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Boosting the photocatalytic performance of Cu_2O for hydrogen generation by Au nanostructures and rGO nanosheets

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Preparation of Au NPs, NRs and NBPs

Preparation of Au NPs: The seed solution was made by adding a freshly prepared, ice-cold $NaBH_4$ solution (0.01 M, 0.65 mL) into an aqueous solution composed of $HAuCl_4$ (0.01 M, 0.25 mL) and CTAB solution (0.1 M, 9.75 mL) under vigorous stirring. The resultant seed solution was kept at room temperature for 3 h before use. The CTAB growth solution was prepared by sequential addition of CTAB (0.1 M, 1.95 mL), $HAuCl_4$ (0.01 M, 0.8 mL) and ascorbic acid (0.1 M, 3 mL) into deionized water (38 mL). The seed solution (0.024 mL) was then added into the growth solution, followed by gentle inversion mixing for 10 s. The reaction solution was left undisturbed overnight at room temperature.

Preparation of Au NRs: The seed solution was made by adding a freshly prepared, ice-cold $NaBH_4$ solution (0.01 M, 0.65 mL) into an aqueous solution composed of $HAuCl_4$ (0.01 M, 0.25 mL) and CTAB solution (0.1 M, 9.75 mL) under vigorous stirring. The resultant seed solution was kept at room temperature for 2 h before use. The CTAB growth solution was prepared by sequential addition of $HAuCl_4$ (0.01 M, 2 mL), $AgNO_3$ (0.01 M, 0.4 mL), HCl (1 M, 0.8 mL), and ascorbic acid (0.1 M, 0.32

mL) into an aqueous CTAB solution (0.1 M, 40 mL). The seed solution (0.1 mL) was then added into the growth solution, followed by gentle inversion mixing for 10 s. The reaction solution was left undisturbed overnight at room temperature.

Preparation of Au NBPs: The citrate-stabilized seed solution was made by adding a freshly prepared, ice-cold $NaBH_4$ solution (0.01 M, 0.15 mL) into an aqueous solution composed of $HAuCl_4$ (0.01 M, 0.125 mL), trisodium citrate (0.01 M, 0.25 mL), and DI water (9.25 mL) under vigorous stirring. The resultant seed solution was kept at room temperature for 3 h before use. The CTAB growth solution was prepared by sequential addition of $HAuCl_4$ (0.01 M, 2 mL), $AgNO_3$ (0.01 M, 0.4 mL), HCl (1 M, 0.8 mL), and ascorbic acid (0.1 M, 0.32 mL) into an aqueous CTAB solution (0.1 M, 40 mL). The seed solution (0.32 mL) was then added into the growth solution, followed by gentle inversion mixing for 10 s. The reaction solution was left undisturbed overnight at room temperature. Then the as grown Au NBP solution (40 mL) of a certain size was centrifuged at 6800 rpm for 10 min. The precipitate was re-dispersed in a CTAC solution (0.08 M, 30 mL), which was followed by subsequent addition and mixing of $AgNO_3$ (0.01 M, 8 mL) and ascorbic acid (0.1 M, 4 mL). The resultant solution was kept in an oven at 60 °C for 4 h, during which Ag was overgrown on the Au nanocrystals to produce bimetallic Au/Ag products. The bimetallic Au/Ag products were then centrifuged at 4000 rpm for 10 min. The precipitate was re-dispersed in CTAB (0.05 M, 30 mL) and left undisturbed overnight at room temperature, and then the supernatant was discarded. The remaining Au/Ag heteronanorods were re-dispersed in water (20 mL). The resultant solution was subsequently mixed gently with $NH_3 \cdot H_2O$ (30 wt%, 0.4 mL) and H_2O_2 (0.1 M, 0.3 mL) and kept undisturbed for 4 h to remove Ag. The clear supernatant was carefully taken out and centrifuged at 6800 rpm for 10 min. The Au NBP product was re-dispersed in a CTAB solution (0.01 M, 20 mL) for further use.

