

## Near-monodisperse Ni-Cu Bimetallic Nanocrystals of Variable Composition: Controlled Synthesis and Catalytic Activity for H<sub>2</sub> Generation

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### Experimental Section

**1. Chemicals.** Nickel(II) acetylacetonate (Ni(acac)<sub>2</sub>, 95%; Sigma-Aldrich), copper(II) acetylacetonate (Cu(acac)<sub>2</sub>, 99.99%; Sigma-Aldrich), oleylamine (OM, tech., 70%; Sigma-Aldrich), 1-octadecene (ODE, 90%; Sigma-Aldrich), sodium borohydride (NaBH<sub>4</sub>, 98%; Sigma-Aldrich), sodium hydroxide (NaOH, GR; EM), dibutyl phthalate (99%; Sigma-Aldrich), and the solvents (analytical grade) including ethanol, methanol, hexanes, and chloroform were used without further purification. Prior to use, oleylamine and 1-octadecene were dehydrated using molecular sieves (deperox/dehydrate; Fluka) for several days.

**2. Synthesis of Ni<sub>1-x</sub>Cu<sub>x</sub> Nanocrystals (Table S1).** Ni(acac)<sub>2</sub> and Cu(acac)<sub>2</sub> in a given amount were pre-dissolved in 1 ml of dry oleylamine at 85 °C in an oil bath. Dry oleylamine and 1-octadecene in a given volume were put into a 50 ml three-necked flask at room temperature. The solvent was heated to 140 °C in a Glas-Col electromantle (60 W; 50 ml) with a Cole-Parmer temperature controller (Digi-sense®), and was evacuated at this temperature for 20 min to remove water and oxygen under magnetic stirring. The solvent was then heated to 230 °C at 10 °C min<sup>-1</sup>. The pre-dissolved metal precursors were injected into the heated solvent inside the flask with a 3 mL plastic syringe in 20 sec, and were allowed to further react for 10 min at this temperature under Ar. When the reaction was complete, an excess of absolute ethanol was added at room temperature to form a cloudy black suspension. This suspension was separated by centrifugation at 4200 rpm for 6 min, and the product was collected.

**3. Fabrication of Langmuir-Blodgett (LB) Films.** Ni<sub>1-x</sub>Cu<sub>x</sub> nanocrystals were washed three times by precipitation/dissolution in hexane (1.5 ml of Ni<sub>1-x</sub>Cu<sub>x</sub> nanocrystal sol in hexane was precipitated by adding 4.5 ml methanol), and re-dispersed in 1.5 ml of hexane with sonication to remove impurities and excess capping ligands. Monolayers of Ni<sub>1-x</sub>Cu<sub>x</sub> nanocrystals were formed by placing drops of the Ni<sub>1-x</sub>Cu<sub>x</sub> nanocrystal chloroform solution onto the water subphase of a LB trough (Nima Technology, M611) at room temperature. Surface pressure was monitored with a Wilhelmy plate, and was adjusted to zero before spreading the nanocrystals. The resulting surface layer was compressed by moving the mobile barrier at a rate of 15 cm<sup>2</sup>/min. At a certain stage of compression, the Ni<sub>1-x</sub>Cu<sub>x</sub> nanocrystal monolayer at the water-air interface was carefully transferred onto continuous carbon-coated copper grids using the Langmuir-Schäffer horizontal lift-off method. Surface coverage was evaluated by counting the particles on the same area of the copper grid. Ni<sub>1-x</sub>Cu<sub>x</sub> nanocrystals were deposited onto Si wafers ((1-1.5) cm × 1 cm) by lift-up of the substrates at a rate of 1 mm min<sup>-1</sup> (Ref.: Zhang, Y.; Grass, M. E.; Habas, S. E.; Tao, F.; Zhang, T.; Yang, P.; Somorjai, G. A. *J. Phys. Chem. C* **2007**, *111*, 12243).

