

Supporting Information

A robust photocatalyst of Au₂₅@ZIF-8@TiO₂-ReP with dual photoreductive sites to promote photoelectron utilization in H₂O splitting to H₂ and CO₂ reduction to CO

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Materials Synthesis

Chemical reagents used were all purchased without further purification. Titanium(IV) isopropoxide (TTIP), sodium tetrahydroborate, ethanol, GSH in the reduced form (Mw = 307), triethanolamine (TEOA), 2-methylimidazole (Melm) and dimethyl imidazole were purchased from Aladdin (Shanghai, China). Zinc nitrate hexahydrate, toluene and diethyl ether were obtained from Guangzhou Guanghua Reagent Plant (Guangzhou, China). Pentacarbonylchlororhenium(I) and hydrogen tetrachloroaurate tetrahydrate, respectively, obtained from Sigma-Aladdin Chemical Reagent Co.Ltd.(Shanghai, China) and Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 2,2'- bipyridine - 4,4'- bisphosphonic acid was obtained from Shanghai yukang biotechnology Co.Ltd(Shanghai, China). Tris(2,2'-bipyridine)dichlororuthenium(II) hexahydrate and methyl cyanide were purchased from Sahn chemical technology Co.Ltd.(Shanghai, China) and Balinway superfine materials Co. Ltd.(Langfang, China), respectively. The deionized water was used with the resistivity of >18 MΩ cm.

Synthesis of Au₂₅(SG)₁₈: Au₂₅(SG)₁₈ was prepared following a previous reported literature¹. Firstly, 1.0 mmol GSH and 0.25 mmol HAuCl₄ was dissolved into 25 ml methanol and the resulting mixture was kept at 0 °C for 30 min. Then, NaBH₄ aqueous solution (6.25mL, 0.2 M) at 0 °C was injected into above mixture and the reaction was kept stirring for 3 h. After that, a dark-brown precipitate, obtained by centrifugation, dissolved in GSH (7 mL, 65.4 mg) aqueous solution and stirred at 328 k for 12 h. Then, the supernatants without large particles removed by centrifugation were loaded into dialysis bag with a molecular-weight cut-off of 3 kDa. Then final products were stored at refrigerator.

Synthesis of ZIF-8: ZIF-8 was synthesized following a previous report. 2.838 g 2-methylimidazole and 0.1462 g Zn(NO₃)₂·6H₂O were dissolved in 1 mL H₂O, respectively. The aqueous solution of Melm was added into Zn(NO₃)₂·6H₂O solution and the mixture was stirring for 15 min. The resulting product was separated out by centrifuging, washed with DI water (repeated three times) and then dried at 55 °C overnight.

Synthesis of Au₂₅(SG)₁₈@ZIF-8: Au₂₅(SG)₁₈@ZIF-8 was prepared following our previous reported literature¹³. 100uL Au₂₅(SG)₁₈ pristine solution was dissolved in Zn(NO₃)₂ aqueous solution. After ultrasonic dispersion for 15 min, the mixture was added into Melm aqueous solution with molar ratio of Zn²⁺ to Melm 1:70 under stirring. After reaction for 10 min, the shallow-brown powders were collected by centrifugation and washed repeatedly twice in H₂O and then vacuum dried at 55°C overnight.

Synthesis of fac-[Re(4,4'-Bis(dihydroxyphosphorylmethyl)-2,2'-bipyridine)(CO)₃Cl]: The RePH sample was prepared according to a previous reported literature with a slight modification². 126.8 mg 2,2'-bipyridine-4,4'-bisphosphonic acid and 140.7 mg Re(CO)₅Cl were dissolved in the mixture of 20 ml toluene and 20 ml methanol in single neck flask. After reflux overnight, the suspension was cooled and filtered to obtain an orange solution, and then the solvent was removed under reduced pressure to collect orange powders.

Synthesis of Au₂₅@ZIF-8@TiO₂, Au NPs@ZIF-8@TiO₂, Au NPs@ZIF-8 and ZIF-8@TiO₂: 64 mg Au₂₅(SG)₁₈@ZIF-8 was added into ethanol and ultrasonic dispersion for 30 min. Then a certain volume of TTIP was rapidly added into the above mixture with molar ratio of ZIF-8 to TiO₂ 1:4 under stirring. After reaction for 1 h, ethanol aqueous solution was dropwise added into the reaction system. The mixture was stirred for 3 h, subsequently transferred to a 50 mL Teflon autoclave. After reaction at 90°C for 24 h, a gray precipitation was obtained and washed with ethanol twice, then dried under vacuum at 55 °C overnight. The molar ratio of H₂O: ethanol: TTIP was 6:400:1. Au NPs@ZIF-8@TiO₂ and ZIF-8@TiO₂ was prepared as the same procedure. Au NPs@ZIF-8 was obtained by reaction at 140 °C.

