Supporting Information

Fabrication of Au/ZnO Nanoparticles Derived From ZIF-8 with Visible Light Photocatalytic Hydrogen Production and Degradation Dye Activities

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EXPERIMENTAL SECTION

Materials. Hydrogen tetrachloroaurate ($HAuCl_4 \cdot H_2O$, ⩾99.99%) were purchased from Sigma (USA). Glutathione (GSH) was obtained from DING GUO. 2-methylimidazole (Hmim) was purchased from Chengdu Kelong Chemical Reagent Company. $Zn(NO_3)_2 \cdot 6H_2O$, commercially available ZnO nanopowder, $Na_2S \cdot 9H_2O$ and Na_2SO_3 were purchased from Tianjin Fengchun Chemical Reagent Technologies Co., Ltd. Methanol and ethanol were purchased from Beijing Chemical Works. All other reagents and solvents for the synthesis were purchased from commercial sources and used as received. All the glassware was cleaned with aqua regia (HCl:HNO_3 volume ratio = 3:1) and thoroughly rinsed with Millipore water (18.0 MΩ cm^{-1}) prior to the experiments. (Caution: Aqua Regia is a very corrosive oxidizing agent, which should be handled with great care).

Characterization. Electron transmission microscopy (TEM) was performed on a JEOL-2100F transmission electron microscope under 200 kV accelerating voltage. Field-emission scanning electron microscope (FE-SEM) images and energy dispersive X-ray (EDX) spectrum were obtained by using an XL 30 ESEM-FEG field-emission scanning electron microscope (FEI Co.). Powder X-ray diffraction (PXRD) patterns were recorded on a Siemens D5005 diffractometer with Cu KR (λ=1.5418 Å) radiation in the range of 3–90°. Thermogravimetric analysis (TGA) experiments were performed on a Perkin-Elmer TGA 7 analyzer heated from 25 to 600 °C under air atmosphere with a heating rate of 10 °C min^{-1}. UV-Vis absorption and diffuse reflectance spectra (DRS) were recorded on a U-3010 spectrophotometer (Hitachi, Japan). Photoluminescence (PL) spectra were performed with FL-4600 fluorescence spectrophotometer (5J2-0004). X-Ray photoelectron spectra (XPS) were measured on an ECSALAB 250 using non-monochromatized Al KR. N_2 sorption measurements were measured on an Autosorb-iQ analyzer (Quantachrome). Before gas adsorption measurements, the samples were activated by drying under a dynamic vacuum at 160 °C overnight. Photocatalytic reactions were performed in a Pyrex inner-irradiation-type reaction vessel with a magnetic stirrer at room temperature. The reactant solution was evacuated using N_2 several times to ensure complete air removal and then irradiated by using a 500 W Xe lamp with a 400 nm cutoff filter. The produced hydrogen was analyzed by a GC9800 instrument with a thermal conductivity detector and a 5 Å molecular sieve column (2 mm × 2 m) with N_2 as carrier gas.

Synthesis of yellow fluorescent GSH-Au NCs. Firstly, a 3 mL $HAuCl_4$ aqueous solution (20 mM) was mixed with 1.2 mL GSH aqueous solution (100 mM). Then 25.8 mL of ultrapure water was poured into them under gentle stirring (500 rpm) at 25 °C and a precipitate was formed. Five minutes later, NaOH solution (0.5 M) was added to the mixture to bring the pH to ~7.0 and the precipitate was dissolved within seconds. Subsequently, the solution was aged for ~1h without stirring in air and the GSH-Au NCs formed as such, which were used without purification and stored at 4 °C in the dark for further use. The product showed yellow fluorescence under 365 nm ultraviolet light based on the volume ratio of the as-obtained GSH-Au NCs solution to methanol with 1: 10.

Synthesis of ZIF-8 and GSH-Au NCs/ZIF-8 NPs. All solutions used methanol as solvent. Firstly, a 2 mL solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.06 mM) was added into 2 mL Hmim solution (0.25 mM). Subsequently, the mixture was allowed to react at room temperature for 24 h without stirring, during which the solution changed the appearance from clear to milky. Finally, the product ZIF-8 NPs were collected by centrifugation at 9000 rpm for 10 min, washed three times with methanol to remove the remaining reactant and then dried under vacuum for 10 h at 50 °C in an oven to get the powder. The GSH-Au NCs/ZIF-8 NPs were obtained by directly mixing 4 mL solution containing 6 mg of ZIF-8 powders and 0.4 mL solution of the as-prepared GSH-Au NCs with stirring for 12 h.

