Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

CdSe on a Mesoporous Transparent Conducting Oxide Scaffold as a Photocathode

Michael R. Norris and Brandi M. Cossairt*

Supplementary Information

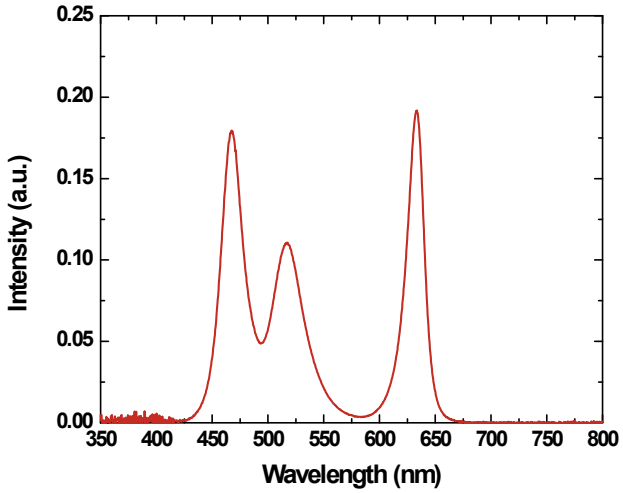

Figure S1. Spectral output of the white LED light strip used for the photochemical and photoelectrochemical experiments.

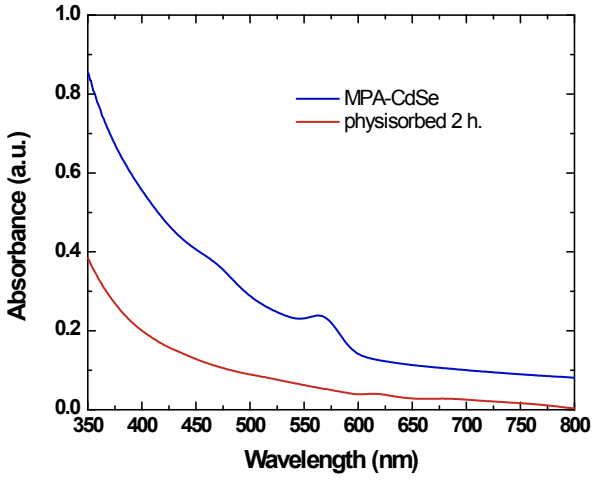

Figure S2. UV/vis comparison of CdSe QDs physisorbed to the surface of a *nano*ITO electrode by immersing the slide in the same CdSe QD solution for 2 h. without having first been dipped in ligand solution. The MPA-CdSe was dipped alternatively in MPA solution followed by the CdSe QD solution.