Synthesis of Au₂₅@ZIF-8@TiO₂-ReP, Au NPs@ZIF-8@TiO₂-ReP and ZIF-8@TiO₂-ReP: The Au₂₅@ZIF-8@TiO₂-ReP was obtained by following a reported literature.³ In a typical procedure, 25 mg Au₂₅(SG)₁₈@ZIF-8@TiO₂ was

dispersed in a aqueous solution of RePH (3mL, 0.36/0.72/1.45 μM) with stirring. After stirring for 4 h, the final product was obtained by centrifugation, and dried at 55°C overnight. In the same way, ZIF-8@TiO₂-ReP was obtained after stirring in 0.72 μM RePH aqueous solution. All these samples derive from the same precursor of Au₂₅(SG)₁₈@ZIF-8, and the Au content in these samples are equivalent.

Characterization

XRD patterns were carried out on a powder X-ray diffractometer (Cu K α radiation, 40 kv, 40 mA, D8 Advance, Bruker, Germany) at a scan rate of 0.02° per second in the 2 θ range from 5° to 70°. The morphology was observed on a JEM-2100F with an acceleration voltage of 200 kV at room temperature. Fourier transform infrared spectroscopy (FTIR) spectra were collected on a VERTEX 70 equipped with a Diamond ATR (attenuated total reflectance) accessory in the wavenumber range of 4000-400 cm⁻¹. Ultraviolet-visible (UV-vis) absorption spectra were observed on a Shimadzu UV-2450 spectrometer. X-ray photoelectron spectroscopy (XPS) observation were obtained on a Physical Electronics PHI 5600 system (Al K α X-ray source, 350W and all binding energies were referenced to the C 1s peak at 284.6 eV. Fluorescent measurements were collected on Edinburgh Instruments Ltd. FLS980 coupled with a continuous Xe 900 Xenon lamp. GC-MS analyses were performed on a DSQ II GC/MS (ThermoFisher) system (column-TG-5SilMS, 30m \times 0.25mm \times 0.25 μm).

Evaluation of photocatalytic performances

The photocatalytic performances were evaluated by conducting at 1 atm pressure in a 40 ml closed glass reactor at room temperature. In a typical test, the reaction system containing 5 mg catalyst, 1 ml TEOA as electron donor, 10 μmol [Ru(bpy)₃]Cl₂·6H₂O as photosensitizer, solvent (5 ml, acetonitrile: H₂O = 4: 1), was stirred and purged with CO₂ for 20 min to remove air and then irradiated under a 300 W Xe lamp (420 nm cut-off filter, PLS-SXE-300C, Beijing Perfect light) with the light intensity of 100 mW·cm⁻² under stirring. After reaction, 0.1 mL of gas was taken from the reactor and analyzed by using a gas chromatograph (FuLi Analytical Instrument Co., Ltd, GC9790 plus) equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD). All the photoreduction tests were repeated three times to ensure the reliability of the data. The apparent quantum yield (AQY)⁴ was measured using the same experimental conditional expect for the addition of a band-pass filter (λ =500nm) with the light intensity of 10mW·cm⁻², and it was calculated using the following equation:

$$\text{AQY(\%)} = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\%$$

$$= \frac{2 \times \text{Number of (H}_2 \text{ molecules + CO molecules evolved in 1 hour)}}{\text{Number of incident photos in 1 hour}} \times 100\%$$

