Supporting Information

Experimental Section

Synthesis of Au$_3$Cu 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 200°C under magnetic stirring. Meanwhile, 50 mg AuPPh$_3$Cl 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 200°C 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$_3$Cu NCs, the amount of added AuPPh$_3$Cl was varied from 10 to 100 mg. AuPPh$_3$Cl was synthesized by reacting HAuCl$_4$•4H$_2$O with C$_8$H$_{15}$P in ethanol according to the literature. After the reaction, the products were washed with hexane three times.

Electrochemical measurements
To prepare the working electrode, 5 mg Au$_3$Cu 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

Figure S1. The phase diagram of Au-Cu at different atom ratios.
<table>
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<tr>
<th>Element</th>
<th>Wt %</th>
<th>At %</th>
</tr>
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<tbody>
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<td>C K</td>
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<td>51.29</td>
</tr>
<tr>
<td>SiK</td>
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<tr>
<td>CuK</td>
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</table>

Figure S2. Energy-dispersive X-ray spectroscopy of Au₃Cu 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$_3$Cl and Cu micro-particles were replaced by presynthesized Au NCs and CuCl$_2$, respectively.
Figure S5. TEM image of the Au₃Cu NCs prepared using the standard procedure except that the Cu micro-particles were replaced by CuCl₂.
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 Au₃Cu NCs and Au nanoparticles in N₂-saturated PBS solution.