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Supporting information for

Heavy Metal-free $CuInS_2$ Quantum Dot Sensitized NiO Photocathode with a Re molecular catalyst for Photoelectrochemical CO_2 Reduction

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Experimental Section

Chemicals

Copper chloride ($CuCl_2 \cdot 2H_2O$), indium chloride ($InCl_3$), were purchased from Merk. Tri-sodium citrate dihydrate ($C_6H_3Na_3O_7 \cdot 2H_2O$, ≥99.0%), L-cysteine (97%), sodium sulfide (Na_2S), tetrabutylammonium iodide (TBAI), tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 98%), *N,N*-dimethylformamide (DMF, 99.8%) were obtained from Sigma-Aldrich. All solvent was used as received.

Synthesis of CIS QDs

Preparation of Stock Solution

Cu stock solution was prepared by dissolving 3.4 mg of copper chloride in 20 ml of deionized water, and in stock solution was obtained by dissolving 221 mg of indium chloride in 1 ml of ethanol. Citrate stock solution was produced by dissolving 294 mg of sodium citrate in 2.5 ml of deionized water, and S stock solution was obtained by dissolving 78 mg of sodium sulfide in 1 ml of deionized water. At last, TBAI passivation stock solution was prepared by dissolving 20 mg of tetrabutylammonium iodide in 5 ml of deionized water.

Synthesis of water-soluble $CuInS_2$ QDs

The $CuInS_2$ QDs were synthesized by following a literature method with moderate modifications.[1] Briefly, 6 ml of Cu stock solution (0.006 mmol), 0.04 ml of In stock solution (0.04 mmol), 0.4 ml of citrate stock solution (0.16 mmol), 2.4 mg of L-cysteine (0.02 mmol) and 17 ml of deionized water were put in a 50-ml flask, followed by injection of 0.062 ml of S stock solution (0.062 mmol) into the flask under stirring at room temperature. Then the reaction system was heated to 95 ^{o}C and kept at this temperate for 40 min. After that, the reaction was stopped by cooling the flask in cold water bath. At last, 1 ml of TBAI solution was injected into the QDs solution at room temperature and stirred for 30 min. The obtained $CuInS_2$ QDs were purified by adding ethanol to the reaction solution and centrifuged at 9600 rpm for 15 min. Finally, the as-synthesized QDs were dispersed in 1.5 ml of deionized water as QDs stock solution (0.027 M).

Re-catalyst was synthesized by following a literature method.[2, 3]

Fabrication of QD-sensitized NiO photocathode

NiO mesoporous electrodes were prepared by screen printing method on Fluorine-doped tin oxide (FTO) glass with homemade NiO paste, followed by annealing at 450 ^{o}C for 30 min. The thickness of the NiO mesoporous layer was around 1 μm, estimated from SEM image (Figure S3). And then the NiO electrodes were cut into small pieces of 1×1 cm^2 for sensitization. QD-sensitized NiO photocathodes were obtained by directly immersing NiO electrodes in $CuInS_2$ QDs stock solution for 24h under ambient environment, and rinsed with water to remove unattached QDs on the sensitized electrodes.

Co-grafting Re-catalyst on QDs sensitized NiO photocathode

The $CuInS_2$ QD-sensitized NiO photocathodes were immersed in Re-catalyst ethanol solution (1.0 mM) for 12 h at room temperature, and then washed with ethanol and water. After that, the photocathodes decorated with QDs and catalyst were stored at ambient environment for further photoelectrochemical measurement.

Photoelectrochemical measurement

All photoelectrochemical measurements were performed with an Autolab PGSTAT302 potentiostat. Linear sweep voltammogram (LSV) measurements of the as-prepared photocathodes was carried out in DMF solution which containing tetrabutylammonium hexafluorophosphate (0.1 M) as electrolyte, in a standard three-electrode cell. A Pt wire was employed as counter electrode and an Ag/$AgNO_3$ (0.1 M $AgNO_3$ in acetonitrile) electrode as reference electrode. Before measurements, the DMF solution was bubbled with Ar and CO_2 for 20 min, respectively. A LED PAR38 module (17 W, Zenaro Lighting GmbH, 420-750 nm) was used as the light source, and the light intensity was comparable to standard 1 sun. The scan rate for LSV measurement was 5 mVs^{-1}, and the chronoamperometry measurement was performed under a bias of -0.87 V Vs NHE.