Control experiment for photocatalytic performance

Au₂₅(SG)₁₈ aqueous solution exhibits 8.7 μmol H₂ output (entry 1), but severe aggregation of Au₂₅ NCs is observed in TEM image (b, Fig. S2) after light irradiation. Au₂₅(SG)₁₈@ZIF-8 (entry 2) gives similar H₂ and CO outputs with that of Au₂₅@ZIF-8@TiO₂ (entry 3), but the sensitivity of ZIF-8 to CO₂ and H₂O incurs the obvious structure variation to carbonate in the lack of TiO₂ protective shell (d, Fig. S2). The highest outputs of 14.9 μmol H₂ and 0.7 μmol CO are detected for Au₂₅@ZIF-8@TiO₂-ReP in entry 5. In contrast, H₂ output of Au₂₅@ZIF-8@TiO₂ falls by half almost and only 0.1 μmol CO is detected as the absence of RePH molecules (entry 3). For ZIF-8@TiO₂-ReP (entry 4), 0.7 μmol CO output is comparable with Au₂₅@ZIF-8@TiO₂-ReP, but only 0.4 μmol H₂ is detected as lack of Au₂₅ NCs. When replacing Au₂₅ NCs by Au NPs (entry 6), both H₂ and CO outputs are nearly half of Au₂₅@ZIF-8@TiO₂-ReP. From these comparisons, it can be summarized that Au centers account for the H₂ evolution while Re(I) sites afford CO generation in as-prepared samples. It should be mentioned that no reduction production is detected for all samples in absence of Ru(bpy)₃²⁺ photosensitizer.

Table S1. ^a Photocatalytic H₂ and CO outputs on different samples.

Entry	photocatalyst	H ₂ (μmol)	CO (μmol)	H ₂ + CO (μmol)
1	Au ₂₅ (SG) ₁₈	8.7	0.3	9.0
2	Au ₂₅ (SG) ₁₈ @ZIF-8	7.9	0.1	8.0
3	Au ₂₅ @ZIF-8@TiO ₂	7.8	0.1	7.9
4	ZIF-8@TiO ₂ -ReP	0.4	0.7	1.1
5	Au ₂₅ @ZIF-8@TiO ₂ -ReP	14.9	0.7	15.6

^a Reaction conditions: 5 mg catalyst, H₂O (1 mL), TEOA (1 mL), acetonitrile (4 mL), [Ru(bpy)₃]Cl₂·6H₂O (10.0 μmol), CO₂ (1 atm), λ > 420 nm, 300 W Xe lamp, 100 mW·cm⁻¹, 25 °C, irradiation time: 1 h.

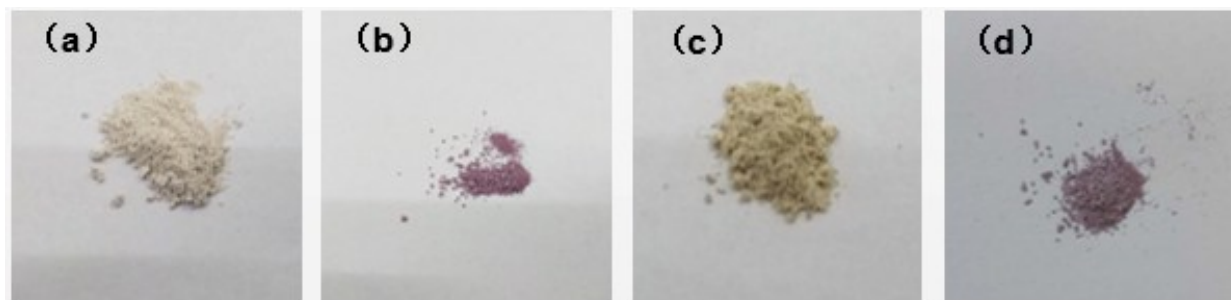


Figure S1. Photo images of (a) Au₂₅(SG)₁₈@ZIF-8, (b) Au NPs@ZIF-8, (c) Au₂₅@ZIF-8@TiO₂-ReP and (d) Au NPs@ZIF-8@TiO₂-ReP.

