#### **Electronic Supplementary Information**

# Coupling CdS Quantum Dots with Polyoxometalate–Supported [Re(CO)<sub>3</sub>]<sup>+</sup> Catalysts for Efficient Photocatalytic CO<sub>2</sub> reduction

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### **Experimental**

#### 1. General Methods and Materials.

All purchased solvents and reagents for synthesis, characterization, and catalytic tests were of analytical reagent grade and used directly without further purification.

The Fourier transform infrared spectroscopy (FT-IR) spectra were conducted on the Bruker Tensor II spectrometer in the range of 4000–400 cm<sup>-1</sup>. The steady-state photoluminescence (PL) quenching spectra were collected in the degassed H<sub>2</sub>O/CH<sub>3</sub>CN (1/5) mixed solution on the Edinburgh Instruments Spectrofluorometer FS5. The morphology of CdS-MPA QDs were characterized on Tecnai G2 F30 S-TWIN Transmissionelectron microscopy (TEM). The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of CdS-MPA QDs were obtained on Techcomp UV 2600 spectrophotometer.

#### 2. Synthesis of Na<sub>9</sub>[XW<sub>9</sub>O<sub>33</sub>] (X=Sb/Bi) and Na<sub>8</sub>[TeW<sub>9</sub>O<sub>33</sub>]

The synthesis of Na<sub>9</sub>[SbW<sub>9</sub>O<sub>33</sub>] (**SbW**<sub>9</sub>) was based on the reported literature method.<sup>1</sup> The detailed synthesis procedures were described as follows. Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (40 g, 121 mmol) was first dissolved in boiling water (80 mL), to which added the concentrated HCl (10 mL) solution containing Sb<sub>2</sub>O<sub>3</sub> (1.96 g, 6.72 mmol). The mixture was then refluxed for 1 h and slowly cooled to room temperature. Colourless crystals of **SbW**<sub>9</sub> were formed after one week.

The synthesis of Na<sub>9</sub>[BiW<sub>9</sub>O<sub>33</sub>] (**BiW**<sub>9</sub>) and Na<sub>8</sub>[TeW<sub>9</sub>O<sub>33</sub>] (**TeW**<sub>9</sub>) was similar to that of **SbW**<sub>9</sub> just replacing Sb<sub>2</sub>O<sub>3</sub> with Bi(NO<sub>3</sub>)<sub>3</sub> (6.5 g, 13.4 mmol) and TeO<sub>2</sub> (2.14 g, 13.44 mmol), respectively.

## 3. Synthesis of $Na_4H_2[(CH_3)_4N]_6[X_2W_{20}O_{70}\{Re(CO)_3\}_2]$ (X=Sb/Bi) and $Na_2H_2[(CH_3)_4N]_6[Te_2W_{20}O_{70}\{Re(CO)_3\}_2]$

The synthesis of Na<sub>4</sub>H<sub>2</sub>[(CH<sub>3</sub>)<sub>4</sub>N]<sub>6</sub>[Sb<sub>2</sub>W<sub>20</sub>O<sub>70</sub>{Re(CO)<sub>3</sub>}<sub>2</sub>] (Sb<sub>2</sub>W<sub>20</sub>Re<sub>2</sub>) was based on the modified literature method and described as follows.<sup>2</sup> 0.1 mmol SbW<sub>9</sub> was first dissolved in 10 mL H<sub>2</sub>O with vigorous stirring for 30 min at the room temperature, and then the pH was adjusted to 5.00 by addition of 1 M HCl. The CH<sub>3</sub>CN solution (3 mL) containing Re(CO)<sub>5</sub>Cl (0.1 mmol) was first refluxed in dark for 30 min to form the orange-red transparent solution, which was then added to the above SbW<sub>9</sub> aqueous solution with continuous stirring for 1 h at 80 °C. Finally, Tetramethylammonium chloride (TMACl) (100 mg) was added to the mixed solution with continued stirring for 10 min. After cooling and filtration, the solution was evaporated slowly at R.T. in dark. The orange block crystals were obtained after one week.