Determination of Faradic efficiency

The experiments were performed in the same three-electrode system as in the LSV measurements, with NiO/QDs/Re as photocathode. Similarly, the electrolyte-DMF solution was bubbled with Ar and CO_2 for 20 min before the measurement, respectively. Then the resulted current of the system was measurement at an applied bias of −0.87 V vs. NHE and under illumination. After 100 minutes, the gas in the headspace of the cell was analyzed by Agilent Technologies 490 Micro gas chromatographic (GC) instrument with COX columns and Ar carrier gas. The amount of produced CO was determined from a CO calibration curve, which is established by injecting a known amount of CO in the GC measurement. A Faradaic efficiency of about 32% was obtained by calculating ratio of the amount of produced CO with that of the consumed charge.

Measurement

Powder X-ray diffraction (XRD) pattern was collected from a X'Pert PANalytical PRO MRD using CuKα1 radiation ($\lambda = 1.54056$ Å), and transmission electron microscopy (TEM) images were obtained from a JEM-2100F (JEOL) microscope. A Leo 1550 and 1530 FEG microscope (Zeiss, Oberjochen, Germany) was used to take scanning electron microscopy (SEM) images, and energy dispersive X-ray (EDX) signal was collected from an 80 mm^2 Silicon Drift EDX detector. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a Varian Cary 5000, and fluorescence spectra were obtained on a Horiba Jobin Yvon Fluorolog with an excitation wavelength of 500 nm. Fourier-transform infrared (FTIR) spectra were collected from solid pellets, prepared by mixing the sample powder with KBr, and recorded from a Bruker IFS 66v/S FTIR spectrophotometer.

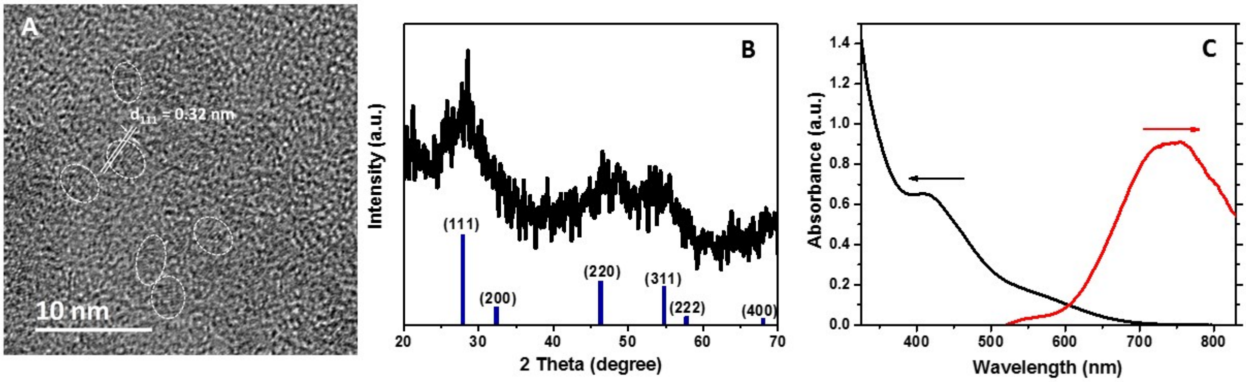

Figure S1. HRTEM image (A) and XRD spectrum (B) of the as-synthesized $CuInS_2$ QDs. Reference of zinc blend phase $CuInS_2$ is also shown (B). UV-Vis absorption spectrum (black curve) and fluorescence spectrum (red curve) of the $CuInS_2$ aqueous solution is also displayed (C).