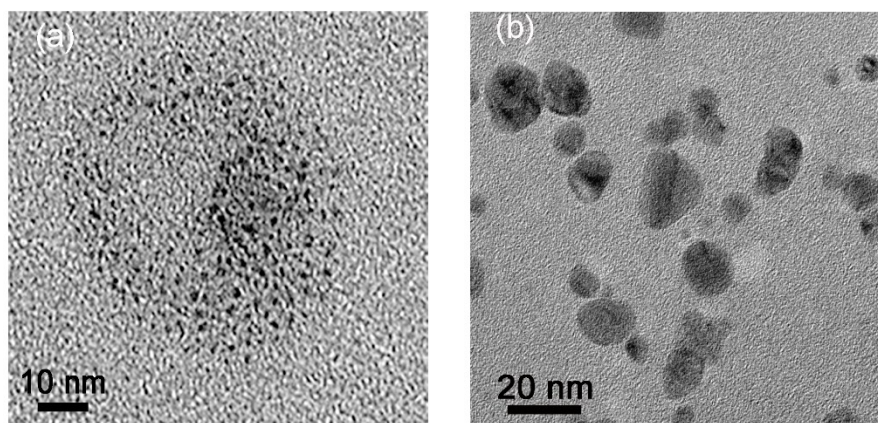


Figure S2. TEM images of (a) Au₂₅(SG)₁₈ and (b) Au₂₅(SG)₁₈ after 1 hour of irradiation.

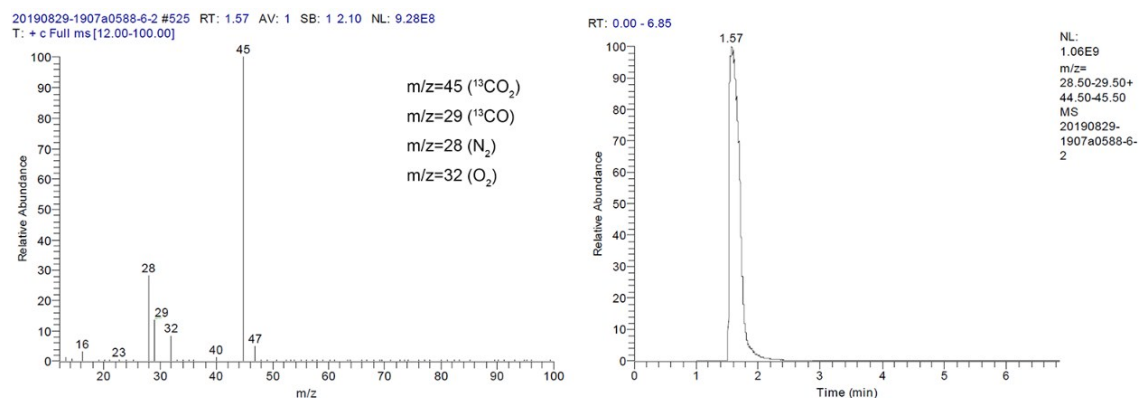


Figure S3. Gas chromatograms and mass spectra (m/z=29) analyses of the produced CO by photocatalytic reduction of ¹³CO₂.

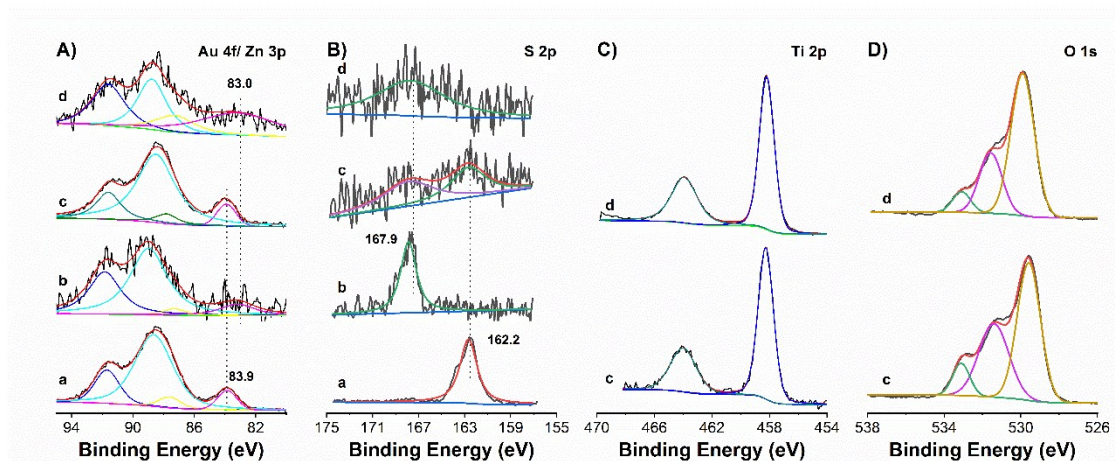


Figure S4. (A) Au 4f/Zn 3p, (B) S 2p, (C) O 1s and (D) Ti 2p XPS spectra of (a) Au₂₅(SG)₁₈@ZIF-8, (b) Au NPs@ZIF-8, (c) Au₂₅@ZIF-8@TiO₂-ReP, and (d) Au NPs@ZIF-8@TiO₂-ReP. The binding energy (BE) is calibrated to adventitious carbon C 1s peak at 284.6 eV.