Characterizations

Scanning electron microscopy (SEM) images were taken on a field emission scanning electron microscope (Regulus8100) with acceleration voltage of 10 kV. Transmission electron microscopy (TEM) images were taken on a transmission

electron microscope (JEM–2100, JEOL, Japan) operated at 200 kV. The high-angle annular dark-field scanning transmission electron microscopy (HAADFSTEM) image, elemental line profiling, and elemental mapping were carried put on an FEI Talos F200X microscope (USA). The crystal structures of the resultant products were characterized by X-ray powder diffraction (XRD) on an Advance D8 instrument (Bruker Corporation, Germany) with Cu Kα (λ=1.54 Å) radiation at a scanning rate of 6°/min. Raman spectroscopy was characterized using a Raman microscope (Raman, DXRTM, Thermo Fisher, America) with laser wavelength at 532 nm. Ultraviolet-visible (UV–vis) absorption spectra were recorded by a Lambda 950 UV–vis-NIR spectrophotometer (Perkin-Elmer, USA). The fluorescence lifetime was measured with steady-state transient fluorescence spectrometer (QM8000, PTI, Japan).

Photocatalytic activity measurement

The photocatalytic behaviors were evaluated by the degradation of MO in an aqueous solution under visible light irradiation (λ>400 nm). Typically, 5 mg of photocatalysts were dispersed into MO aqueous solution (30 mg/mL, 50 mL) by ultrasonic treatment. Then, the solution was stirred for 1 h in the dark to achieve adsorption−desorption equilibrium. After that, the photocatalytic measurement was carried out under visible and infrared light using a 300 W Xe arc lamp (PLS-SXE300UV, Beijing Perfect Light Co., Ltd.) with a UV cutoff filter to cut off light of wavelength less than 400 nm. After illumination, aliquots (5 mL) were taken out every 5 min and centrifuged to remove the photocatalytic particles. The absorption of the supernatant MO solution was determined spectrophotometrically at λmax=464 nm.

Electrochemical impedance spectra (EIS) measurement

The samples with same concentration were collected on cellulose membranes by suction filtration. Before testing, the cellulose membranes were pressed at 10 MPa for 1 min and cut into 0.5×0.5 cm pieces. A mixture containing 10mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) and 0.5M KCl was used as electrolyte, while a Pt foil and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively. The EIS measurement was performed with an electrochemical

workstation (CHI760E, Chenhua, Shanghai, China) in a frequency region from 10 MHz to 100 mHz and an AC amplitude of 5 mV at room temperature.