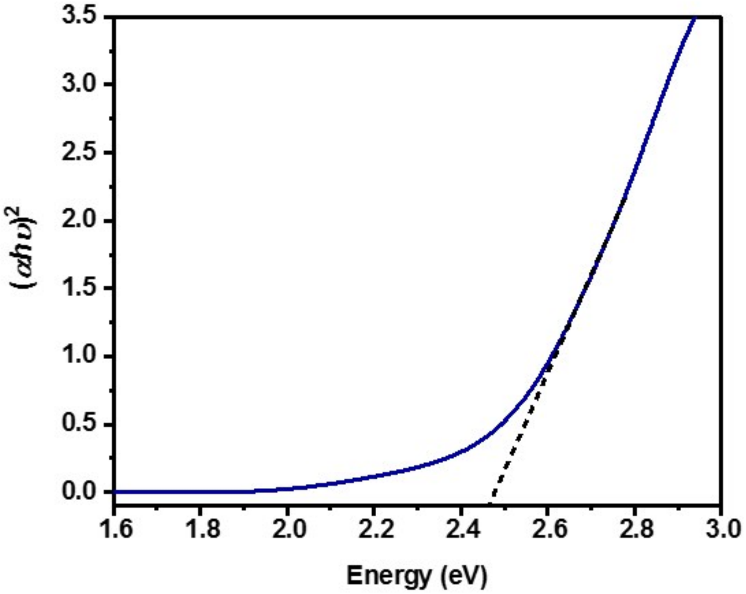

Figure S2. Plots of $(\alpha h\nu)^2$ against photon energy(hν) for as-synthesized $CuInS_2$ QDs.

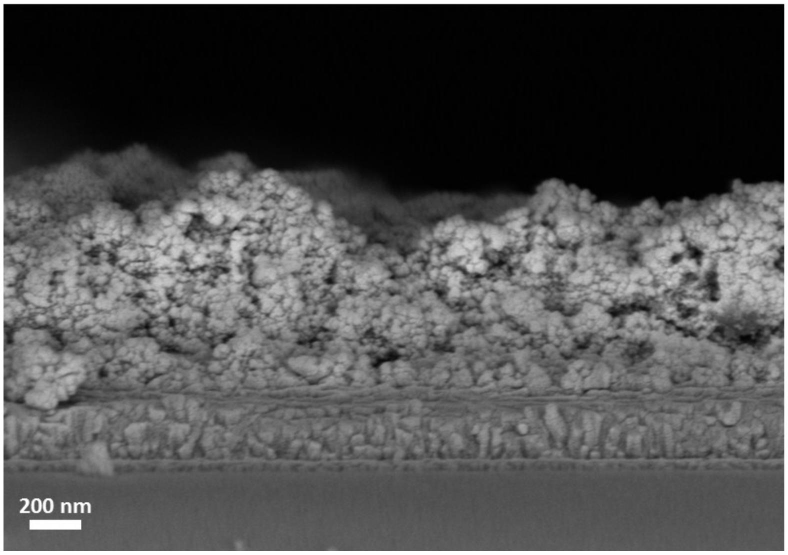

Figure S3. SEM image of the blank NiO electrode. Thickness of the blank NiO substrate was around 1μm, which is much thinner than other reported works[4, 5]

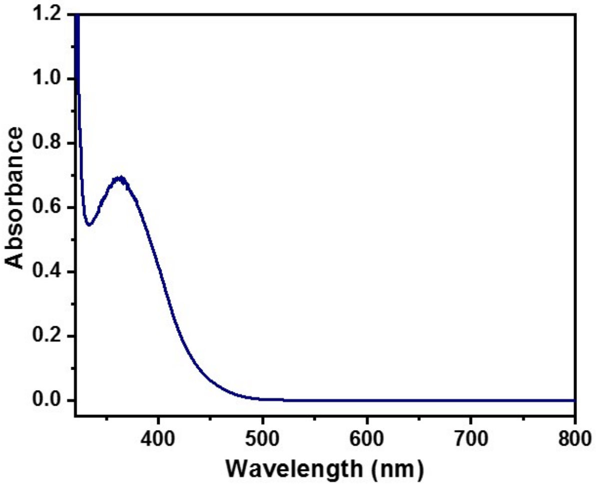

Figure S4. UV-Vis absorption spectrum of the Re catalyst in ethanol.

