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Supporting Information for

Breaking the Short-Range Proximity Requirement in Quantum Dot/Molecular Catalyst Hybrids for CO_2 Reduction via Long-Range Hot Electron Sensitization

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1. Experimental Details

Structural and optical characterization

Transmission electron microscopy (TEM) images of the QDs dispersed on a TEM grid were obtained on a FEI-Tecnai G2 F20 ST FE-TEM electron microscope. The absorption spectra of the quantum dots were obtained using a CCD absorption spectrometer (Ocean Optics). The photoluminescence spectra were collected using a fiber-coupled CCD fluorescence spectrometer (QE65pro, Ocean Optics). The time-dependent Mn luminescence intensity was measured using a pulsed nitrogen laser (NL100 SRS, 337 nm, 3.5 ns pulse width) as the excitation source and a PMT (R928, Hamamatsu) as the detector.

Quantum efficiency (QE) calculation for CO generation.

The quantum efficiency of the CO generation (QE) was calculated from the ratio of the number of CO molecules produced (n_{CO}) and the number of photons absorbed by the quantum dots (n_{ph}). The factor of 2 comes from the number of electrons needed to produce one CO molecule via reduction.

$$QE = 2\frac{n_{CO}}{n_{ph}}$$

n_{ph} for a given illumination time (t) was calculated from the average fraction of photons absorbed by the QDs across the reactor (f = 0.20), the area of illumination (A=15 cm^2) for a given excitation intensity (I =0.1W/cm^2) and photon energy (E_{ph} = 4.41· 10^{-19} J).

$$n_{ph} = (I \times f \times A \times t)/E_{ph}$$

For t =8 hrs (28800 s) and n_{CO}= 6.5μM × 6.02·10^{23}, we get QE of 0.04 %

Calculation of extinction coefficient and QD concentration

The extinction coefficient of the QDs and concentration of QDs in the solution were obtained in the following ways from the size of the QDs estimated from the TEM images and total metal ion concentration of the QDs solution sample determined from the elemental analysis. The total concentration of metal ions (Cd^{2+} and Zn^{2+}) in the acid-digested QD samples were determined from employing inductively coupled plasma mass spectrometry (NexIon 300D). The sample for the elemental analysis was prepared by first drying 1 mL of QD solution with absorbance of 0.1 at

460 nm and then digesting the dried QD sample in concentrated nitric acid. The calibration curve for the elemental analysis was built by measuring the various diluted element standard ICP solutions (Aldrich). The concentration of Cd^{2+} and Mn^{2+} ($[Cd^{2+}]$ and $[Mn^{2+}]$) of each sample could be calculated to determine the absorption coefficient. The molar extinction coefficient (ε) was calculated using Beer's law:

$$\varepsilon = \frac{A}{(b * [QD])}$$

Where A is the absorbance of the sample, b is 1 cm, and [QD] is the molar concentration of the QDs. [QD] is calculated from $[Cd^{2+}]/\langle n_{Cd} \rangle$, where $\langle n_{Cd} \rangle$ is the average number of cadmium ions per QD. The number of Cd^{2+} ions was calculated from the radius of the CdSSe core in the TEM images then used to determine the number of Cd^{2+} ions per QD (~420). [QD] is then calculated by:

$$[QD] = \frac{[Cd^{2+}]}{420}$$

Resulting in $\varepsilon = 1.93 \times 10^5\ M^{-1}\ cm^{-1}$ at 460 nm.

2. Additional Figures

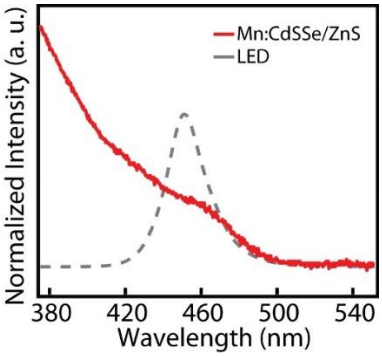

Figure S1. Overlap of excitation light source (450 nm LED) and QD absorption.

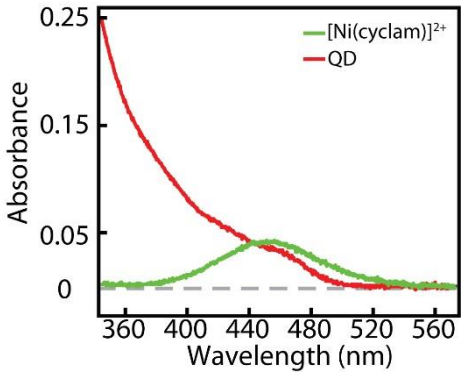

Figure S2. Absorption of QD and $[Ni(cyclam)]^{2+}$.

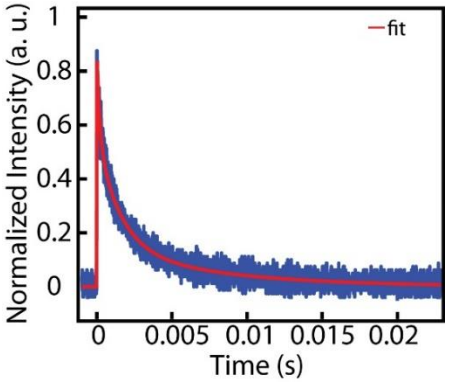

Figure S3. Time dependent luminescence lifetime of Mn-doped CdSSe/ZnS QD

3. Tables

Table S1. CO and H_2 production by four different catalyst combinations under Ar atmosphere.

Catalyst	CO (μmol @ 8hrs)	H_2 (μmol @ 8hrs)
Undoped QD	below detection limit	7.6
Undoped QD/$[Ni(cyclam)]^{2+}$	below detection limit	123
Mn-doped QD	below detection limit	75
Mn-doped QD/$[Ni(cyclam)]^{2+}$	below detection limit	368