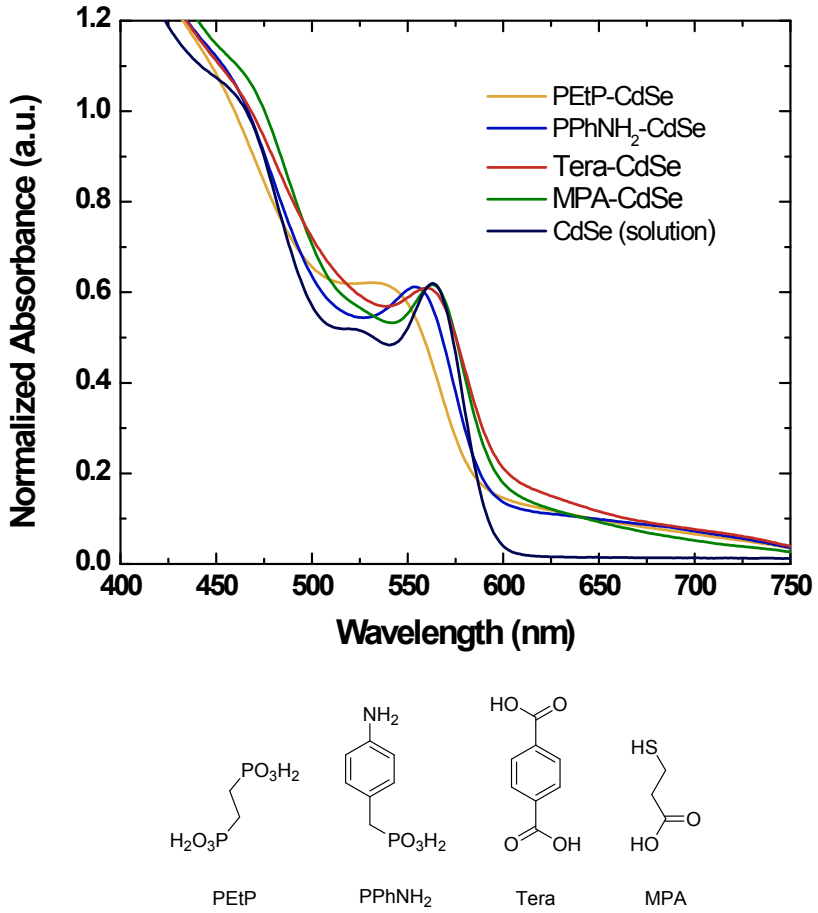

Figure S3. UV/vis comparison (top) of CdSe QDs attached to *nano*ITO via four different bi-functional organic linkers (bottom). The *nano*ITO slides were first dipped in 0.1 M (or saturated) methanolic solutions of the ligand for 10 minutes, followed by a dip in CdSe QD solution in pentane for 10 min. Cycles were repeated 3 times and the resulting UV/vis spectra were normalized to compare LEET broading and shift.

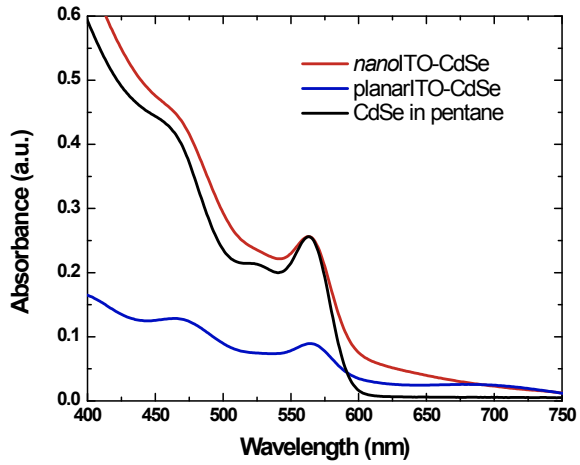

Figure S4. UV/vis comparison of CdSe loaded onto planar FTO slides (blue) to CdSe loaded onto *nano*ITO slides (red). Both slides had a 10 mm x 10 mm active area and were dipped 3 times in MPA and CdSe QDs.

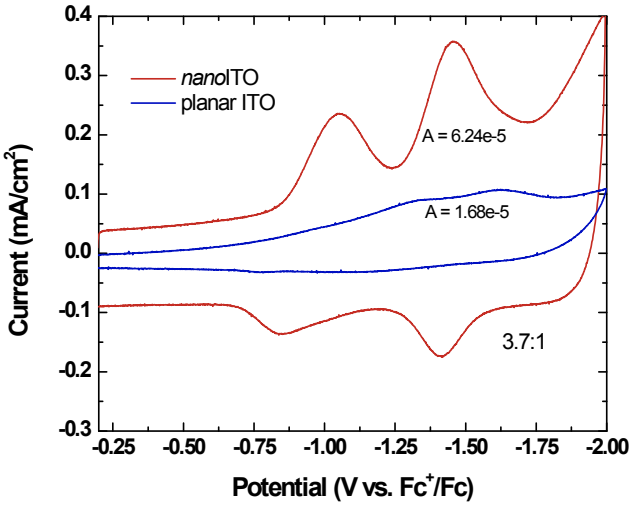

Figure S5. CVs using either the FTO (blue) or *nano*ITO (red) as the working electrode with a Pt counter electrode and $Ag/AgNO_3$ reference electrode in a 0.1 M TBAH solution of CH_3CN. Each slide had a 10 mm x 10 mm geometric surface area and was loaded with propionic acid-derivatized viologen and the charge passed in each case was compared to obtain the surface area ration.