Table S1. Comparation of QDs concentration on NiO photocathode between this work with colloidal $CuInS_2$ QDs and a reported work with CdSe QDs prepared from OPAR method.[4, 6]

Electrode	Absorbance	Absorption coefficient ($M^{-1}cm^{-1}$)	Thickness of NiO layer (μm)	Concentration of QDs (mM)
NiO/CdSe QDs	0.415 (525 nm)	2×10^5	5.6	3.67
NiO/$CuInS_2$ QDs	0.404 (400 nm)	6×10^5	1	6.73

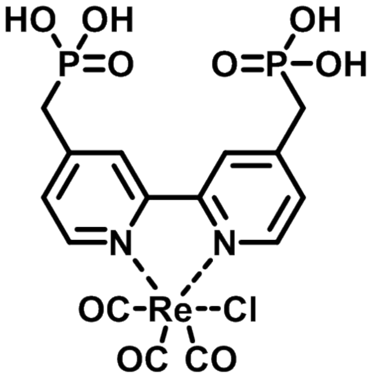

Figure S5. Molecular structure of the Re catalyst.

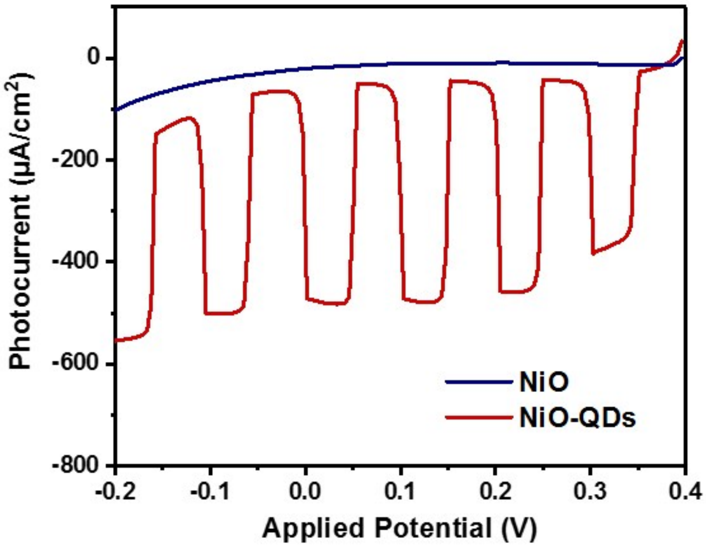

Figure S6. LSV plots of blank NiO photocathode and NiO photocathode sensitized by $CuInS_2$ QDs in the presence of pentaamminechlorocobalt(III) chloride in electrolyte solution, under chopped light irradiation.

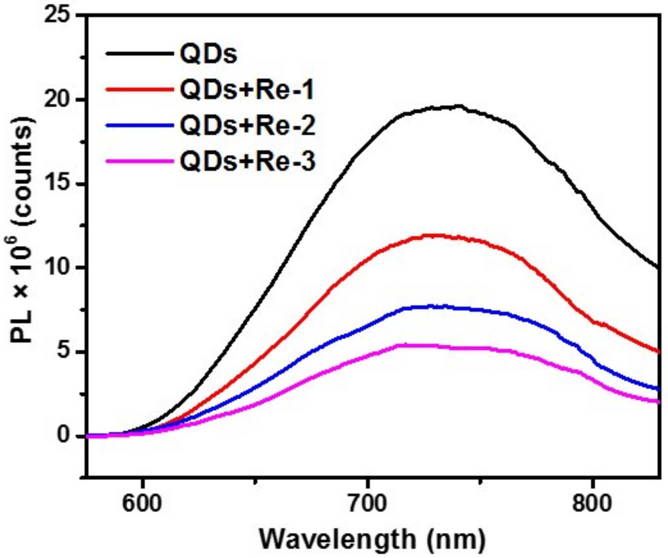

Figure S7. Fluorescence spectra of $CuInS_2$ QDs upon addition of Re catalyst upon excitation at 500 nm. The concentration of $CuInS_2$ QDs in each sample was 0.05 mM, and the concentration of Re catalyst was 0.01 mM, 0.02 mM, 0.03 mM for the samples of QDs+Re-1, QDs+Re-2, QDs+Re-3 respectively.

