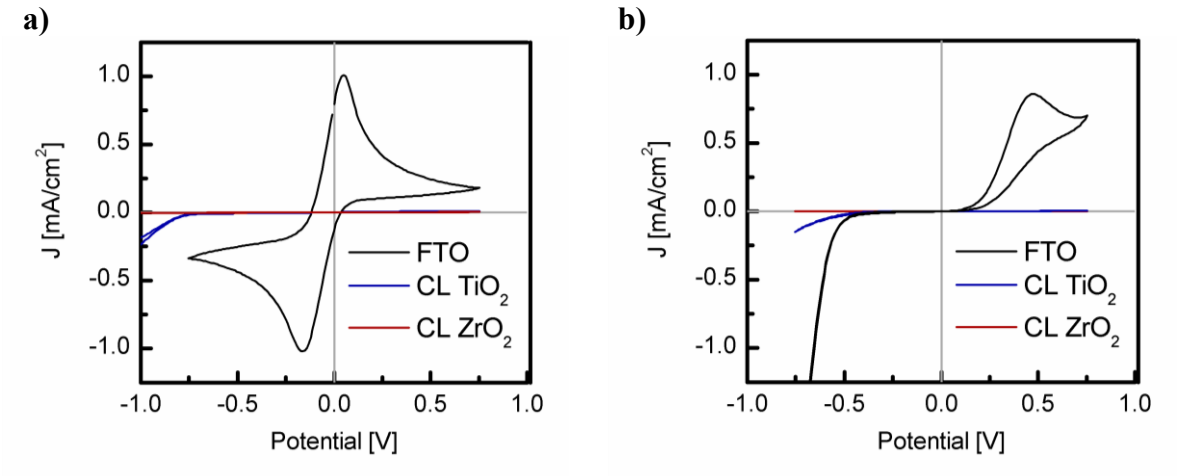

Figure S2: *Cyclic voltammetry (CV) of a FTO substrate (black), a compact TiO_2 (blue) and a compact ZrO_2 layer (red) both deposited onto a FTO substrate, a) using an aqueous electrolyte containing the $Fe(CN)_6^{2+}$ / $Fe(CN)_6^{3+}$ redox couple and b) with the polysulfide electrolyte. In both cases a Pt wire was used as a pseudo reference electrode.*

High Resolution Scanning Electron Microscopy (SEM)

The SEM image shows a cross section of a porous ZrO_2 film, deposited onto a FTO substrate which was covered with a compact ZrO_2 layer. One can see that the ZrO_2 layer thickness is very homogeneous and free of holes. Furthermore, it is clearly visible that the deposition of ZrO_2 nano-crystals onto the ZrO_2 layer (including subsequent sintering) is not damaging it (see white arrow pointing to the ZrO_2 nano-crystal that is in contact with the compact ZrO_2 layer).

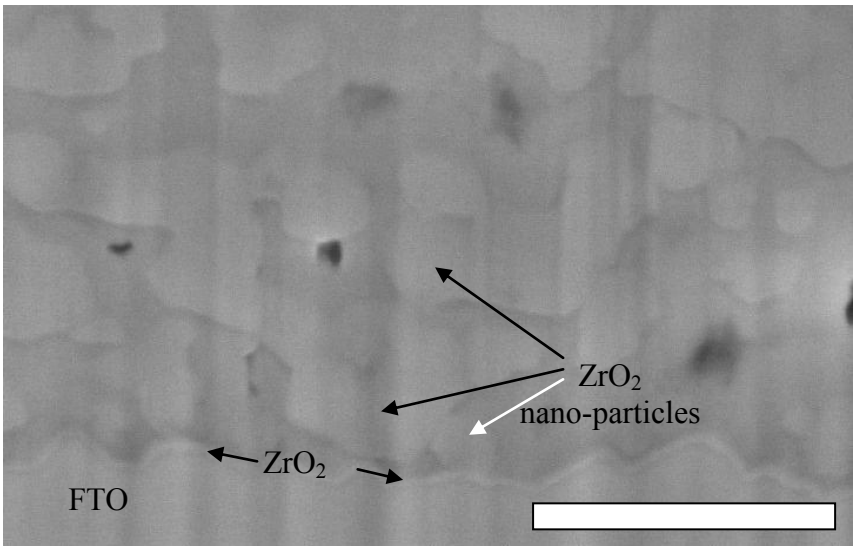

Figure S3: *SEM image of a cross section that was prepared with a focused ion beam. The FTO substrate can be seen at the bottom which is covered with a ~20 nm thin ZrO_2 layer, followed by a porous ZrO_2 film. The scale bar represents a length of 400 nm.*