Supporting Information

Experimental Section

Synthesis of Au_3Cu NCs

In a standard synthesis, 5 mg Cu micro-particles were firstly dispersed in oleylamine (OAm, 6 mL) in a 20 mL vial. After the vial had been capped, the solution was transferred into an oil bath and heated at 200ºC under magnetic stirring. Meanwhile, 50 mg $AuPPh_3Cl$ precursor was dissolved in TOP (5.0 mL), and pumped into the Cu micro-particle OAm solution at the rate of 0.1ml/min. The reaction was kept at 200ºC for 6 hours. As the reaction proceeded, the solution changed its color from pale red to wine red and finally reddish brown. To tune the size of Au_3Cu NCs, the amount of added $AuPPh_3Cl$ was varied from 10 to 100 mg. $AuPPh_3Cl$ was synthesized by reacting $HAuCl_4$. $4H_2O$ with $C_8H_{15}P$ in ethanol according to the litterature.[1] After the reaction, the products were washed with hexane three times.

Electrochemical measurements

To prepare the working electrode, 5 mg Au_3Cu NCs was dispersed in 5 ml hexane to form an ink, and 10 μl of the ink was pipetted onto a glassy carbon (GC) substrate (Ø = 4 mm), which had been buff-polished with an alumina suspension prior to use. Then, 10 μl 0.1% nafion was dropped onto the coated electrode, and dried under an infrared lamp.

Electrochemical experiments were conducted on an Autolab electrochemistry station, which was equipped with a rotating disk electrode (RDE) system (No.1154-R65WHPL) in a thermostatic glass cell. Cyclic voltammetry (CV) was carried out in N_2 saturated solution. A sheet of Platinum was used as the counter electrode. The reference electrode was an Ag/AgCl. The electrochemical reduction reaction of CO_2 was carried out in a CO_2-saturated 0.1 M PBS solution. The CV curves were recorded by scanning the potential from -0.6 V to -1.4 V at a rate of 50 mV s^{-1}. All measurements were conducted at room temperature.

Characterization

Powder XRD patterns were recorded using a diffractometer (X-ray Diffractometer SmartLab(3), Rigaku) operated at 3 kW. SEM images were obtained with an FEI field-emission scanning electron microscope (Sirion XL) operating at an accelerating voltage of 30 kV and a HITACHI field-emission scanning electron microscope (S4800) operating at an accelerating voltage of 3 kV. TEM and HRTEM images were performed at a transmission electron microscopy (TEM, JEM-2100F), and EDX mapping images were performed with an EDX system attached to a JEM-2100F TEM. The adsorption spectra were obtained with an ocean optic UV/Vis spectrometer. Electrochemical measurements were conducted on AutoLab (PGSTAT302N) electrochemical station. Faradaic efficiencies of the major products are expressed by monitoring the product distribution using gas chromatography (Techcomp, GC7900).