The syntheses of  $Na_4H_2[(CH_3)_4N]_6[Sb_2W_{20}O_{70}\{Re(CO)_3\}_2]$  (**Bi**<sub>2</sub>**W**<sub>20</sub>**Re**<sub>2</sub>) and  $Na_2H_2[(CH_3)_4N]_6[Te_2W_{20}O_{70}\{Re(CO)_3\}_2]$  (**Te**<sub>2</sub>**W**<sub>20</sub>**Re**<sub>2</sub>) were similar to that of

#### Sb<sub>2</sub>W<sub>20</sub>Re<sub>2</sub> just replacing SbW<sub>9</sub> with BiW<sub>9</sub> or TeW<sub>9</sub>, respectively.<sup>2, 3</sup>

#### 4. Synthesis of cadmium sulfide quantum dots (CdS QDs)

#### 4.1 Synthesis of oleic acid-capped CdS (CdS-OA) QDs

The CdS-OA QDs were synthesized based on the modified literature method<sup>4</sup> and the detailed procedures are described as follows. 4.4 mL 1-Octadecene (ODE) solution containing 23 mg (CH<sub>3</sub>COO)<sub>2</sub>Cd·3H<sub>2</sub>O (0.1 mmol) and 508 mg Oleic acid (OA) (1.8 mmol) was heated to 260 °C under Ar atmosphere to form the uniform transparent solution. The previously prepared ODE solution (1 mL) containing sulfur (0.05 mmol, 1.6 mg) was rapidly injected to the transparent solution described above. The mixture solution was kept at the temperature of 230 °C for 7 minutes before being rapidly cooled to room temperature using an ice bath. The resulting QDs were isolated using 5 mL methanol, 5 mL hexane and excess acetone, followed by centrifugation at 12000 rpm for 5 minutes and re-dissolved in 5mL hexane.

#### 4.2 Synthesis of mercaptopropionic acid-capped CdS (CdS-MPA) QDs

The ligand exchange of CdS-OA QDs with MPA was prepared based on the reported procedure. MPA (1 mmol, 106 mg) and KOH (1.2 mmol, 67 mg) were dissolved in methanol (20 mL), followed by the addition of the as-synthesized CdS-OA hexane solution (5 mL) and stirring for 30 minutes in dark. The excessive acetone was added to the above solution and the resulting CdS-MPA QDs were collected by centrifugation (12000 rpm, 5 minutes) and washing with acetone in sequence. The CdS-MPA QDs were re-dispersed in 2 mL water and stored in dark.

#### 5. Photocatalysis Experiments.

The photocatalytic CO<sub>2</sub> reduction was conducted in a homemade reactor equipped with a quartz window under Xe lamp irradiation (300 W, Xenon Lamp Source Microsolar300, Beijing Perfectlight). The typical photocatalytic test was described as follows. CdS-MPA (2  $\mu$ M), POM (1  $\mu$ M), and TEOA (0.4 M) were subsequently added to the H<sub>2</sub>O/CH<sub>3</sub>CN (1/5, 6 mL) mixed solvent under vigorous stirring at 600 rpm. After degassing with CO<sub>2</sub> for 15 min, the reaction solution was irradiated by Xe lamp equipped with 400 nm cut-off filter and water-cooling system. After photocatalysis, the gas product was analyzed by GC (Shimadzu GC-2030N) equipped with a BID detector and MP-01 column, while the liquid product was determined by ion chromatography (Thermo Scientific ICS-1100). The repeated experiments have been conducted for all photocatalytic reactions to guarantee the accuracy.



Fig. S1 Ball-and-stick models of  $Sb_2W_{20}Re_2$ ,  $Bi_2W_{20}Re_2$  and  $Te_2W_{20}Re_2$ . W, blue; O, red; Re, yellow; C, black; Sb, orange; Bi, green; Te, purple.



Fig. S2 The time profiles of  $Sb_2W_{20}Re_2$  catalyst using CdS-MPA QDs (2uM) and  $[Ru(bpy)_3]Cl_2$  (2uM) as photosensitizer. Standard reaction conditions: CdS-MPA QDs (2  $\mu$ M), POM-Re catalyst (1  $\mu$ M), TEOA (0.4 M), H<sub>2</sub>O/CH<sub>3</sub>CN (1:5), 6 mL, Xe lamp ( $\lambda > 400$  nm), R.T.



Fig. S3 The photocatalytic activity as a function as the concentration of CdS-MPA QDs. Standard reaction conditions: CdS-MPA QDs (2  $\mu$ M), POM-Re catalyst (1  $\mu$ M), TEOA (0.4 M), H<sub>2</sub>O/CH<sub>3</sub>CN (1:5), 6 mL, Xe lamp ( $\lambda > 400$  nm), R.T.



Fig. S4 The photocatalytic activity as a function as the concentration of  $Sb_2W_{20}Re_2$  catalyst. Standard reaction conditions: CdS-MPA QDs (2  $\mu$ M), POM-Re catalyst (1  $\mu$ M), TEOA (0.4 M), H<sub>2</sub>O/CH<sub>3</sub>CN (1:5), 6 mL, Xe lamp ( $\lambda > 400$  nm), R.T.