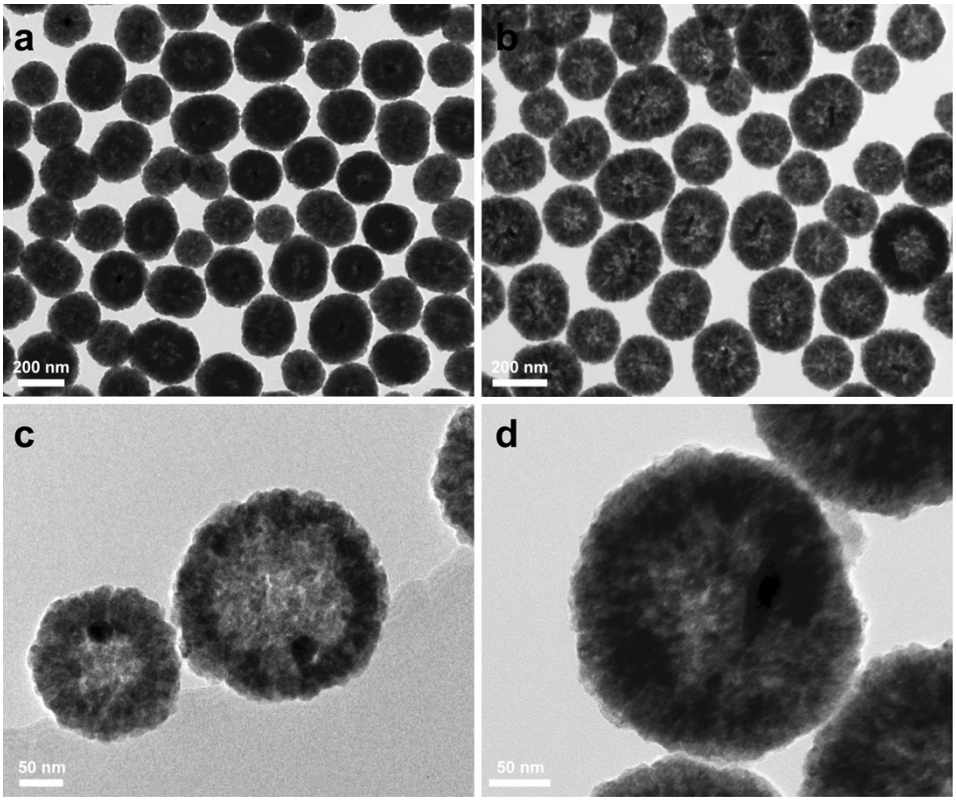

Figure S1. (a-d) TEM images of solid Au NR@Cu_2O, yolk-shelled Au NR@Cu_2O, yolk-shelled Au NP@Cu_2O and yolk-shelled Au NBP@Cu_2O, respectively. In the solid core-shelled Au@Cu_2O, Au core locates in middle of the sphere. When cavity occurs in the yolk-shelled Au NBP@Cu_2O, Au core can move and always be found in the side of the sphere.

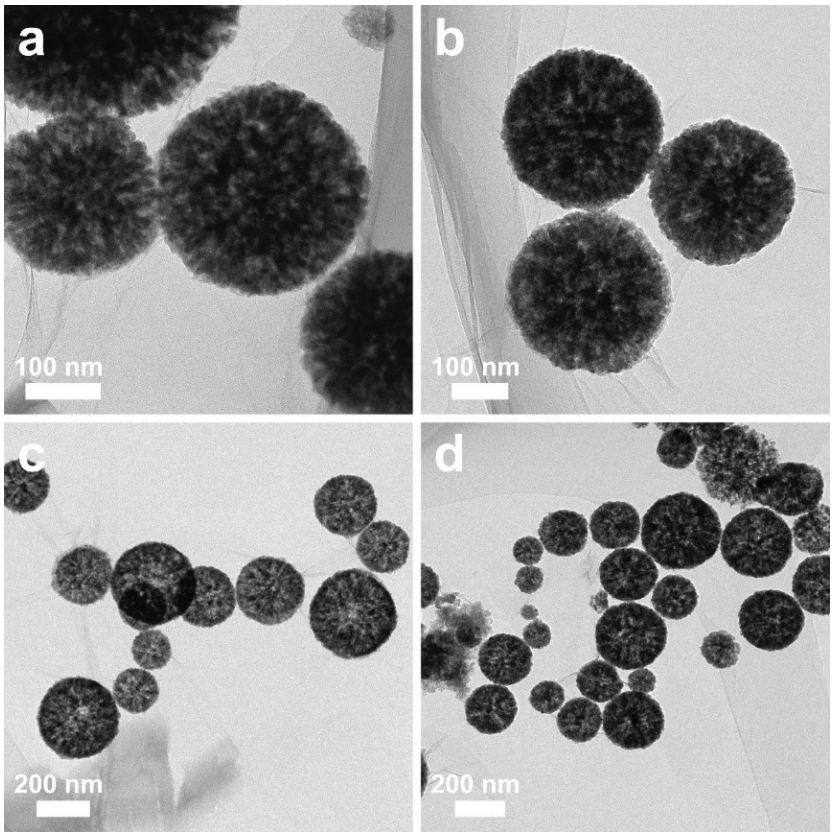

Figure S2. (a-d) TEM images of Cu_2O/rGO composites obtained at 5, 30, 60 and 90 min, respectively.

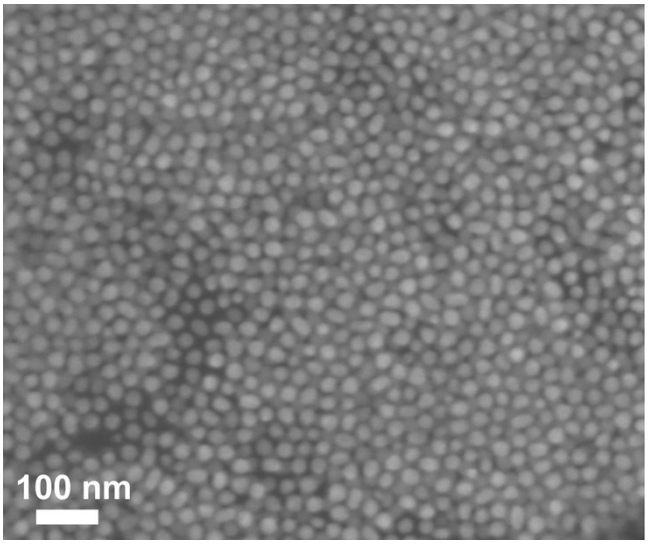

Figure S3. SEM image of Au NPs.