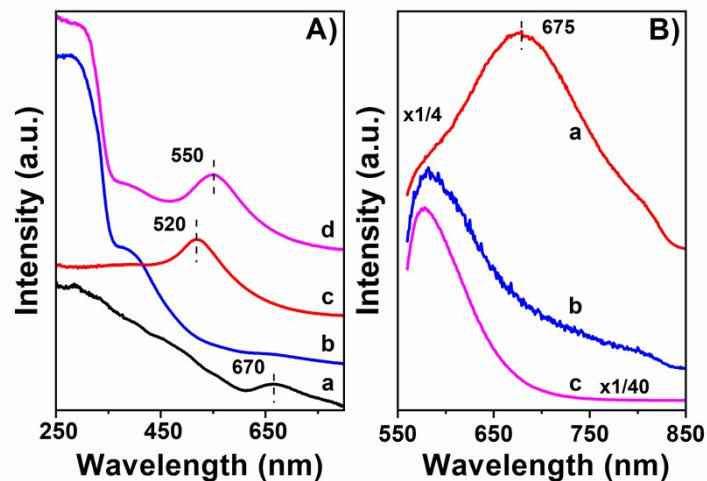


Figure S5. (A) UV-visible absorption of (a) Au₂₅(SG)₁₈@ZIF-8, (b) Au NPs@ZIF-8, (c) Au₂₅@ZIF-8@TiO₂-ReP and (d) Au NPs@ZIF-8@TiO₂-ReP; (B) Photoluminescence spectra of (a) Au₂₅(SG)₁₈@ZIF-8, (b) Au NPs@ZIF-8 and (c) ZIF-8@TiO₂. PL spectra was excited at 520 nm.

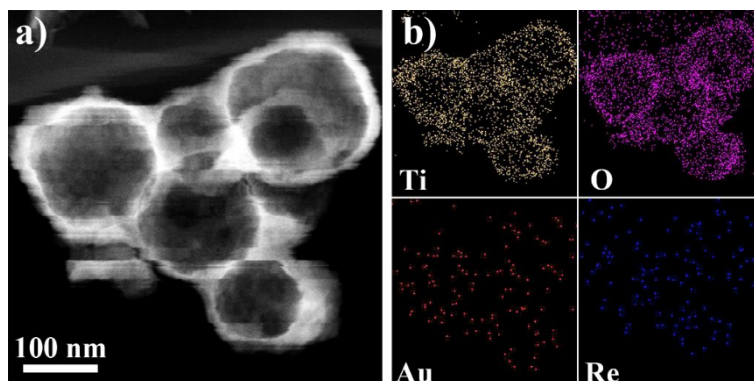


Figure S6. a) HAADF-STEM images and b) Elemental maps of Au₂₅@ZIF-8@TiO₂-ReP after three times sequential recycle reaction.

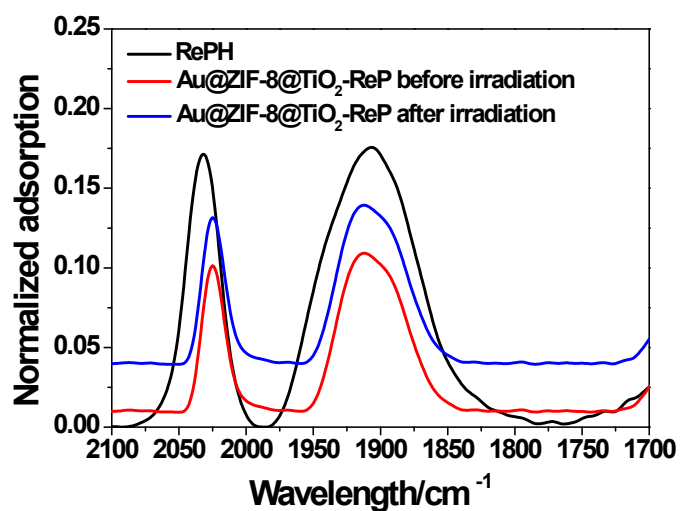


Figure S7. ATR-IR spectra of RePH and Au₂₅@ZIF-8@TiO₂-ReP before and after photocatalytic reaction.

References

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