Supporting Information

Fast Synthesize of Nanoporous Cu/Ag Bimetallic Triangular Nanoprisms by Galvanic Replacement for Efficient 4-Nitrophenol Reduction

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Experimental Sections

Materials

Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, ≥99.0%), sodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$, ≥99.0%), potassium bromide (KBr, ≥99.0%), sodium borohydride ($NaBH_4$, ≥99.0%), polyvinyl pyrrolidone (PVP, K30), L-ascorbic acid (L-AA, ≥99.7%), citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, ≥99.5%), silver nitrate ($AgNO_3$, ≥99.8%) and 4-nitrophenol (4-NP, ≥99.0%). All commercial compounds were directly used without purification.

The preparation of Cu NPs

Cu NPs were synthesized by a seed mediated growth method. Firstly, 1.0 mL of $CuSO_4$ (1.0 M) solution and 2.0 mL of PVP (40 mg/mL) solution were added to 6.8 mL of deionized (DI) water. Afterward, 0.2 mL of freshly prepared $NaBH_4$ (0.1 M) was slowly dropped into the solution in 1 min under vigorous stirring and stirred for another 5 min. The solution gradually changed from light blue to yellow-green, indicating the formation of Cu seeds. The freshly prepared Cu nanoparticles were used as seeds for next step.

For the growth of Cu NPs, typically, 1.0 mL of $CuSO_4$ solution (1.0 M) were added into 30 mL DI water, and then the 1.0 mL of sodium citrate (1.0 M) was added directly under magnetic stirring. Afterward, 0.1 mL of KBr and 2.0 mL of fresh prepared Cu seeds were added respectively. The mixture was transferred into a water bath at 80^{o}C. Finally, 1.0 mL of L-ascorbic acid (1.5 M) was dropped into the mixture. After heated at 80^{o}C for 30 min, Cu NPs were collected and centrifuged at 8500 rpm for 5 min, finally, the samples were re-dispersed in 50 mL deionized water.

Synthesis of nanoporous Cu/Ag BTNPs

Cu/Ag BTNPs were synthesized by a galvanic replacement method. Firstly, 5.0 mL of freshly prepared Cu NPs was added into a 20 mL vial, then 0.5 mL of citric acid and 0.5 mL of silver nitrate aqueous solution (0.2 M) were added under ultrasonication at room temperature. After 5 min of reaction, the nanoporous Cu/Ag BTNPs could be obtained. The samples were collected and centrifuged at 8500 rpm for 5 min, and finally re-dispersed in 2 mL DI water.

Catalytic activity

To evaluate the catalytic performance, the reduction of 4-NP was carried out by using Cu/Ag BTNPs and $NaBH_4$ as catalyst and reducing agent, respectively. Typically, 0.5 mL of 4-NP aqueous solution (25 mM) was mixed with 0.5 mL freshly prepared $NaBH_4$ solution (1.25 M, stored in ice bath) and a yellow solution was prepared in a double transparent quartz cuvette. Then 50 μL of Cu/Ag BTNPs sample was injected into the solution. The absorbance was monitored by UV–vis spectrophotometer at different time intervals. The color of solution changed from yellow into colorless, indicating the completely degradation of 4-NP. For the next cycle of catalysis, the catalyst was collected by centrifugation and washed thoroughly with deionized water, and used repeatedly under the same reaction conditions.

Calculation of rate constants k and TOF values

The catalytic efficiency k is the slope coefficient of the following equation:

$$\ln (C_t/C_0) = \ln (A_t/A_0) = -kt$$

where the ratios of C_t to C_0 are obtained from the intensity ratios of classic absorbance of 4-NP (A_t/A_0) at 400 nm. A_0 and A_t are on behalf of the absorbance at the initial

time and the reaction time t.

The turnover frequency (TOF) is regarded as the number of moles of reduced 4-NP per unit time per mole of catalyst.