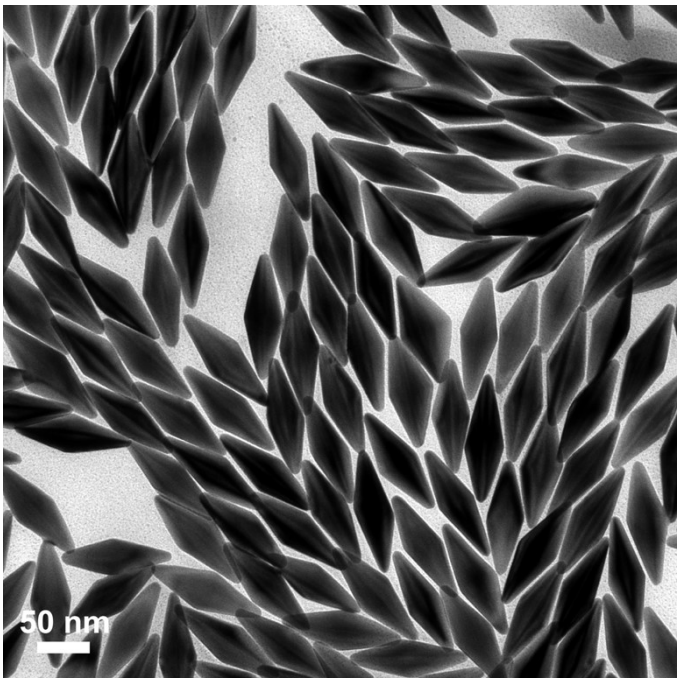

Figure S4. TEM image of Au NBPs.