Synthesis of ZnO and Au/ZnO NPs. The as-synthesized ZIF-8 and GSH-Au NCs/ZIF-8 NPs powder were calcined in air at 550 °C for 2 h by 2 °C per minute from room temperature, respectively. Then the ZnO and Au/ZnO NPs were collected after the products were cooled to the room temperature.

Photocatalytic Hydrogen Generation Measurement. To explore the visible light photocatalytic hydrogen evolution activity of Au/ZnO or ZnO NPs, 100 mg photocatalyst powder was dispersed in 200 mL of aqueous solution containing 3.6 g $Na_2S \cdot 9H_2O$ and 1.89 g Na_2SO_3. The catalyst solution was irradiated under a 500 W Xe lamp with a 400 nm cutoff filter and the amount of hydrogen generation was determined using a gas chromatograph.

Photocatalytic degradation of RhB Measurement. RhB was chosen as a representative dye to test the potential photodegradation activity under visible light irradiation. Firstly, a 20 mL 1×10^{-5} M RhB aqueous solution was mixed with 20 mL aqueous solution containing 20 mg catalyst powder of Au/ZnO NPs, ZnO NPs or commercially available ZnO nanopowder. Then they were stirred for 3 h in the dark to reach adsorption-desorption equilibrium between the RhB and the photocatalyst. Subsequently, they were irradiated by a 500 W Xe lamp with a 400 nm cutoff filter under magnetic stirring in air. Finally, samples of the suspension were draw out at regular intervals, centrifuged to completely remove the catalyst and measured using a UV-Vis spectrophotometer to detect the degree of RhB degradation.

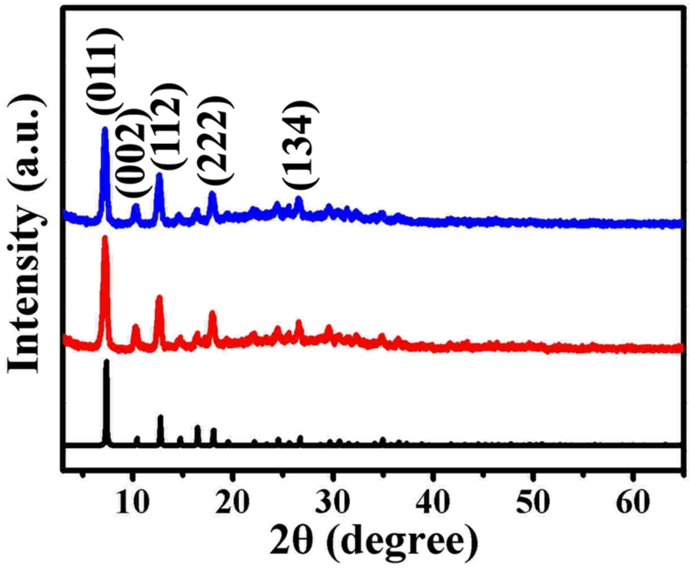

Fig. S1 PXRD patterns of simulated ZIF-8 (black), as-synthesized ZIF-8 (red) and GSH-Au NCs/ZIF-8 (blue).

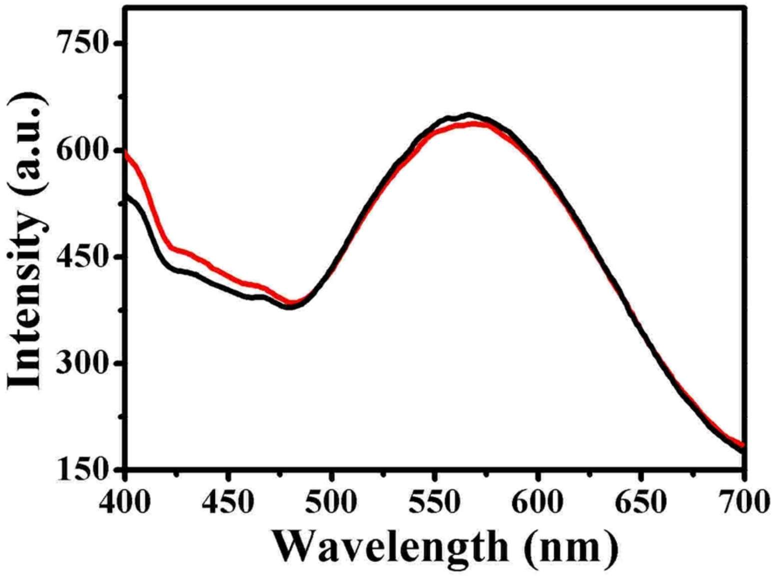

Fig. S2 PL spectra of the as-prepared GSH-Au NCs/ZIF-8 before (black) and after (red) washed with methanol for ten times.