Calculation of conversion rate

Kinetic rate constant (k) was used to determine the conversion rate list in Fig. 3d with the equation:

$$\text{Conversion rate} = (k_t/k_{0)} \times 100\%$$

The k_0 was the kinetic rate constant of the fresh Cu/Ag BTNPs and the k_t was the kinetic rate constant of the Cu/Ag BTNPs that were recycled. The (t) was the times of recycling.

Characterization of materials

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy-dispersive X-ray (EDX) spectroscopy were carried out by a JEOL JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV. The high angle annular dark field-scanning transmission electron microscopy (HADDF-STEM) images and EDX mapping were performed on the FEI Tecnai G2 F20 transmission electron microscope. The samples were dropped on nickel (Ni) grids for TEM inspection. The structure properties of freeze-dried powders were analyzed by X-ray diffraction (XRD, Panalytical, Netherlands) with Cu Kα (λ = 1.5406 Å) radiation at 40 kV and 20 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a KratosAxis spectrometer with monochromatic Al Ka (1486.71 eV) X-ray radiation (15 kV and 10 mA) and a hemispherical electron energy analyzer. UV-Vis measurements were conducted on a Shimadzu 2550 spectrophotometer.

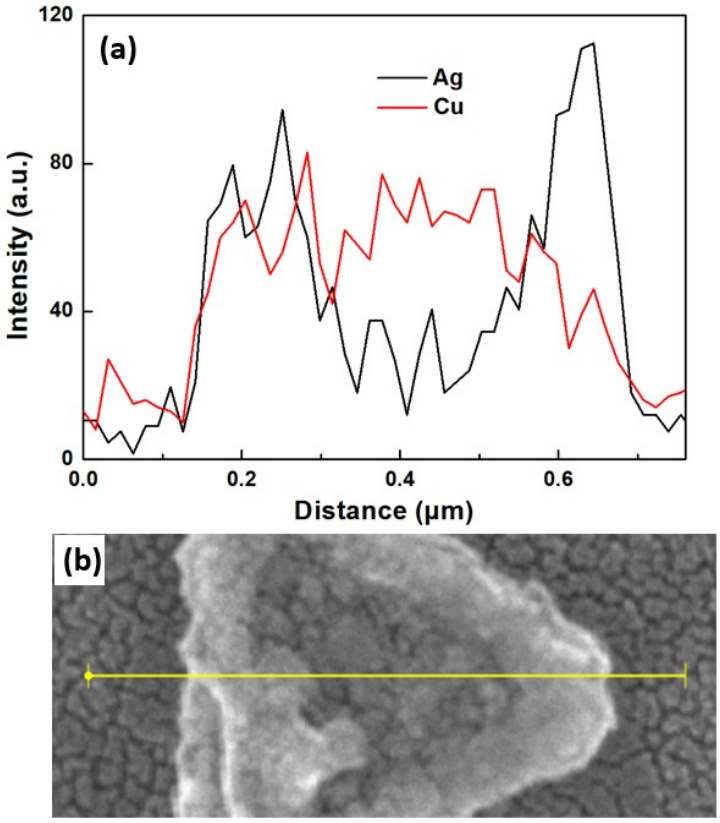

Fig. S1 EDS analysis result (a) along line across the Cu/Ag BTNPs showed in SEM image (b).