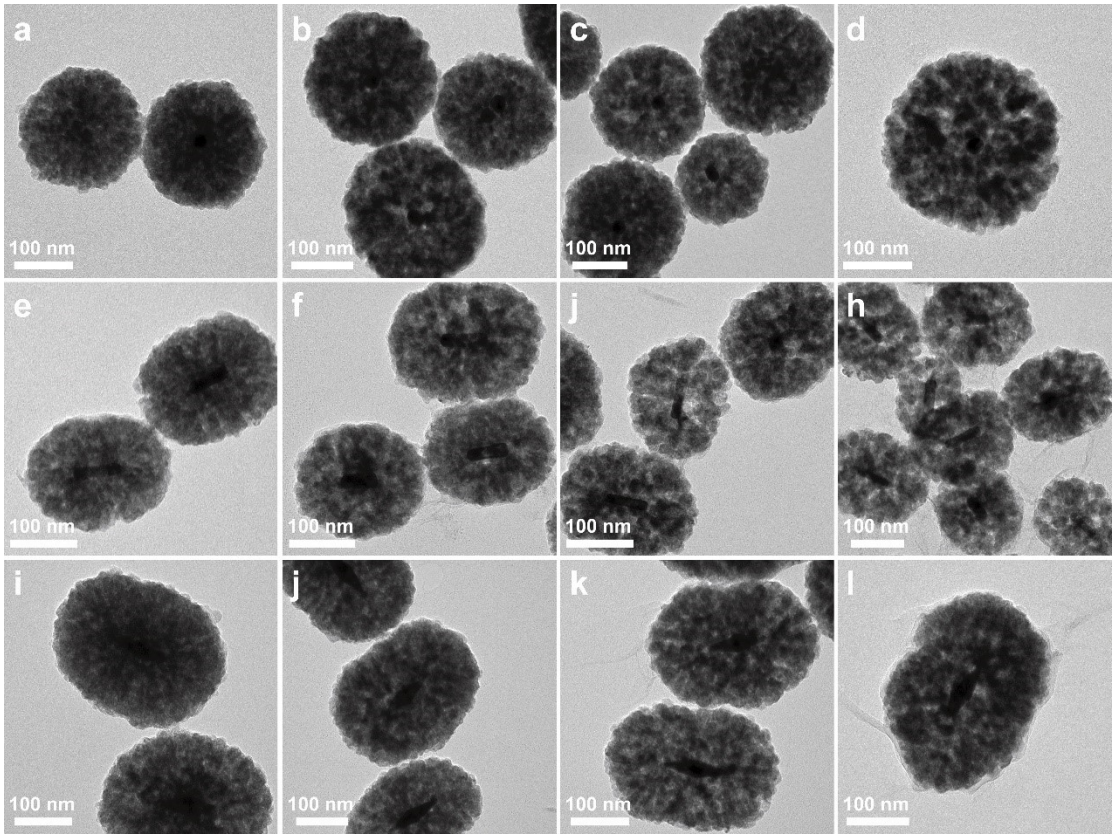

Figure S5. (a-d) TEM images of Au NP@Cu_2O/rGO obtained at 5, 20, 40 and 60 min, respectively. (e-h) TEM images of Au NR@Cu_2O/rGO obtained at 5, 20, 40 and 60 min,

respectively. (i-l) TEM images of Au NBP@Cu_2O/rGO obtained at 5, 20, 40 and 60 min, respectively.

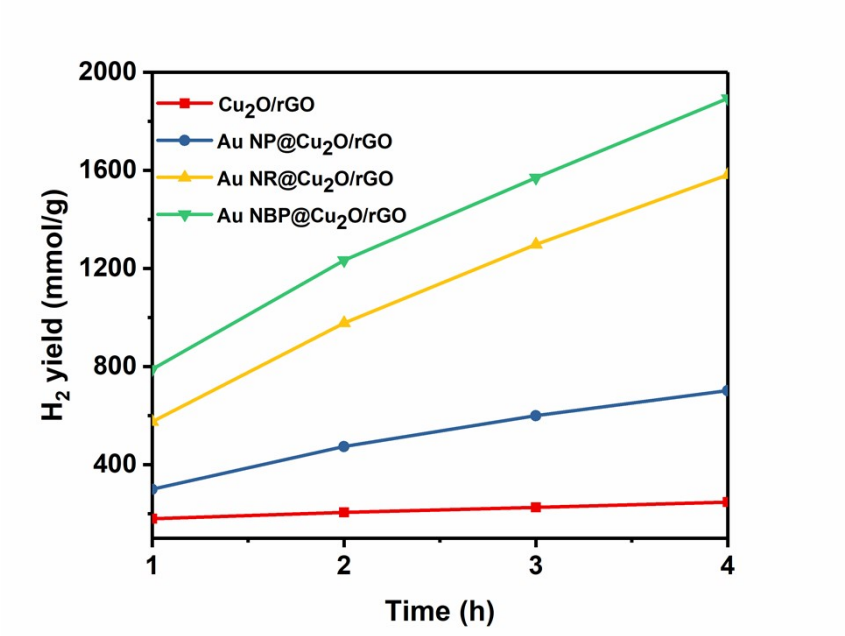

Figure S6. The H_2 yield of Cu_2O/rGO, y-Au NP@Cu_2O/rGO, y-Au NR@Cu_2O/rGO and y-Au NBP@Cu_2O/rGO during 4 hours.