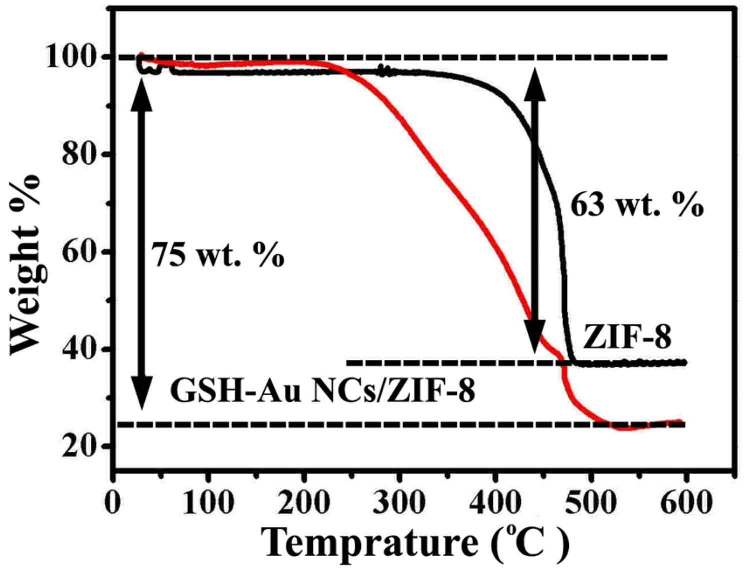

Fig. S3 TGA analysis of the ZIF-8 (black) and GSH-Au NCs/ZIF-8 (red).

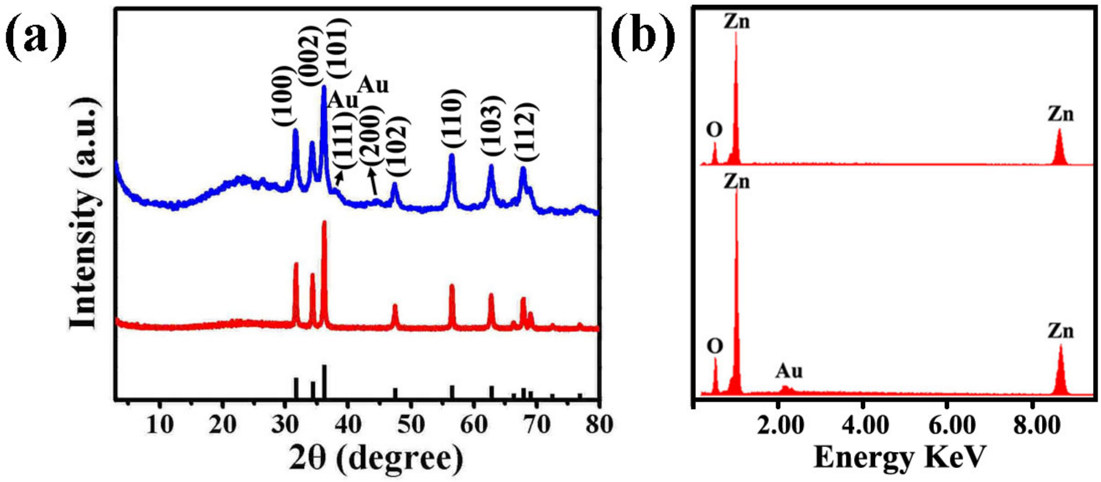

Fig. S4 (a) PXRD patterns of simulated ZnO (black), as-synthesized ZnO (red) and Au/ZnO (blue) NPs. (b) EDX spectra of ZnO (top) and Au/ZnO NPs (bottom) measured on copper substrate.

