Supporting Information

A robust photocatalyst of Au$_{25}$@ZIF-8@TiO$_2$-ReP with dual photoreductive sites to promote photoelectron utilization in H$_2$O splitting to H$_2$ and CO$_2$ reduction to CO was obtained by following a reported literature.

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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), and 2,2'-bipyridine-4,4'- bisphosphonic acid and 140.7 mg Re(CO)$_5$ were dissoved in 1 mL H$_2$O and then vacuum dried at 55°C overnight. The molar ratio of H$_2$O: ethanol: TTIP was 6:400:1. Au NPs@ZIF-8 (SG)$_{18}$ was prepared following a previous reported literature.$^3$ Firstly, 1.0 mmol GSH and 0.25 mmol HAuCl$_4$ was dissolved into 25 ml methanol and the resulting mixture was kept at 0 °C for 30 min. Then, NaBH$_4$ 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 Au$_{25}$@ZIF-8@TiO$_2$: Au$_{25}$@ZIF-8 was prepared following a previous report.$^4$ Firstly, 1.0 mmol GSH and 0.25 mmol HAuCl$_4$ was dissolved into 25 ml methanol and the resulting mixture was kept at 0 °C for 30 min. Then, NaBH$_4$ 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 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(NO$_3$)$_2$6H$_2$O were dissolved in 1 mL H$_2$O, respectively. The aqueous solution of Melm was added into Zn(NO$_3$)$_2$6H$_2$O 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 Au$_{25}$@ZIF-8@TiO$_2$: Au$_{25}$@ZIF-8@TiO$_2$ was prepared following our previous reported literature.$^1$ 100μL Au$_{25}$@ZIF-8@TiO$_2$ pristine solution was dissolved in Zn(NO$_3$)$_2$ aqueous solution. After ultrasonic dispersion for 15 min, the mixture was added into Melm aqueous solution with molar ratio of Zn$^{2+}$ to Melm 1:70 under stirring. After reaction for 10 min, the shallow-brown powders were collected by centrifugation and washed repeatedly twice in H$_2$O and then vacuum dried at 55°C overnight.

Synthesis of fac-[Re(4,4’-Bis(dihydroxyphosphorylmethyl)-2,2’-bipyridine)(CO)$_3$Cl]: The RePH sample was prepared according to a previous reported literature with a slight modification.$^2$ 126.8 mg 2,2’-bipyridine-4,4’- bisphosphonic acid and 140.7 mg Re(CO)$_5$Cl 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 Au$_{25}$@ZIF-8@TiO$_2$: Au NPs@ZIF-8@TiO$_2$: Au NPs@ZIF-8 and ZIF-8@TiO$_2$: 64 mg Au$_{25}$@ZIF-8(SG)$_{18}$ 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 TiO$_2$ 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 H$_2$O: ethanol: TTIP was 6:400:1. Au NPs@ZIF-8@TiO$_2$: Au NPs@ZIF-8 was obtained by following a reported literature.$^3$ In a typical procedure, 25 mg Au$_{25}$@ZIF-8(SG)$_{18}$ 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 TiO$_2$ 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 H$_2$O: ethanol: TTIP was 6:400:1. Au NPs@ZIF-8@TiO$_2$: 64 mg Au$_{25}$@ZIF-8(SG)$_{18}$ 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 TiO$_2$ 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 H$_2$O: ethanol: TTIP was 6:400:1. Au NPs@ZIF-8@TiO$_2$: Au NPs@ZIF-8 was obtained by following a reported literature.$^3$ In a typical procedure, 25 mg Au$_{25}$@ZIF-8(SG)$_{18}$ 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 TiO$_2$ 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 H$_2$O: ethanol: TTIP was 6:400:1. Au NPs@ZIF-8@TiO$_2$: Au NPs@ZIF-8 was obtained by following a reported literature.$^3$ In a typical procedure, 25 mg Au$_{25}$@ZIF-8(SG)$_{18}$ 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 TiO$_2$ 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 H$_2$O: ethanol: TTIP was 6:400:1. Au NPs@ZIF-8@TiO$_2$: Au NPs@ZIF-8@TiO$_2$: Au NPs@ZIF-8@TiO$_2$: Au NPs@ZIF-8 was obtained by following a reported literature.$^3$ In a typical procedure, 25 mg Au$_{25}$@ZIF-8(SG)$_{18}$ 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 TiO$_2$ 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 transf
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 Kα radiation, 40 kv, 40 mA, D8 Advance, Bruker, Germany) at a scan rate of 0.02° per second in the 2θ 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 Kα X-ray source, 350Wand 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 × 0.25mm × 0.25μm).

**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) 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:

\[
\text{AQY} = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\%
\]

\[
= \frac{2 \times \text{Number of (H2 molecules + CO molecules evolved in 1 hour)}}{\text{Number of incident photons in 1 hour}} \times 100\%
\]

**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 generation in as-prepared samples. It should be mentioned that no reduction production is detected for all samples in absence of Ru(bpy)3Cl2 photosensitizer.

**Table S1.** Photocatalytic H2 and CO outputs on different samples.

<table>
<thead>
<tr>
<th>Entry</th>
<th>photocatalyst</th>
<th>H2 (μmol)</th>
<th>CO (μmol)</th>
<th>H2 + CO (μmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au25(SG)18</td>
<td>8.7</td>
<td>0.3</td>
<td>9.0</td>
</tr>
<tr>
<td>2</td>
<td>Au25(SG)18@ZIF-8</td>
<td>7.9</td>
<td>0.1</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>Au25@ZIF-8@TiO2</td>
<td>7.8</td>
<td>0.1</td>
<td>7.9</td>
</tr>
<tr>
<td>4</td>
<td>ZIF-8@TiO2-ReP</td>
<td>0.4</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>Au25@ZIF-8@TiO2-ReP</td>
<td>14.9</td>
<td>0.7</td>
<td>15.6</td>
</tr>
</tbody>
</table>
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⁻², 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) Au$_{25}$(SG)$_{18}$@ZIF-8, (b) Au NPs@ZIF-8, (c) Au$_{25}$@ZIF-8@TiO$_2$-ReP, and (d) Au NPs@ZIF-8@TiO$_2$-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) Au$_{25}$(SG)$_{18}$@ZIF-8, (b) Au NPs@ZIF-8, (c) Au$_{25}$@ZIF-8@TiO$_2$-ReP and (d) Au NPs@ZIF-8@TiO$_2$-ReP; (B) Photoluminescence spectra of (a) Au$_{25}$(SG)$_{18}$@ZIF-8, (b) Au NPs@ZIF-8 and (c) ZIF-8@TiO$_2$. PL spectra was excited at 520 nm.

Figure S6. a) HAADF-STEM images and b) Elemental maps of Au$_{25}$@ZIF-8@TiO$_2$-ReP after three times sequential recycle reaction.
Figure S7. ATR-IR spectra of RePH and Au$_{25}$@ZIF-8@TiO$_2$-ReP before and after photocatalytic reaction.

References