Reference

1 Z. Y. Jiang, Q. F. Zhang, C. Zong, B.J. Liu, B. Ren, Z. X. Xie, L. S. Zheng, *J. Mater. Chem.*, 2012, **22**, 18192.

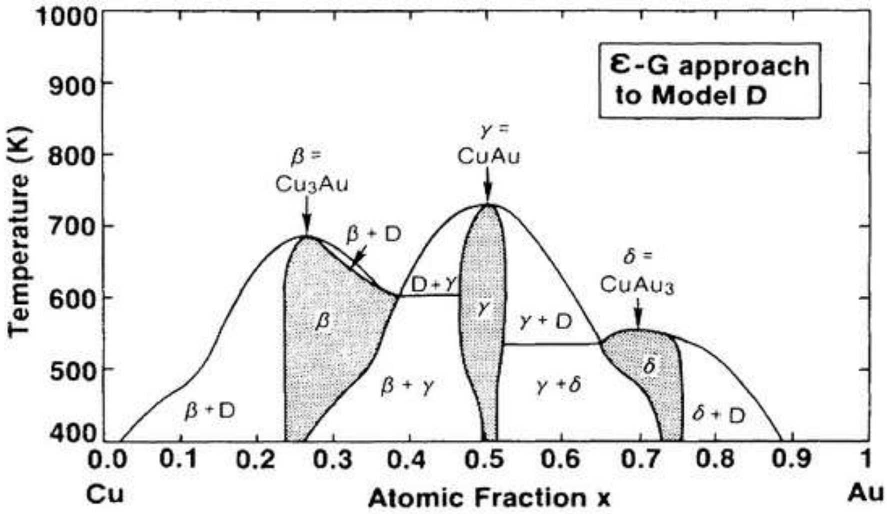
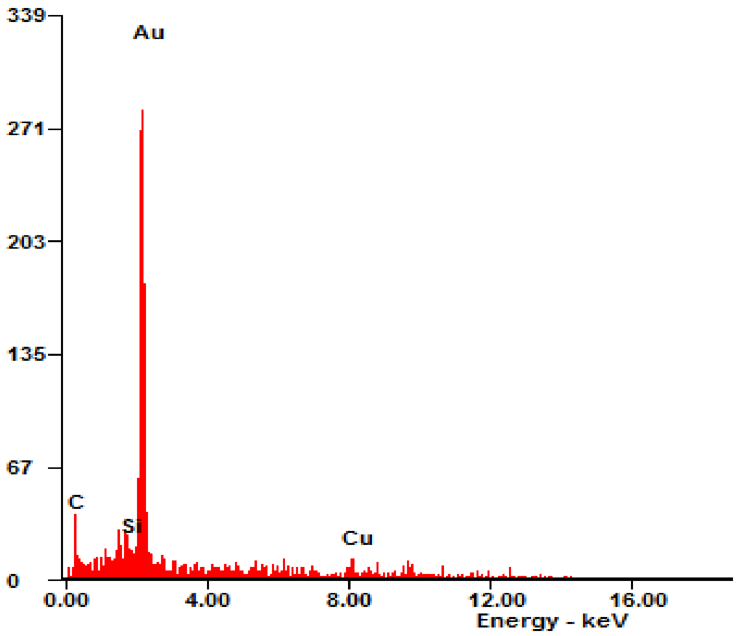


Figure S1. The phase diagram of Au-Cu at different atom ratios.



Element	***Wt %***	***At %***
C K	07.37	51.29
SiK	00.69	02.05
AuM	83.40	35.41
CuK	08.55	11.25

Figure S2. Energy-dispersive X-ray spectroscopy of Au_3Cu NCs.

Figure S3. A photograph of the Cu^{2+}-based complex, formed by adding 20 mg $CuCl_2$ into the solution of oleylamine and heated for 6h under 200℃.

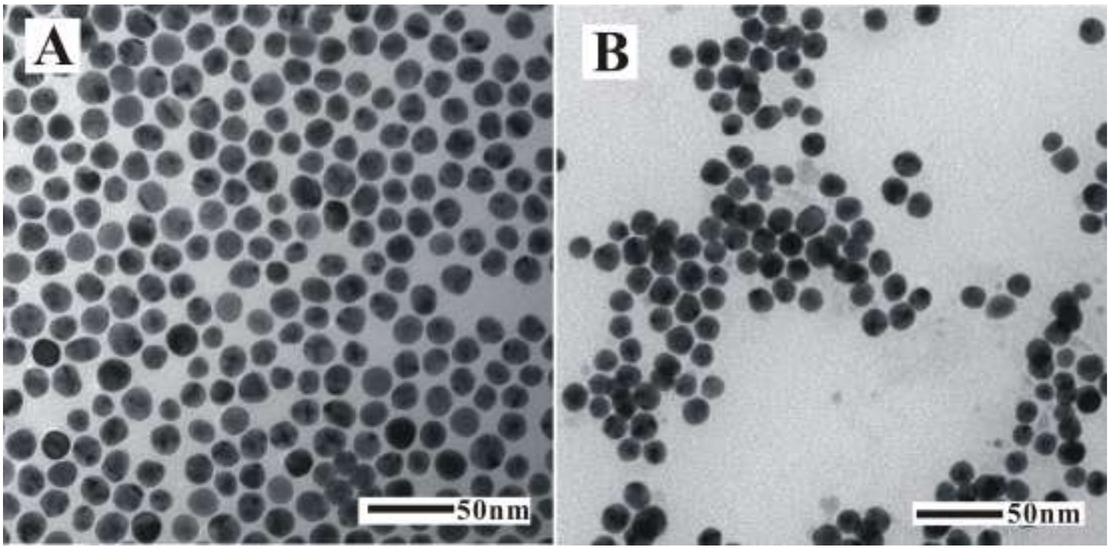


Figure S4. (A) TEM image of Au NCs that were used as seeds; (B) TEM image of the product that were prepared using the standard procedure except that the $AuPPh_3Cl$ and Cu micro-particles were replaced by presynthesized Au NCs and $CuCl_2$, respectively.