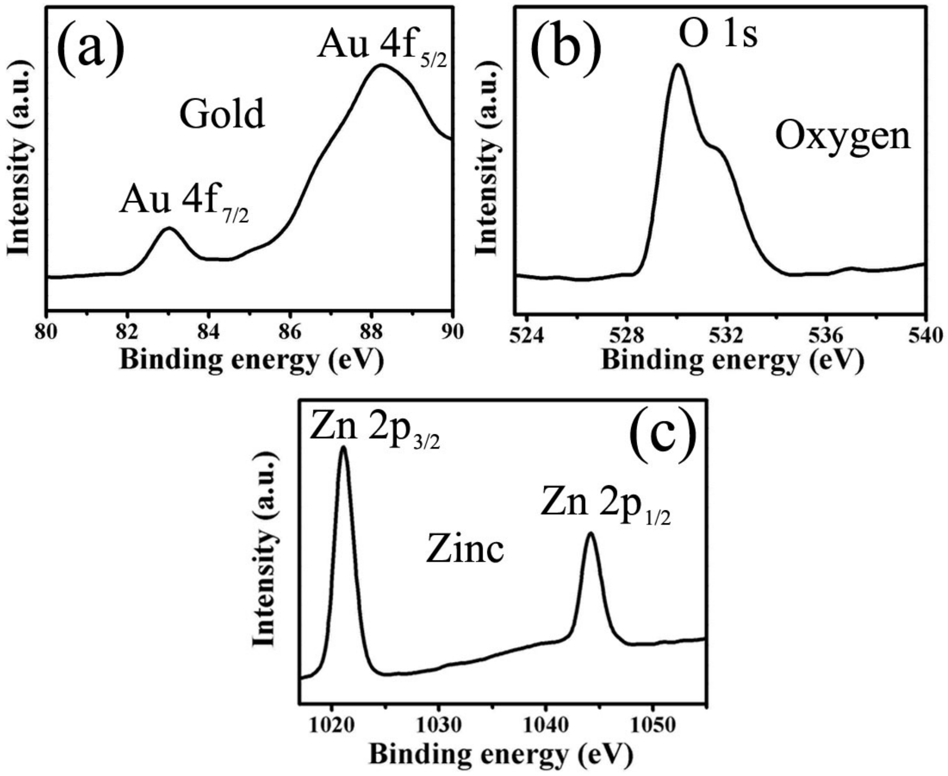

Fig. S5 XPS spectra of Au/ZnO NPs (a) Au, (b) O, (c) Zn.

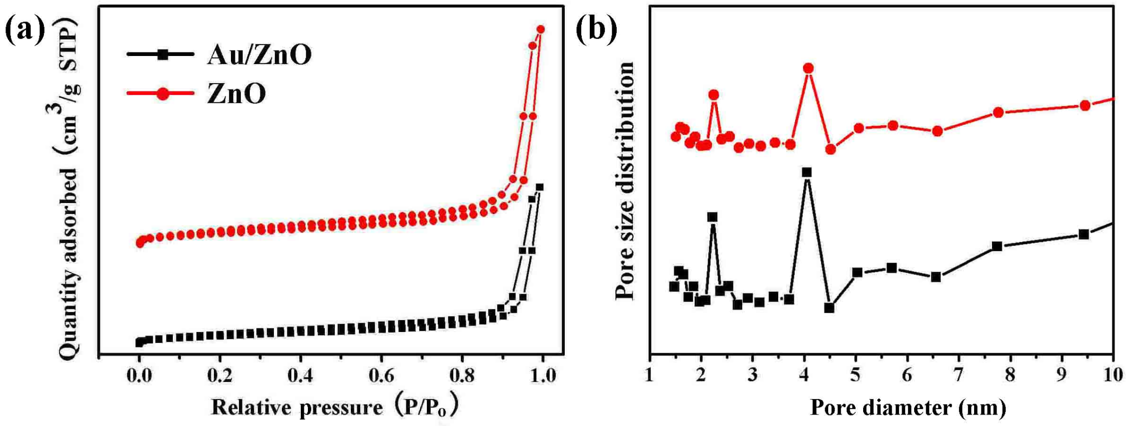

Fig. S6 (a) N_2 sorption isotherms of Au/ZnO NPs (black) and ZnO NPs (red) collected at 77.35 K. (b) Pore size distribution curves of the corresponding Au/ZnO NPs (black) and ZnO NPs (red).

