Electronic Supplementary Information

# **Compositional dependence of the stability of AuCu alloy nanoparticles**

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## **Experimental details**

## Au<sub>x</sub>Cu<sub>v</sub> NP synthesis

Au<sub>x</sub>Cu<sub>y</sub> NPs were synthesized by reducing HAuCl<sub>4</sub> and Cu(acac)<sub>2</sub> in oleylamine. In a typical synthesis of Au<sub>1</sub>Cu<sub>1</sub>, 0.25 mmol HAuCl<sub>4</sub>, 0.25 mmol Cu(acac)<sub>2</sub>, and 2 mmol 1,2-hexadecanediol were mixed and dissolved in 10 mL oleylamine at 40 °C under an Ar blanket. The solution was then heated to 160 °C at a heating rate of 2 °C min<sup>-1</sup>. The reaction was maintained at 160 °C for 2 h and then cooled down to room temperature. As-prepared AuCu NPs were collected and washed by adding ~100 mL ethanol and following centrifugation. The composition was varied by changing the precursor ratio. Au<sub>x</sub>Cu<sub>y</sub> NPs dispersed well in non-polar solvents such as hexane and toluene.

## Cu synthesis

Cu NPs were synthesized by reducing Cu(acac)<sub>2</sub> in a mixture of oleylamine and oleic acid. Typically, 0.25 mmol Cu(acac)<sub>2</sub> was mixed and dissolved in 10 mL oleylamine and 1 mL oleic acid at 40 °C under an Ar blanket. The solution was then heated up to 160 °C with a heating rate of 2 °C min<sup>-1</sup>. The reaction was maintained at 160 °C for 2 h and then cooled down to room temperature. As-prepared Cu NPs were collected and washed by adding ~100 mL ethanol and following centrifugation.

#### Au synthesis

Au NPs were synthesized by reducing HAuCl<sub>4</sub> in oleylamine. Typically, 0.25 mmol HAuCl<sub>4</sub> was mixed and dissolved in 10 mL oleylamine under an Ar blanket. The solution was then heated up to 120 °C with a heating rate of 2 °C min<sup>-1</sup>. The reaction was maintained at 120 °C for 1 h and then allowed to cool down to room temperature. As-prepared Au NPs were collected and washed by adding ~100 mL ethanol and following centrifugation.

#### Stability with respect to oxidation tests

As-prepared NPs were dissolved in toluene and the solutions were treated at a certain temperature for 24 or 48 hours. The temperature inside the reaction flask was controlled by an oil bath. To keep the solvent from evaporating, a circulator is used to provide ~4 °C cooling water for condenser. At each time stage, a small amount of sample was taken from the solution for recording the surface plasmon absorption.

#### Nanoparticle Characterization

The TEM study was carried out on a JEOL 200CX transmission electron microscope at 120 kV. The samples were prepared by dropping NP solutions onto nickel TEM grids with amorphous carbon film. The UV-Vis absorption spectra were recorded by a Cary 100 UV-Vis

spectrometer. The X-ray diffraction pattern was collected on a PANalytical X'pert Pro with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). The samples were prepared by dropping highly concentrated NP solution onto glass slides. The composition of nanoparticles was determined by ICP-MS. The EDS analysis on single nanoparticles was conducted on a JEOL 2010F transmission electron microscope at 200 kV. The sample was prepared on a Ni TEM grid.

## Electrochemical Measurements

The nanoparticles were loaded onto Vulcan carbon (XC-72) with a mass ratio of 40 wt% and then washed with isopropanol for three times to remove excess surfactant. As-prepared catalysts were dispersed in de-ionized water to give a catalyst ink solution of 1 mg/mL. 10  $\mu$ L ink solution was dropped onto a glass carbon electrode (GCE, 5mm in diameter) and then dried slowly in a water vapor to form a flat thin film fully covering the surface of GCE. The electrochemical measurements were performed on a Pine Instrument. A Pt wire and a saturated calomel electrode (SCE, Analytical Sensor, Inc.) were used as the counter electrode and the reference electrode, respectively. The cyclic voltammograms of catalysts were recorded in Ar- and CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> with a scan rate of 10 mV/s at the potential window from -1.3 to 0.7 V (vs RHE). The electrolyte has a pH of 7.6 at room temperature and the potential was calibrated to versus the reversible hydrogen electrode (RHE) by a factor of 692 mV.

