Supporting Information

Probe Binding Mode and Structure of Photocatalytic Center: Hydrogen Generation by Quantum Dots and Nickel Ions

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1. Chemicals

S powder (Alfa, 99%), CdO (99%), oleic acid (90%), octadecene (ODE, 95%) Na_2S (99.5%), toluene (99.5%) formamide (FA, 99.5%) and isopropanol (99.5%) were purchased from Sigma-Aldrich. Other chemicals are of analytical grade and used without further purification unless otherwise noted. Ultrapure water with 18.2 MΩ cm (Mettler Toledo, FE20, China) was used thorough.

2. Experiments

The synthesis of oleic acid stabilized CdS (CdS-OA) QDs. The synthesis method of CdS-OA QDs was slightly modified based on the literature.[1] A mixture of CdO (1 mmol, 128 mg) and oleic acid (6 mL) in octadecene (ODE, 18 mL) was heated under an Ar atmosphere to 250 °C. Sulfur (16 mg) in ODE (5 mL) was added rapidly and the solution allowed cooling to 240 °C. This temperature was maintained for 3 min before quenching by rapid cooling. The particles were precipitated from toluene using excess acetone, centrifuged at 8000 rpm for 5 min, and re-dispersed in toluene.

The synthesis of S^{2-} stabilized CdS (CdS-S^{2-}) QDs. The ligand exchange steps were referenced to literature.[2] Firstly, $Na_2S \cdot 9H_2O$ was added to the formamide solution (0.05 M). 2 mL CdS-OA toluene solution was added to the formamide solution (2 mL) under vigorous stirring conditions. After adding excess acetone, the precipitate was washed with formamide/acetone (1:1) and re-dispersed into water for further photocatalytic H_2 evolution.

Determine the diameter of CdS QDs. According to Peng's method,[3] diameter (D) of the CdS

QDs can be determined according to following equations (1),

$$D = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + 13.29 \tag{1}$$

where, D (nm) is the diameter of CdS QDs; λ is the wavelength of the first absorption peak (from low energy) of CdS QDs.

Photocatalytic H$_2$ evolution (standard system). Typically, the above prepared CdS-S^{2-} QDs (6.67×10^{-7} M) aqueous solution 3 mL and 1.3 μmol NiCl$_2 \cdot$6H$_2$O were added into 3 mL isopropanol. The system was adjusted to 6.0 by HCl or NaOH before the photocatalytic experiment. The reaction mixture was degassed through bubbling argon gas for 30 min to remove the residual oxygen gas, and then irradiated 2 W 440 nm LED lamps at room temperature. The molecular H$_2$ evolved was determined by Gas chromatography (GC) taking CH$_4$ as internal standard.

Determine TON and TOF. Turnover number (TON) is usually defined by the number of reacted molecules to the number of photosensitizers or catalysts. We determined the TON in this system by using the following equation (2):

$$TON = \frac{n(H_2)}{n(QDs)} \tag{2}$$

The number of evolved H$_2$ is determined by the gas collected in a certain time and the number of the photocatalyst is regarded as equal to the number of CdS QDs. The hydrogen generation amounts were 2.76 mmol/6 h, so we calculated the TON values as 1.38×10^6/per QD in 6 h. The corresponding turnover frequency (TOF) can be obtained through dividing TON by time.

3. Characterizations

UV-Vis absorption spectra were recorded with a Shimadzu 1601PC spectrophotometer. Photoluminescence (PL) measurements were performed at room temperature using a Hitachi 4500 fluorescence spectrophotometer. All optical measurements were performed at room temperature under ambient conditions. Fourier transform infrared (FT-IR) spectra were taken on Excalibur 3100 system (Varian, USA). High-resolution transmission electron microscopy (HR-TEM) was performed on a JEM 2100F (Japan) electron microscope operated at an accelerating voltage of 200 kV. Gas chromatography (GC) was performed on a Shimadzu GC2014CAFC/APC using a 5 Å molecular sieve column and a thermal conductivity detector. The X-ray photoelectron spectra (XPS) measurements were performed on an ESCALAB 250 spectrophotometer with Al-Kα radiation. The binding energy calibration was using the C 1s peak at 284.8 eV.

EPR spectra were obtained by using X Band Brucker E500 Electron Spin Resonance Spectrometer. The aqueous solution sample was injected into a sealed paramagnetic tube and bubbled with argon (Ar) atmosphere about 20 min. Room temperature is ~20 ^oC. All samples were measured with microwave power of 10.02 mW, modulation frequency 100 kHz, modulation amplitude 2 G, center field 3010 G, sweep width 6000 G, conversion time 40 ms, and sweep time 80 s.

XAS were acquired at beamline 1W1B at the Beijing Synchrotron Radiation Facility (BSRF). The X-ray source was 2.5 GeV with a current of 250 mA in top-up mode. Powder samples were prepared for measurement by milled and smeared onto a metal-free polyimide tape, and liquid samples were injected into polyimide tape encapsulated groove. Before collecting the data, K-edge energy calibration was performed with a metallic nickel foil standard.

Extended X-ray absorption fine structure (EXAFS) spectra were transformed using the Athena

software.[4] Firstly, the EXAFS spectra were obtained by subtracting the pre-edge background

(−150 to −50 eV vs. absorption edge) from the overall absorption and then normalizing with range

of 150−700 eV. Subsequently, $\chi(k)$ data in the k-space were Fourier transformed to R space using

a hanning window (k-weight = 2, k is ranged from 2.8 to 11.40 Å^{-1}) to separate the EXAFS

contributions from different coordination shells. EXAFS spectra were fitting using the Artemis

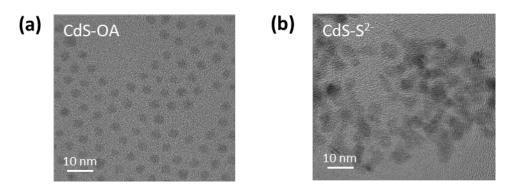software and amplitude attenuation factor (amp) were calculated from Ni foil (amp = 0.785).