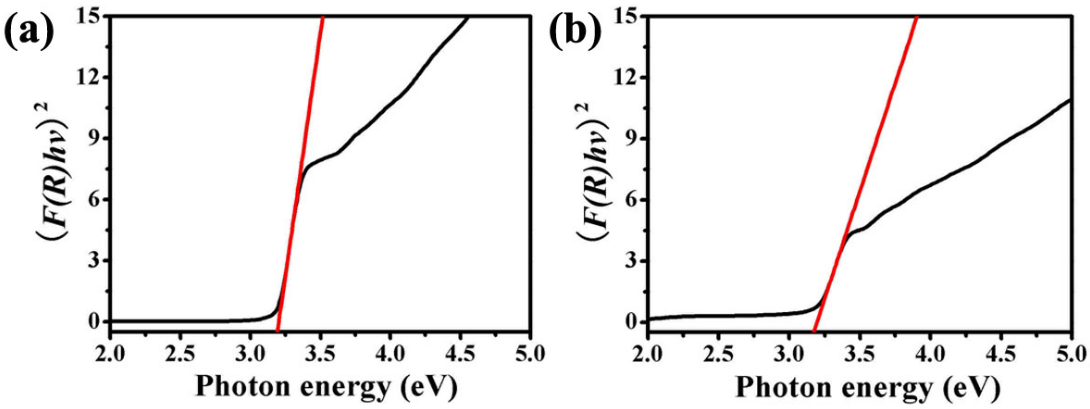

Fig. S7 The plots of $(F(R)h\nu)^2$ *vs*. photon energy for the ZnO NPs (a) and Au/ZnO NPs (b).

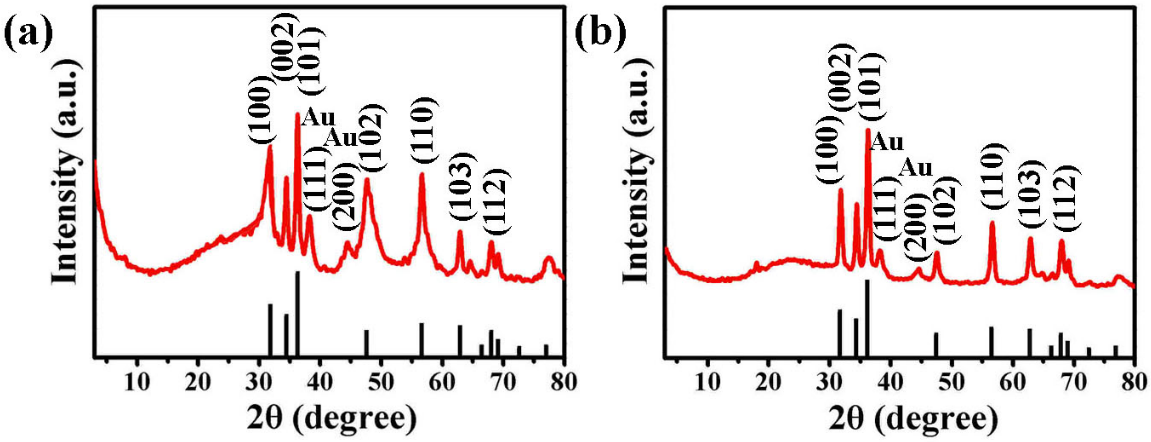

Fig. S8 PXRD images of simulated ZnO (black) and the collected product (red) that obtained after the visible light photocatalytic hydrogen evolution (a) and degradation of RhB under visible light irradiation (b) through centrifugation at 9000 rpm and washing several times to remove the impurity.

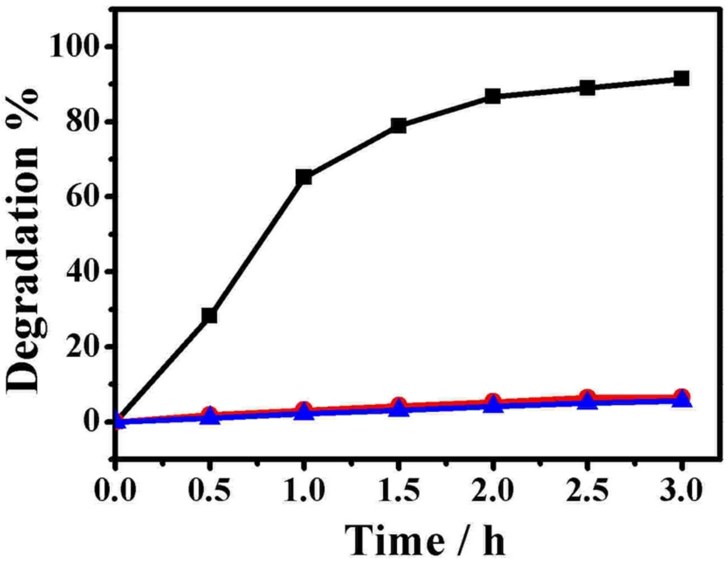

Fig. S9 Degradation rate of RhB under visible light with the as-prepared Au/ZnO NPs (black), ZnO NPs (blue) and commercially available ZnO nanopowder (red).