## **Tables and Figures**

Table S1. Elemental	composition	determined	by ICP-MS.
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Sample	Au <sub>2</sub> Cu <sub>1</sub>	Au <sub>1</sub> Cu <sub>1</sub>	$Au_1Cu_2$
Atomic% Au	64.4	47.2	33.9
Atomic% Cu	35.6	52.8	66.1
Ratio Au:Cu	1.8:1	1:1.1	1:1.9

#### Table S2. Oxidation rate constants.

Sample	Au	Au <sub>2</sub> Cu <sub>1</sub>	Au <sub>1</sub> Cu <sub>1</sub>	$Au_1Cu_2 \\$	Cu
<i>k</i> <sub>A</sub> (OD min <sup>-1</sup> )	0	0	1.26X10 <sup>-4</sup>	2.16X10 <sup>-3</sup>	2.61X10 <sup>-2</sup>
<i>k</i> ₄ (nm min⁻¹)	0	0.0121	0.0297	0.105	2.07



**Figure S1**. TEM images and size histograms of Au<sub>2</sub>Cu<sub>1</sub> (a,d), Au<sub>1</sub>Cu<sub>1</sub> (b,e), and Au<sub>1</sub>Cu<sub>2</sub> (c,f) NPs.



Figure S2. TEM images and size histograms of Au (a,c) and Cu (b,d) NPs.



Spot	Element	Weight%	Atomic%
1	Cu K	26.06	52.22
	Au L	73.94	47.78
2	Cu K	28.98	55.85
	Au L	71.02	44.15
3	Cu K	29.20	56.11
	Au L	70.80	43.89

Figure S3. EDS elemental analysis results on single nanoparticles (Au<sub>1</sub>Cu<sub>1</sub>).



Figure S4. XRD patterns of Au<sub>2</sub>Cu<sub>1</sub>, Au<sub>1</sub>Cu<sub>1</sub>, and Au<sub>1</sub>Cu<sub>2</sub> NPs.



**Figure S5.** XRD patterns of carbon supported  $Au_2Cu_1$  before and after oxidation in air. The d-spacing (*a*) shifted from 4.026Å to 4.064 Å, indicating that the oxidation leads to the segregation of copper oxides on the surface and depletes Cu in the nanoparticle core and thus the d-spacing of remaining Au core shifts toward the value of pure Au.



Figure S6. Photos of the  $Au_1Cu_1$  solution before oxidation (1), after oxidation for 5, 10, 30, 60, 120, 300, 600, and 1440 min (from 2 to 9).



**Figure S7**. TEM images of NPs after oxidation: a) Au, b)  $Au_2Cu_1$ , c)  $Au_1Cu_1$ , d)  $Au_1Cu_2$ , and e) Cu after oxidation at 110°C. f)  $Au_1Cu_1$  after oxidation at 95°C.



**Figure S8** (a) Toluene supernatant of AuCu NPs after stability test at 110 °C; (b) toluene supernatant of Cu NPs after oxidation at 110 °C; (c) copper (II) ions heated in the mixture of oleylamine and toluene; (d) the mixture of oleylamine and toluene.



**Figure S9.** Temperature dependence of oxidation of Au<sub>1</sub>Cu<sub>1</sub>. (a)  $\lambda_{peak}$  as a function of oxidation time for Au<sub>1</sub>Cu<sub>1</sub> at 25°C (circles), 75°C (up triangles), 95°C (down triangles), and 110°C (diamonds). (b) A<sub>peak</sub> as a function of oxidation time for Au<sub>1</sub>Cu<sub>1</sub> at 25°C (circles), 75°C (up triangles), 95°C (down triangles), and 110°C (diamonds).



Figure S10. (a)  $\lambda_{peak}$  of Cu NPs oxidized at 25°C, (b)  $A_{peak}$  of Cu NPs oxidized at 25°C