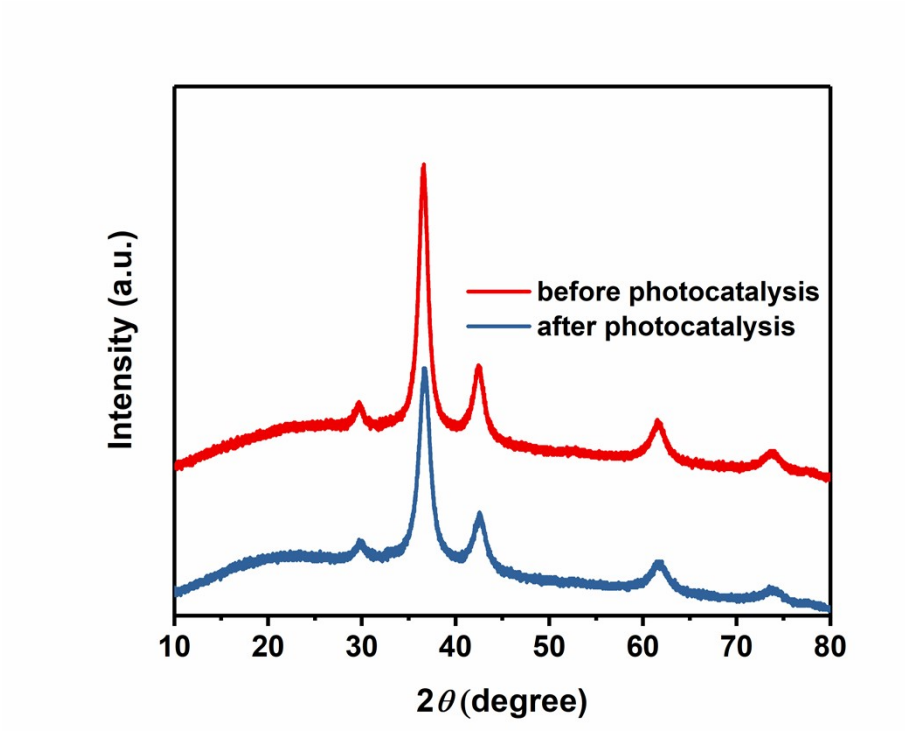

Figure S7. XRD patterns of Cu_2O/rGO composites before and after photocatalysis.

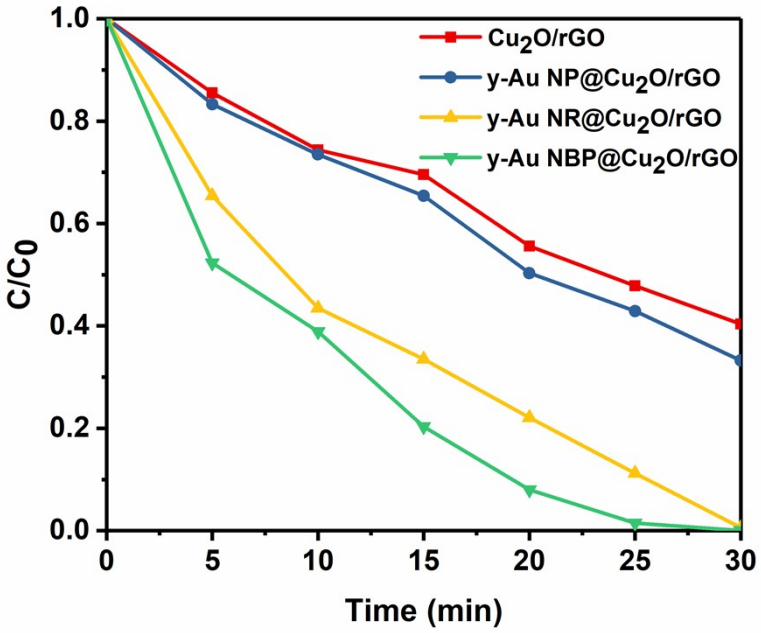

Fig. S8. Photocatalytic degradation of MO in the presence of Cu_2O/rGO, y-Au NP@Cu_2O/rGO, y-Au NR@Cu_2O/rGO and y-Au NBP@Cu_2O/rGO.

Table S1. The photoluminescence decay for y-Au NP@Cu_2O/rGO, y-Au NR@Cu_2O/rGO and y-Au NBP@Cu_2O/rGO, respectively.

Samples	τ_1 (ns)	τ_2 (ns)	χ_1 (%)	χ_2 (%)	τ_{avg} (ns)
Cu_2O/rGO	1.60	47.72	29.65	70.35	34.05
y-Au NP@Cu_2O/rGO	2.20	39.80	45.50	54.50	22.69
y-Au NR@Cu_2O/rGO	1.79	43.61	54.85	45.15	20.67
y-Au NBP@Cu_2O/rGO	1.89	35.04	61.46	38.54	14.67