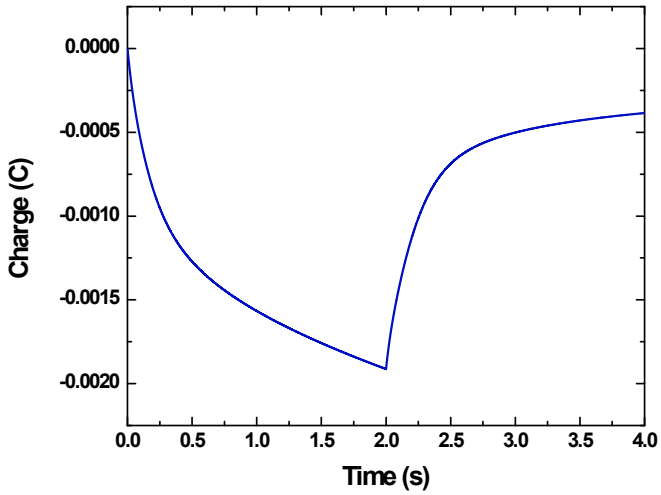

Figure S6. Cottrell Plot taken from the current response vs. time in a chronoamperometry experiment. A *nano*ITO slide was used as the working electrode with a Pt auxiliary and pseudo Ag reference with 10 mM Fc in 0.1 M CH_3CN. A potential 200 mV below the oxidation of $Fc^{+/0}$ was held for 2 s, then instantaneously stepped to a point 200 mV beyond the $Fc^{+/0}$ couple with data recorded every 1 ms.

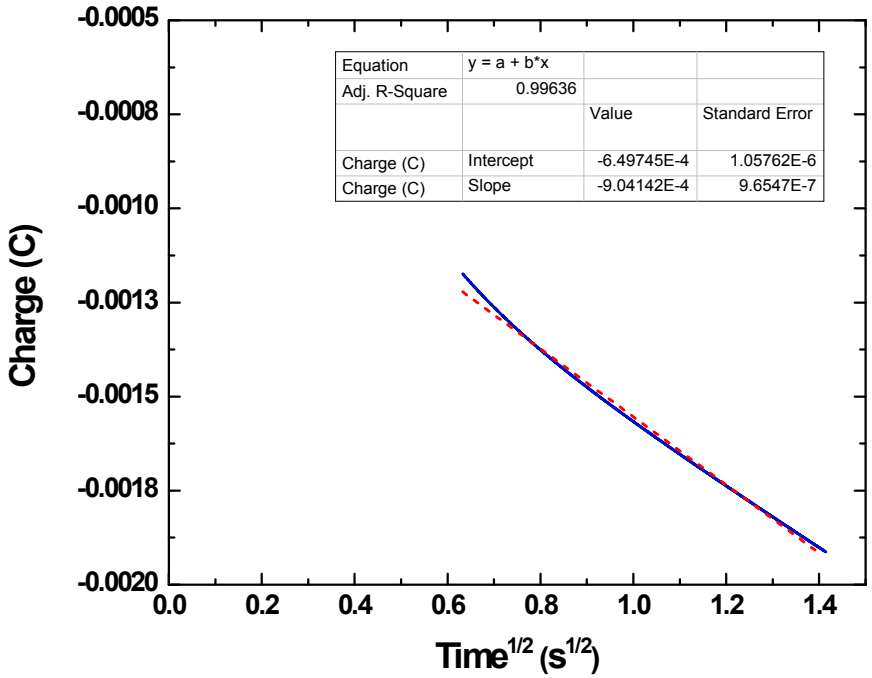

Figure S7. Linear portion of the derivative of the Cottrell Plot from Figure S3 which gave a slope for the Anson equation used to calculate the electro-active surface area of the *nano*ITO electrode.