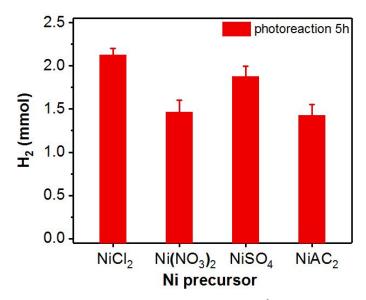**Figure S1.** TEM images of CdS QDs before (a) and after (b) ligand exchange with S^{2-}.

Figure S2. Comparison of hydrogen evolution after CdS-S^{2-} QDs were added with different Ni^{2+} salts, illumination time 5 h.

Compared with SO$_4$$^{2-}$, NO$_3$$^-$, and OAc$^-$, Cl$^-$ is endowed with the smallest ionic radius, so NiCl$^+$ intermediate species are easier to migrate from the solution to the surface of CdS-S^{2-}, making NiCl$_2$ behaves a better hydrogen evolution activity. [5–7]
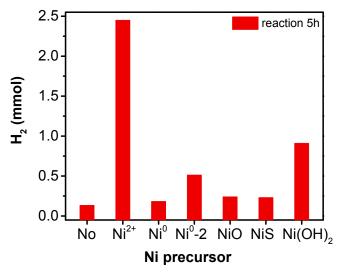
Figure S3. Comparison of hydrogen evolution after CdS-S^{2-} QDs were added with different insoluble Ni^{2+} salts and zero-valence metal nickel (Ni^0) powder, illumination time 5 h. The comparative experiments with different Ni additions use the same amount of Ni, wherein Ni^0-2 uses a fivefold amount of Ni metal sample.
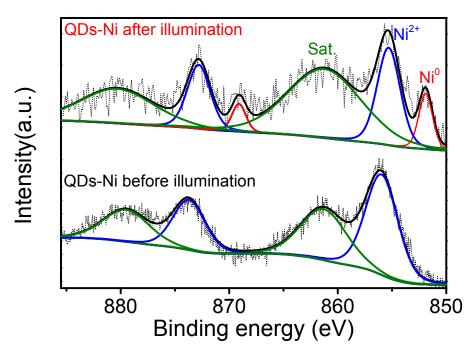
Figure S4. The fine XPS of Ni 2p attached to the CdS-S^{2-} QDs before and after light illumination.
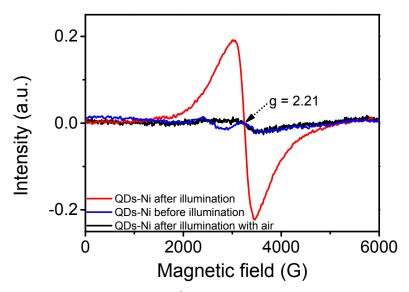
Figure S5. The EPR results of the CdS-S^{2-} QDs-Ni-IPA hydrogen production system before light illumination, after, and after light illumination with air.
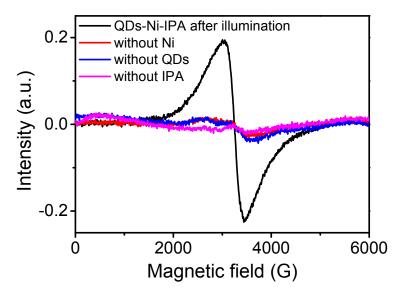
Figure S6. EPR spectra of CdS-S^{2-}-Ni^{2+}-IPA hydrogen evolution system in the absence of single condition after illumination.
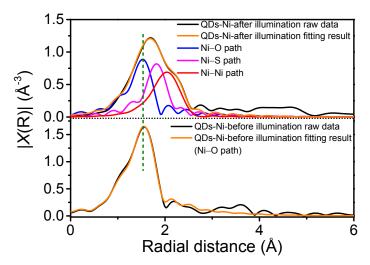
Figure S7. EXAFS raw data and fitting results of QDs-Ni-IPA systems before and after light reaction.

Table S1. Quantitative analysis of the Ni content in the supernatant and the precipitate under different conditions.

	sediment (μg)	supernatant (μg)	sediment (%)	supernatant (%)
without light	2.23	61.63	3.5	96.5
light for 0.5 h[a]	11.31	53.13	17.6	82.4
light for 0.5 h[b]	32.95	33.32	49.7	50.3
light for 0.5 h[c]	3.11	61.71	4.8	95.2

[a]Centrifugation under Air atmosphere (Air). [b]Centrifugation under Argon. [c]Centrifugation after aerating O_2 for 20 minutes.

Table S2. EXAFS fitting parameters of QDs-Ni-IPA systems before and after light reaction.

Sample	Atomic scatter	Coordination Number (CN)	Coordination distance (Å)	Debye-Waller factor ($10^{-3} \times Å^2$)	ΔE_0 (eV)
QDs-Ni-before illumination	Ni–O	6.00	2.04	7.09	−4.76
QDs-Ni-after illumination	Ni–O	2.78	2.00	2.14	−8.42
	Ni–S	1.40	2.29	0.48	−8.42
	Ni–Ni	5.48	2.48	15.49	−8.42

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