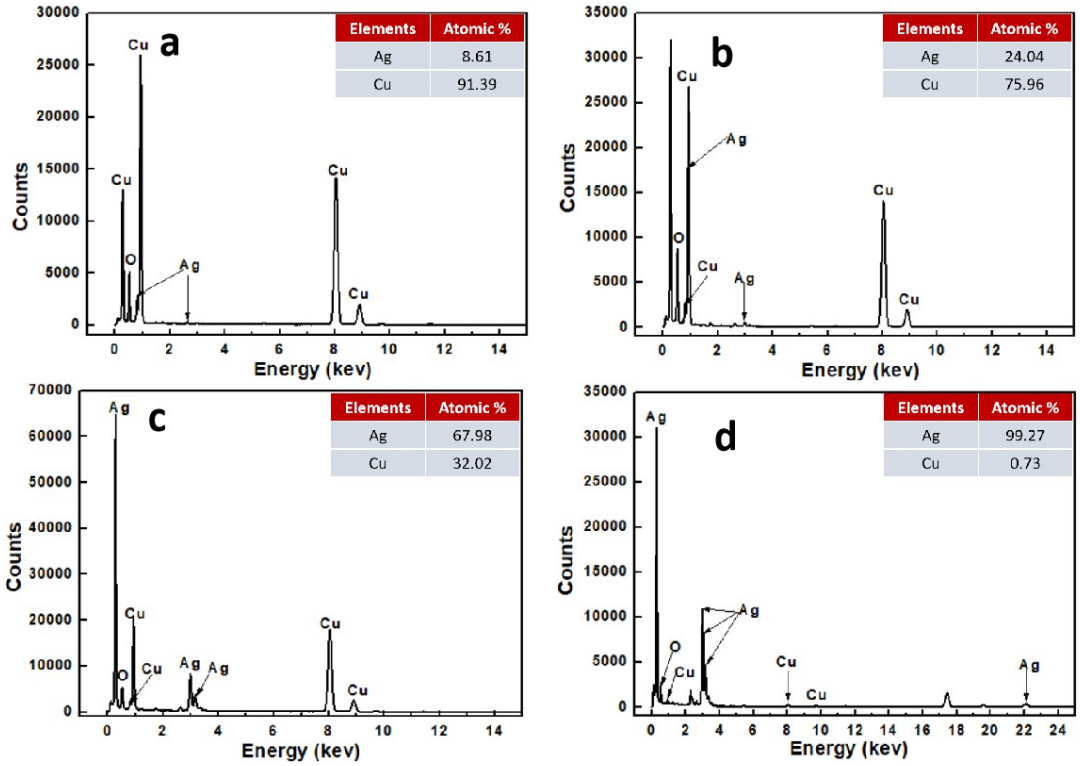

Fig. S2 EDX spectra of Cu/Ag BTNPs by the Cu/Ag molar ratio of (a) 10 : 2, (b) 10 : 5, (c) 10 : 10 and (d) 10 : 20.

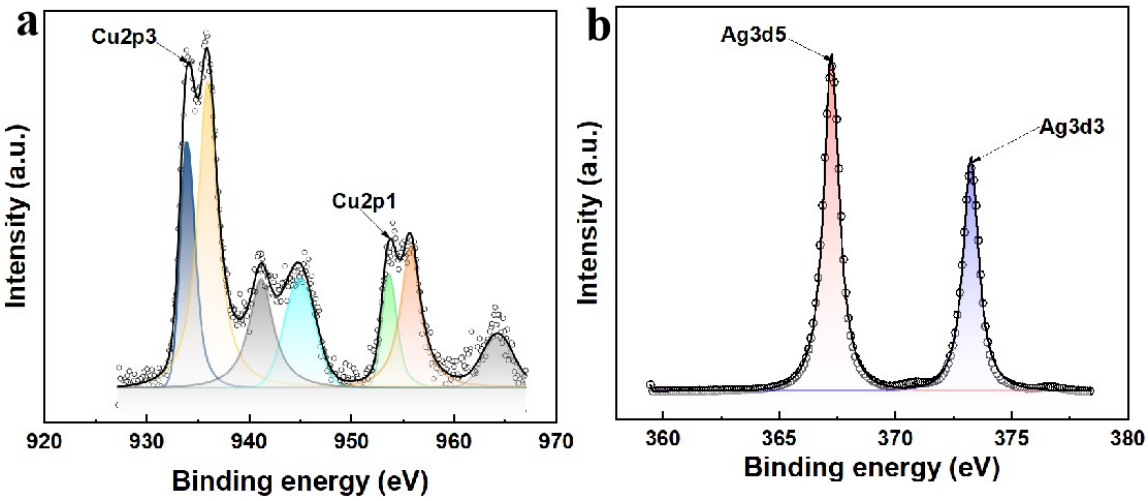

Fig. S3 XPS spectra of (a) Cu and (b) Ag in the sample of Cu/Ag BTNPs.