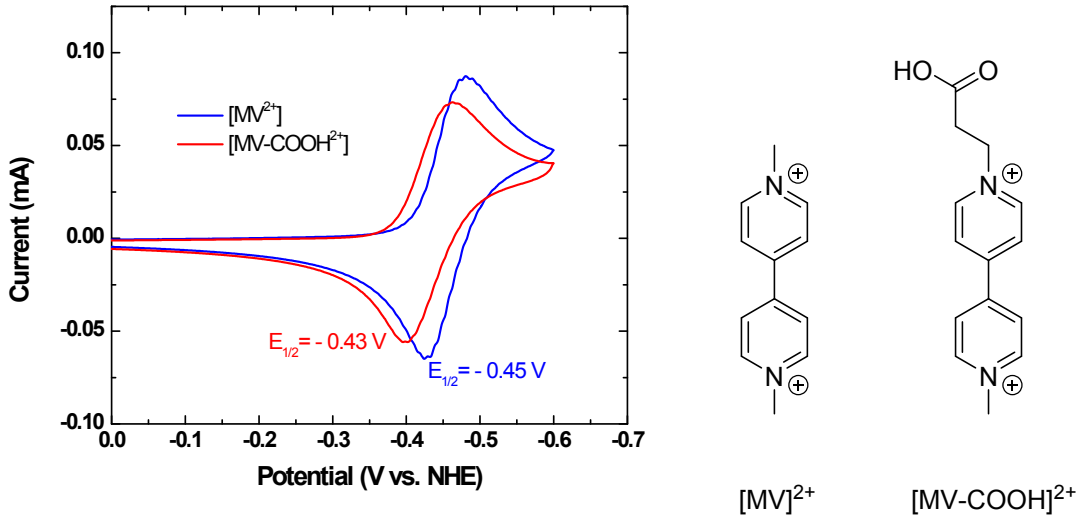

Figure S8. CVs of $[MV]^{2+}$ (blue) and $[MV\text{-}COOH]^{2+}$ (red) in PBS pH = 7.4 buffer showing the first reduction to the radical cation using a GC working electrode, Pt auxiliary electrode, and Ag/AgCl reference electrode (*left*). ChemDraw images of methyl viologen and derivatized viologen (*right*).

Figure S9. Photograph of the experimental set-up used to measure the generation of $MV^{+\bullet}$ over time with LED illumination. The reaction vessel fitted with a septum cap was de-aerated with N_2 and placed in a water bath surrounded by white LED lights to help dissipate heat and act as a UV filter.

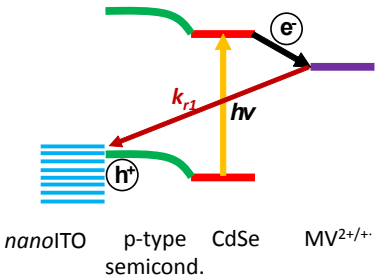

Figure S10. Cartoon of the relative energy levels of CdSe conduction and valance bands with the $MV^{2+/+\bullet}$ couple with a thin layer of a p-type semiconductor added to the *nano*ITO slide.

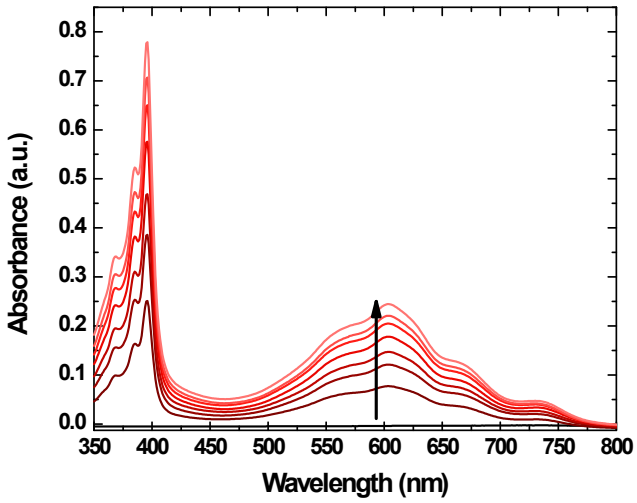

Figure S11. UV/vis spectra of the appearance of $MV^{+\bullet}$ over time in one of the quenching experiments with MPA. The underlying CdSe spectrum was subtracted for clarity.