Fig. S5 The photocatalytic activity as a function as the concentration of TEOA. Standard reaction conditions: CdS-MPA QDs (2  $\mu$ M), POM-Re catalyst (1  $\mu$ M), TEOA (0.4 M), H<sub>2</sub>O/CH<sub>3</sub>CN (1:5), 6 mL, Xe lamp ( $\lambda$  > 400 nm), R.T.



**Fig. S6** The time profile of  $Sb_2W_{20}Re_2$ . Standard reaction conditions: CdS-MPA QDs (2  $\mu$ M), POM-Re catalyst (1  $\mu$ M), TEOA (0.4 M), H<sub>2</sub>O/CH<sub>3</sub>CN (1:5), 6 mL, Xe lamp ( $\lambda$  > 400 nm), R.T.



Fig. S7 FT-IR spectra of the fresh and isolated  $Sb_2W_{20}Re_2$  after photocatalysis.



**Fig. S8** The photocatalytic recycling tests using fresh and isolated 2  $\mu$ M CdS-MPA QDs. Standard reaction conditions: CdS-MPA QDs (2  $\mu$ M), POM-Re catalyst (1  $\mu$ M), TEOA (0.4 M), H<sub>2</sub>O/CH<sub>3</sub>CN (1:5), 6 mL, Xe lamp ( $\lambda > 400$  nm), R.T.



Fig. S9 (a) Emission spectra of CdS-MPA QDs as a function as the concentration of Bi<sub>2</sub>W<sub>20</sub>Re<sub>2</sub>.
(b) The Stern–Volmer plot as a function as the concentration of Bi<sub>2</sub>W<sub>20</sub>Re<sub>2</sub>.



**Fig S10** (a) Emission spectra of CdS-MPA QDs as a function as the concentration of TEOA. (b) The Stern–Volmer plot as function as the concentration of TEOA.

Table S1. The quenching rate constant and quenching rate of  $Sb_2W_{20}Re_2$ ,  $Bi_2W_{20}Re_2$ , and  $Te_2W_{20}Re_2$ .

	quenching rate constant (M <sup>-1</sup> S <sup>-1</sup> )	concentration	quenching rate (S <sup>-1</sup> )
$Sb_2W_{20}Re_2$	1.24×10 <sup>11</sup>	1 µM	1.24×10 <sup>5</sup>
$Bi_2W_{20}Re_2$	1.11×10 <sup>11</sup>	1 µM	1.11×10 <sup>5</sup>
$Te_2W_{20}Re_2$	$8.49 \times 10^{10}$	1 µM	8.49×10 <sup>4</sup>

Table S2. Comparison of photocatalytic  $CO_2$  reduction activities among  $Re(CO)_3$ -based photocatalysts.

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Catalyst	Photosensitizer	Sacrificial agent	Product	TO N	Tim e	Ref.
$Te_2W_{20}Re_2$	CdS-MPA QDs	TEOA	НСООН	1533	10 h	
Bi <sub>2</sub> W <sub>20</sub> Re <sub>2</sub>	CdS-MPA QDs	TEOA	НСООН	2097	10 h	This work
$Sb_2W_{20}Re_2$	CdS-MPA QDs	TEOA	НСООН	2532	10 h	
Ru+Re complex	Ir complex	BNAH	НСООН	110	15 h	5
Re complex	Ru complex	AscNa	НСООН	25	24 h	6
Ru–Re complex	Os complex	TEOA	СО	239	10 h	7
Re complex	Ru complex	TEOA	CO	707	60 h	8
Re complex	Re complex	TEOA	CO	125	2 h	9
Re(bpy)(CO) <sub>3</sub> Br	InP/ZnS QDs	TEOA	CO	52	6 h	10
Re(bpy)(CO) <sub>3</sub> Cl	Ru(bpy) <sub>3</sub> Cl <sub>2</sub>	TEOA	CO	7.1	1 h	11
Re(bpy)(CO) <sub>3</sub> SCN	Re complex	TEOA	СО	30	25 h	12
Re(bpy)(CO) <sub>3</sub> MeCN	Re complex	BIH	СО	526	16 h	13

Re(bpy)(CO) <sub>3</sub> MeCN	Re complex	TEOA	CO	98	15 h	14
Re(PyNHC-PhCF <sub>3</sub> )(CO) <sub>3</sub> Br	Ir(ppy) <sub>3</sub>	BIH	CO	51	4 h	15
Re(bpy)(CO) <sub>3</sub> Br	Zn complex	BIH	СО	360	24 h	16

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