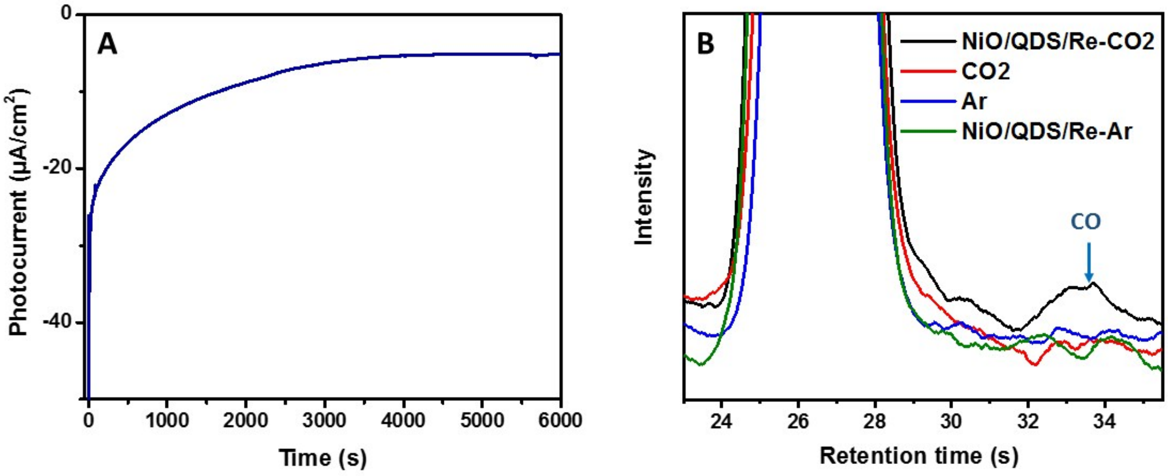

Figure S8. (A)Long-term photoelectrocatalytic performance of NiO/QDs/Re photocathode for CO_2 reduction at the external bias of -0.87 V vs NHE. (B) GC spectra of gas sample from CO_2 gas cylinder, Ar cylinder, head space of PEC cell based on NiO/QDs/Re photocathode in CO_2 atmosphere and head space of PEC cell based on NiO/QDs/Re photocathode in Ar atmosphere.

Table S2. QD/Dye and molecular catalysts immobilized NiO photocathodes for CO_2 reduction

Photosensitizer	Catalyst	Applied Potential	Light source/intensity	Solvent	Photocurrent $(\mu A\cdot cm^{-2})$	Faradaic efficiency	Ref
Porphyrin	Re catalyst	-	430 nm, 6 mW	0.1 M TBAPF6 in DMF	20	6.2% (CO)	J. Cata., 2014, 310, 57-66
P1 dye	Enzyme	-0.27 vs. SHE	White light , 50 $mW\cdot cm^{-2}$	0.2 M MES buffer	30	-	J. Am. Chem. Soc. 2014, 136, 13518−13521
Ru dye	Re catalyst	−1.2 V *vs.*Ag/$AgNO_3$	>460 nm, 300 W Xe lamp	0.1 M Et4NBF4 acetonitrile	8	98%	*Chem. Commun.***,** 2015, 51, 10722-10725
Ru dye	Re catalyst	-0.54 V vs. NHE	Solar simulator, 100 $mW\cdot cm^{-2}$	0.1 M LiClO4 in acetonitrile	65	85% (CO)	Chem. Sci., 2019, 10, 4436–4444
Ru dye	Re catalyst	-0.7 V vs. Ag/AgCl	Solar simulator, 100 $mW\cdot cm^{-2}$	50 mM NaHCO3 buffe	15	65% (CO)	ACS Energy Lett. 2019, 4, 629−636
Ru dye	Re catalyst	−0.7 V vs Ag/AgCl	>460 nm, 300 W Xe lamp	CO2 purged 50 mM NaHCO3 (aq) (pH 6.6)	20	85%	ACS Appl. Mater. Interfaces 2019, 11, 5632−5641
CuInSe2 QD	Re catalyst	-0.87 V vs NHE	White LED 420-750 nm (50 $mW\cdot cm^{-2}$)	0.1 M TBAPF6 in DMF	25	32% (CO)	This work

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