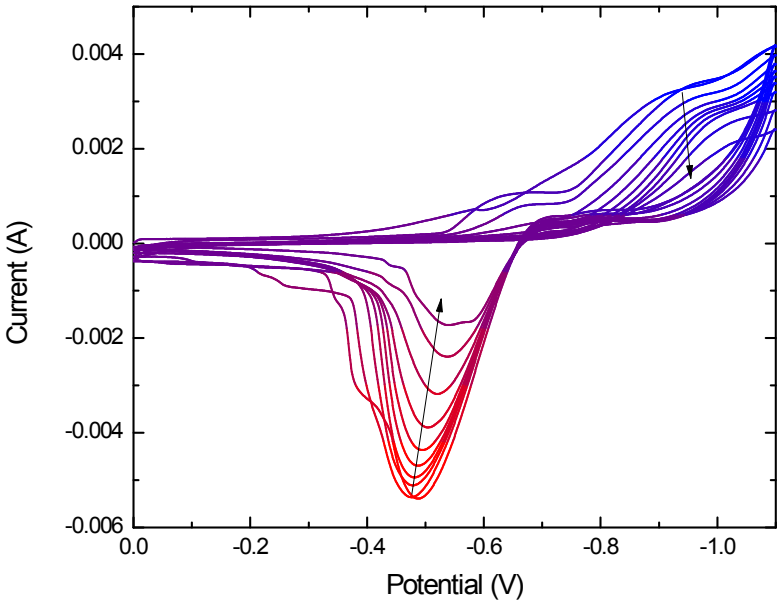

Figure S12. Electrodeposition of ZrO_2 onto exposed (electroactive) *nano*ITO. Conditions: nanoITO-CdSe slide was used as the working electrode with a Pt wire counter electrode and Ag/AgCl reference. Cyclic voltammetry was performed at 20 mV/s for 10 cycles from -1.1 V to 0 V in aqueous solution containing 5.0 mM $ZrOCl_2$ x $8H_2O$ and 0.1 M KCl. Potentials reported vs. Ag/AgCl.

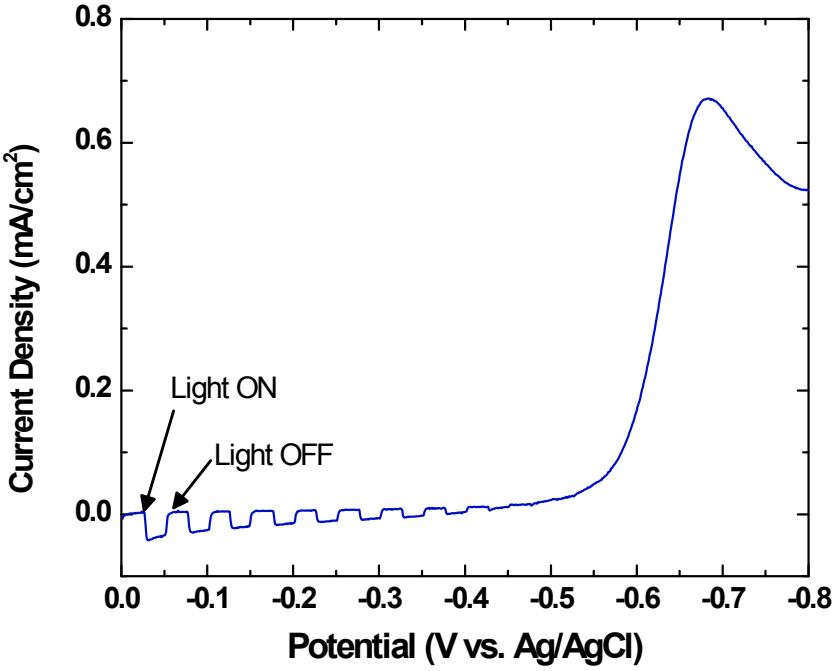

Figure S13. Linear sweep voltammagram of 5 mM MV^{2+} in pH = 7 phosphate buffer with a *nano*ITO-MPA-CdSe slide as a working electrode with the electrodeposited ZrO_2, Pt wire counter electrode, and Ag/AgCl reference. Scan rate 5 mV/s with a chopped white light cycled on and off every 5 seconds.

