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Supporting Information

Tuning of visible light-driven CO₂ reduction and hydrogen evolution activity by using POSS-modified porous organometallic polymers

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1. General Information

1.1 Characterization methods

The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer with KBr pellets. Solid-state NMR experiments were performed on a Bruker AVANCE NEO 400 MHz wide-bore (89 mm) spectrometer with ¹³C frequency of 100.63 MHz. A conventional HX NMR probe with a rotor diameter of 4 mm was used. ¹³C ramped cross-polarization (CP) NMR spectra were acquired under a magicangle-spinning (MAS) rate of 5 kHz. High-power proton decoupling with a radio frequency (RF) field strength of 100 kHz and TOSS (total suppression of spinning sidebands) were adopted during ¹³C signal acquisition. The power X-ray diffraction (PXRD) patterns were measured on Rigaku SmartLab operating at (40 kV, 150 mA) with a scan rate of 8°/min from 2° to 60°. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic Al Ka X-ray source (1486.6 eV) operated at 100 W. Samples were analyzed under vacuum (P<10-8 mbar) with a pass energy of 150 eV (survey scans) or 30eV (high-resolution scans). All peaks would be calibrated with C1s peak binding energy at 284.8 eV for adventitious carbon. The experimental peaks were fitted with Avantage software. Re contents in POSS-Re-n and R-POSS-Re-2 were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, SpectroBlue). Field emission scanning electron microscopy (SEM) images and field emission transmission electron microscopy (TEM) images were obtained on JSM-7500F

at an acceleration voltage of 5 kV and Tecnai G2 F20 at an acceleration voltage of 200 kV, respectively. N_2 and CO_2 sorption of the polymers were measured by Micromeritics ASAP 2020 and Micromeritics ASAP 2460, respectively. Pore size distributions were obtained from the adsorption branches of the isotherms using the non-local density functional theory (NLDFT) method and isosteric heat of adsorption (Q_{st}) for CO_2 was calculated with the Clausius–Clapeyron equation. Solid UV-Vis spectra were recorded on a UV-visible absorption spectroscopy (Shimadzu, UV-2700).

Electrochemical measurements were carried out on a CHI660d electrochemical workstation with an ITO conductive glass(1 cm*1 cm) coated with the synthesized samples (the coated area is 1 cm²) as the working electrode, a Ag/AgCl electrode (saturated KCl solution) as the reference electrode, a platinum plate as the counter electrode. The coated samples were prepared by mixing photocatalyst (5 mg) and Nafion solution (30 µL, 5 wt%) in ethanol (1 mL), then dried in air. The Mott-Schottky tests were carried out in 0.1 M TBABF6 DMF solution, with the measured potentials calibrated by ferrocene/ferrocenium (Fc/Fc⁺). The electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI 660d electrochemical work station in 5 mM potassium ferricyanide/5 mM tetrapotassium hexacyanoferrate trihydrate/0.1 M potassium chloride electrolyte. Linear sweep were performed in 0.1 voltammograms measurements Μ tetrabutylammonium hexafluorophosphate. The photocurrent was recorde in 0.2 M Na₂SO₄ aqueous solution electrolyte.

1.2 Experimental Section/Methods

Materials

5,5'-dibromo-2,2'-bipyridine and $Pd(PPh_3)_4$ were purchased from Energy Chemical; POSS was purchased from Heowns Scientific Ltd.in Tianjin, Re(CO)₅Cl (98%) was purchased from Sigma Aldrich, CO₂ (99.99% purity) was purchased from Liquefied Air (Tianjin) Co., Ltd.. DMF as solvent was purchased from J&K Scientific Ltd..

Synthesis of POSS-Bpy-n (n=2,4)

The following synthesis was described in the previous literature.^[1] POSS-Bpy-n (n=2,4) were prepared from the Heck reaction of POSS with DBr-Bpy. In a typical run, POSS (0.2 mmol, 126.6 mg) was dissolved in 10 mL of dimethylformamide (DMF), and DBr-Bpy (0.4 mmol, 125.6 mg) was dispersed in 10 mL of DMF. Then, the mixture was transferred to a 25 mL

Teflon-lined autoclave. At the same time, K_2CO_3 (2.0 mmol, 276.6 mg) dissolved in 2 mL of water was poured into the mixture solution, followed by the addition of Pd(PPh₃)₄ (0.04 mmol, 46.4 mg) with stirring for 30 min. Next, the sealed Teflon-lined autoclave was placed in a 120 °C constant temperature oven for 72 h. After the completion of the reaction, the solid product was recovered by filtration and thoroughly washed with DMF, H₂O, and ethanol. The greyish green powder POSS-Re-2 was obtained by drying in a vacuum for 12 h at 80 °C and yield at 47%. A series of POSS-Bpy-n were also obtained by varying the molar ratios of DBr-Bpy to POSS (n= 2, and 4).

Synthesis of POSS-Re-n (n=2,4)

Using a typical molar ratio of $\text{Re}(\text{CO})_5\text{Cl}$ to the Bpy ligand in POSS-Bpy-2 (1: 1), the catalyst POSS-Re-2 was prepared by the following process: POSS-Bpy-2 (50 mg) was suspended in 20 mL of methanol by adding $\text{Re}(\text{CO})_5\text{Cl}$ (0.14 mmol, 100 mg) at Ar atmosphere, and the resultant mixture solution was heated at 80 °C for 24 h. The solid was filtered and washed with methanol and hexane and then dried at 80 °C under vacuum for 12 h to give a yield at 70%.