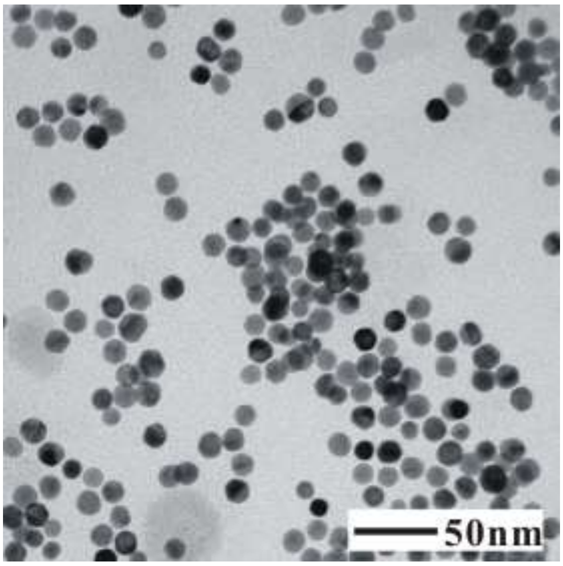


Figure S5. TEM image of the Au_3Cu NCs prepared using the standard procedure except that the Cu micro-particles were replaced by $CuCl_2$.

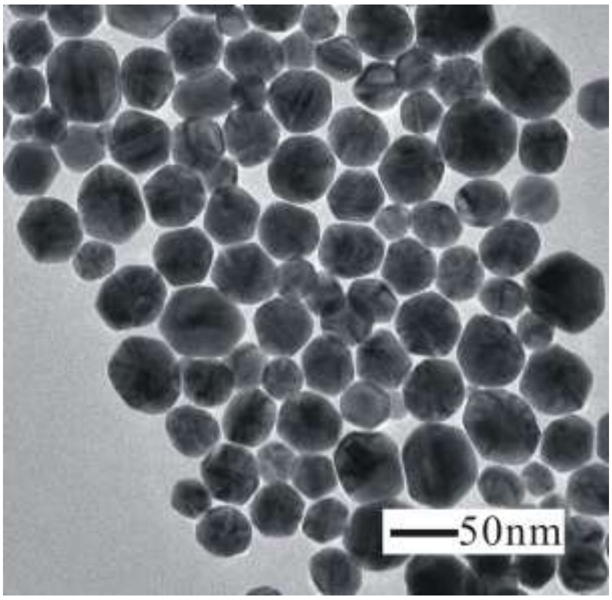


Figure S6. The TEM image of Au particles prepared under the standard procedure but without the addition of Cu micro-particles.

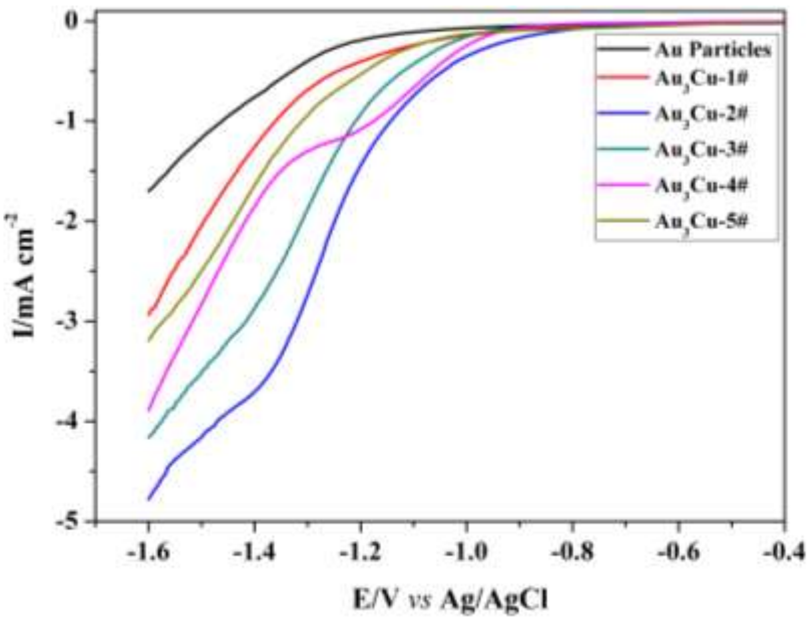


Figure S7. Electroreduction performance of Au_3Cu NCs and Au nanoparticles in N_2-saturated PBS solution.