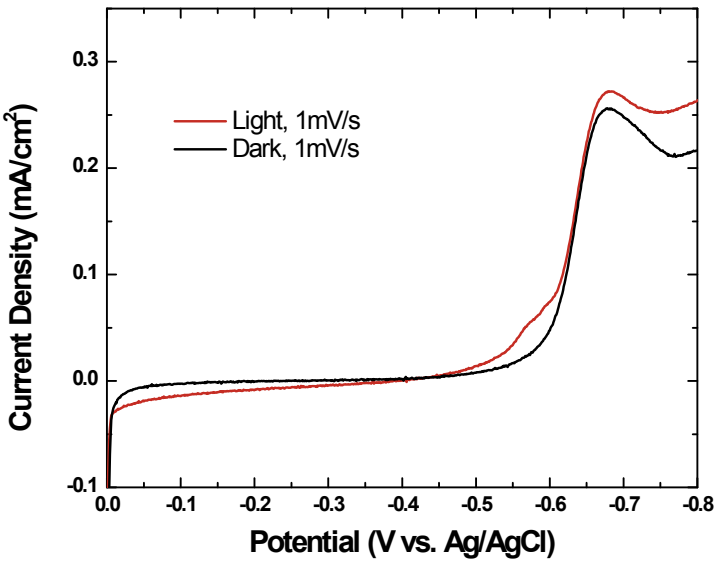

Figure S14. Linear sweep voltammagram of 5 mM MV^{2+} in pH = 7 phosphate buffer with a *nano*ITO-Tera-CdSe slide as a working electrode, Pt wire counter electrode, and Ag/AgCl reference. Scan rate 1 mV/s with either white light illumination (red) or in the dark (black).

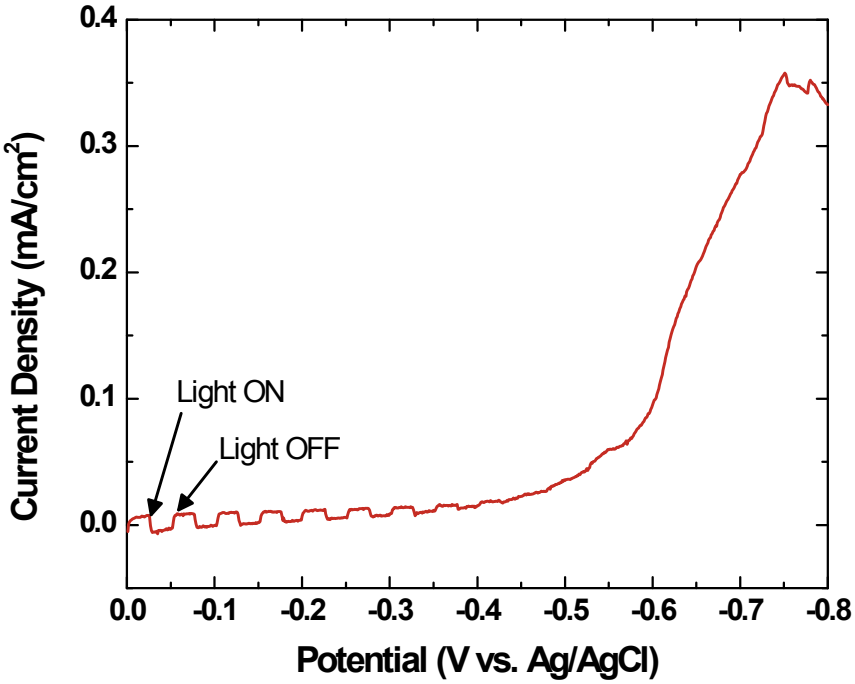

Figure S15. Linear sweep voltammagram of 5 mM MV^{2+} in pH = 7 phosphate buffer with a *nano*ITO-Tera-CdSe slide as a working electrode, Pt wire counter electrode, and Ag/AgCl reference. Scan rate 5 mV/s with a chopped white light cycled on and off every 5 seconds.