Synthesis of R-POSS-Re-2

The following synthesis was referred to the previous literature.^[2] Diborane, generated from the addition of (56 mmol, 1 g) of sodium borohydride to 4 mL (57.4 mmol) of boron trifluoride-etherate, was passed into the reaction flask containing 30 mg of POSS-Bpy-2 in 10 mL of diglyme. The reaction temperature was controlled through an ice/water bath. The reaction steps were all under protection of Ar atmosphere for 16 h. The reaction flask was disconnected, and quenched the reaction by water, then filtered and washed the residue with water and ethanol. Then the grey powder product was dried at 80 °C under vacuum for 12 h to give a yield at 96%.

*General Procedure for Photocatalytic CO*₂ *Reduction.*

To a 25 mL Schlenk tube, photocatalyst (2 mg), TEOA (0.9 g, 0.8 mL) and DMF (3 mL) were successively added. Then, the reaction mixture was sonicated to allow the polymer to disperse evenly in the whole solution for 15 min. Air in the Schlenk tube was replaced by CO₂ through the freeze-pump-thaw method. Then, the reaction tube was sealed and placed under a 500W long-arc Xenon lamp ($\lambda \ge 400$ nm) for desired time at room temperature. After the reaction, partial gaseous products (1 mL) were taken from the tube using a syringe and then analyzed by gas chromatography with a TCD detector.

Recycling test Procedure

After the reaction, the gas in the Schlenk tube was replaced by CO_2 through the freeze-pumpthaw method 3 times and then reused for the next run.

2. Supplementary Figures

2.1 Characterization of the structure composition and morphology



Fig. S1 (a) XPS spectrum survey, (b) C 1s, (c) N 1s, (d) Si 2p.



Fig. S2 XRD patterns of POSS-Bpy and POSS-Re-2.



Fig. S3 Pore size distributions calculated by NLDFT. (a) POSS-Re-2; (b) POSS-Re-4; (c) R-POSS-Re-2.

Entry	Cat.	Metal	Concen. (measured value)	Theoretical value	TON(H ₂ /CO)
1	POSS-Re-2	Re	15.7%	18.8%	<mark>7.5 / 3.8</mark>
2	R-POSS-Re-2	Re	12.3%	16.0%	12.2 / 4.1
3	POSS-Re-4	Re	20.2%	22.4%	<mark>21.9 / 0.3</mark>

Table S1 Comparison of Re content ^a

^a Re contents in POSS-Re-n(n=2,4) and R-POSS-Re-2 were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, SpectroBlue)

2.2 Electrochemical properties



Fig. S4. EIS spectra of POSS-Re-2, R-POSS-Re-2 and POSS-Re-4 under dark and visible light irradiation (λ >420nm)



Fig. S5 Linear sweep voltammograms of electrodes coated with POSS-Re-2, R-POSS-Re-2 and POSS-Re-4.



Fig. S6. Mott-Schottky plots of (a) POSS-Re-2; (b) POSS-Re-4;(c)R-POSS-Re-2 in 0.1 M TBABF₆ DMF solution at 500 and 1000 Hz.



Fig. S7. Tauc plots of (a) POSS-Re-2; (b) POSS-Re-4;(c)R-POSS-Re-2.

2.3 The stability tests of catalyst



Fig. S8. The stability tests over POSS-Re-2.



Fig. S9 SEM images of fresh POSS-Re-2 and used POSS-Re-2.



Fig. S10. FT-IR of fresh POSS-Re-2 and used POSS-Re-2.

Catalyst	Photosensitizer	Sacrificial	Light	Major	Reference
	/Cocatalyst	reagent	source	product	
				evolution	
				$(\mu mol g^{-1})$	
POSS-Re-2	-	BIH/TEOA	500 W Xe	CO:4055	This and the
			$(\lambda > 400 \text{ nm})$	H ₂ :9000(24 h)	THIS WOLK
Fe-SAs/N-C	$[Ru(bpy)_{3}]Cl_{3}$	TEOA	5 W white LED	CO: 18000	S 3
			light (400 nm $\leq \lambda$	H ₂ : 19800	
			\leq 800 nm)	(4 h)	
Ni COFs	$Ru(bpy)_{3}Cl_{2} \cdot 6H_{2}O$	TEOA	5 W white LED	CO: 4530	S4
			light (400 nm $\leq \lambda$	H ₂ : 580 (1 h)	
			\leq 800 nm)		~ -
Rel/Colli	Dye	BIH	three LED	CO:773	85
modified 110 ₂			$\operatorname{lamps}\left(\lambda > 400\right)$	H ₂ :221 (10	
			nin, 60 w)	h)	
	Ru(bpy) ₃ Cl ₂ ·6H ₂ O	TEOA	300 W Xe	CO: 8360	56
Co-ZIF-9		TEOA	$(\lambda > 420 \text{ nm})$	П ₂ . 3980 (0.3	50
Au/CdS	a^{2+}	TEOA	300 W Xe	II) CO: 2758	\$7
Au/Cu5	$Co(bpy)_3^{-1}$	TEOA	$(\lambda > 400 \text{ nm})$	H ·1588 (1 h)	57
Dt/C In O	Dt	TEOA	300 W Xe	$11_2 \cdot 1500 (1 \text{ II})$	58
$100-1120_3$	11	ILOA	$(\lambda > 420 \text{ nm})$	н · 910	50
			()	CH : 558 (4 h)	
CuPt/TiO		No SO	100 mW/cm^2	CO(1010)	50
Curvino ₂	-	Na ₂ SO ₃	AM 1 5G	Н -2020 (12	57
		solution	illumination	$11_{2}.2020(12)$	
SnS /SnO	_	H O	300 W Xe	$CO^{-245} 6$	
5115 ₂ , 5110 ₂	_	1120	$(\lambda > 420 \text{ nm})$	$O_{12} = 104 (20 h)$	S10
			```	2. I C . (= C II)	

Table S2 Comparison of syngas production from different kinds of catalysts for  $CO_2$  photoreduction.

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