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Electronic Supplementary Information

$CuInS_2$ Quantum Dots Coated with CdS as High-Performance Sensitizers for TiO_2 Electrodes in Photoelectrochemical Cells

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Determination of the electron transfer rate constant, k_{et}

We estimate the rate constant of electron injection from $CuInS_2$ quantum dots (QDs) into TiO_2 based on an empirical equation derived from estimation of the driving force-dependent rate constant in the CdSe–TiO_2 system reported by Kamat et al.[1] In the determination of the rate constants they first measured the time-resolved recovery of absorption bleaching recorded at the bleaching maximum following 387 nm laser pulse excitation of different size CdSe QDs with and without linking to TiO_2 particles via mercaptopropionic acid bifunctional molecule. The multiexponential of recovery was analyzed using a universal stretch exponential kinetic expression:

$$\Delta A(t) = \Delta A(0) \times \exp[-(t/\tau)^{\beta}]$$

where τ is the characteristic lifetime, β value fitted is in the 0.4–0.5 range, and A is the bleaching of absorption. An enhanced recovery was observed with decreasing QD size. Assuming that photoexcited electron in CdSe transferred to the conduction band of TiO_2 is the only additional deactivation pathway, the rate constant can be estimated by comparing the recovery lifetimes and given by the following equation:

$$k_{et} = 1/\tau_{(CdSe+TiO_2)} - 1/\tau_{(CdSe)}$$

where $\tau_{(CdSe+TiO_2)}$ and $\tau_{(CdSe)}$ represent the recovery lifetimes of QDs with and without linking to the TiO_2 particles, respectively. Based on this estimation principle, Figure S1 shows the driving force-dependent rate constant as a function of the conduction band energy difference between the sensitizer and TiO_2.[1] We use the correlation shown in Figure S1 to estimate the k_{et} values of electron injection from $CuInS_2$ QDs to TiO_2.

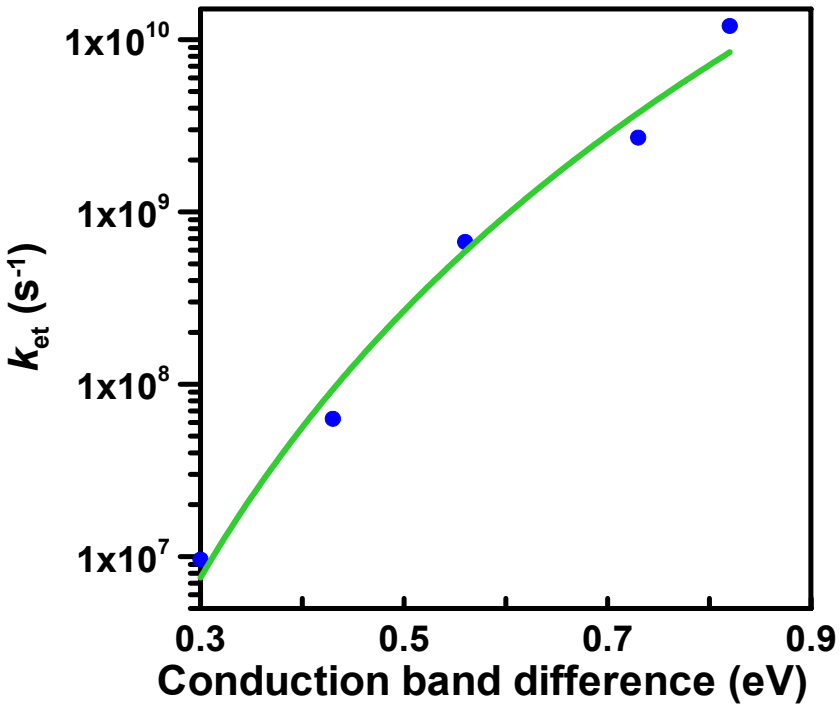

Fig. S1 Plot of electron transfer rate constant vs. conduction band energy difference between QD sensitizer and TiO_2. This correlation is determined based on CdSe–TiO_2 system.

Effect of coating ZnS on $CuInS_2$ QDs

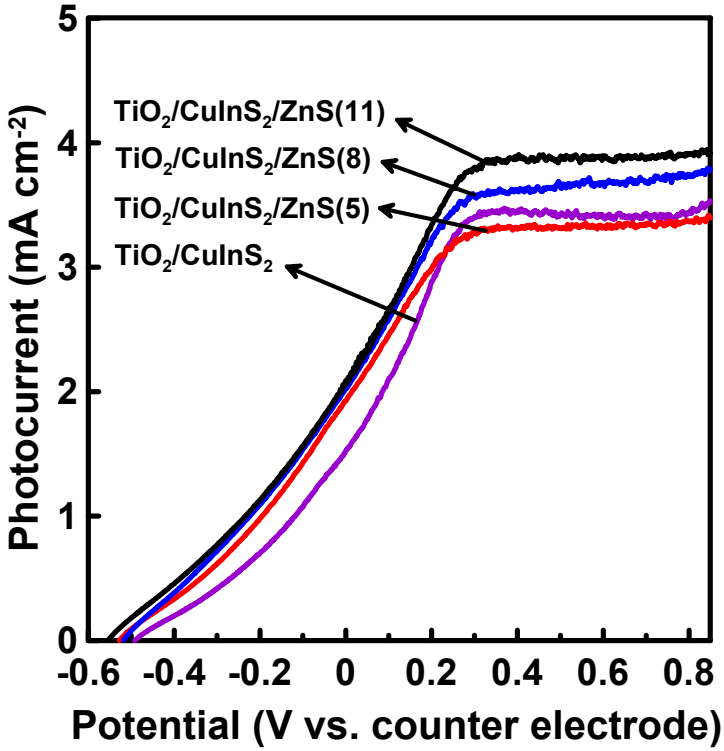

Fig. S2 Photocurrent density versus bias potential (*I–V* characteristics) of the TiO_2 nanocrystalline films with varying sensitization levels of ZnS under 100 mW cm^{-2} AM 1.5G illumination. The size of $CuInS_2$ QDs is 3.5 nm. The concentration of $Zn(NO_3)_2$ and Na_2S in the SILAR deposition of ZnS is 0.05 M, the solvent used is ethanol and methanol, respectively.

References

1. I. Robel, M. Kuno and P. V. Kamat, *J. Am. Chem. Soc.*, 2007, **129**, 4136.