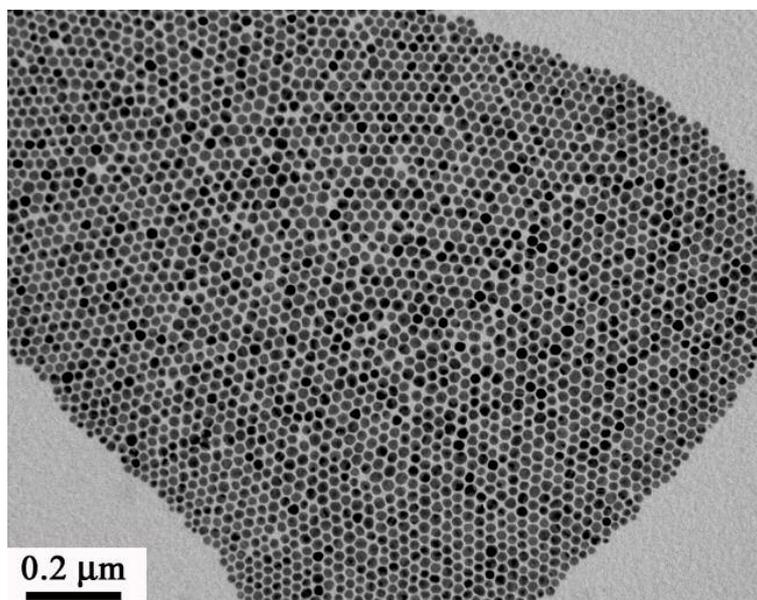
**4. Characterization Methods.** Shape, size and lattice structure of the Ni<sub>1-x</sub>Cu<sub>x</sub> nanocrystals were analyzed using a Philips FEI Tecnai 12 transmission electron microscope (TEM) and a Philips CM200/FEG high-resolution TEM (HRTEM), operated at 100 and 200 kV, respectively. Samples were prepared by placing a drop of Ni<sub>1-x</sub>Cu<sub>x</sub> nanocrystal sol in hexane onto a continuous carbon-coated copper TEM grid. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 GADDS diffractometer using Co-K $\alpha$  radiation ( $\lambda = 1.79 \text{ \AA}$ ). Lattice parameters of the nanocrystals were calculated with the least-squares method.

**5. H<sub>2</sub> Generation Test.** The catalytic hydrolysis of NaBH<sub>4</sub> was carried out batchwise at 1 atm in a 25 ml three-necked flask reactor over the temperature range of 298-308 K in an oil bath. In the beginning, one LB sample was placed in the flask with the Ni<sub>1-x</sub>Cu<sub>x</sub> nanocrystal monolayer facing the bottom, and flushed with Ar for 10 min. Then, 5 ml of 15 wt.% NaOH water solution containing 0.16 g of NaBH<sub>4</sub> was injected into the flask to encapsulate the LB sample completely, and Ar was bubbled through the solution for 10 min. The volumetric amount of H<sub>2</sub> evolved was determined by the liquid-replacement method with dibutyl phthalate as the reservoir solvent. (Ref.: Chung, Y. M.; Ahn, W. S.; Lim, P. K. *J. Catal.* **1998**, *173*, 210. Ingersoll, J. C.; Mani, N.; Thenmozhiyal, J. C.; Muthaiah, A. *J. Power Sources* **2007**, *173*, 450. Niu Y.; Yeung L. K.; Crooks, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 6840). H<sub>2</sub> generation rates were calculated by dividing the collected H<sub>2</sub> volume (after calibration for results over a bare Si wafer) by both the reaction time and the mass of the Ni<sub>1-x</sub>Cu<sub>x</sub> nanocrystals. The mass of the Ni<sub>1-x</sub>Cu<sub>x</sub> nanocrystals was estimated from their surface coverage, crystallite size, and shape (assuming non-overlapping spherical particles).

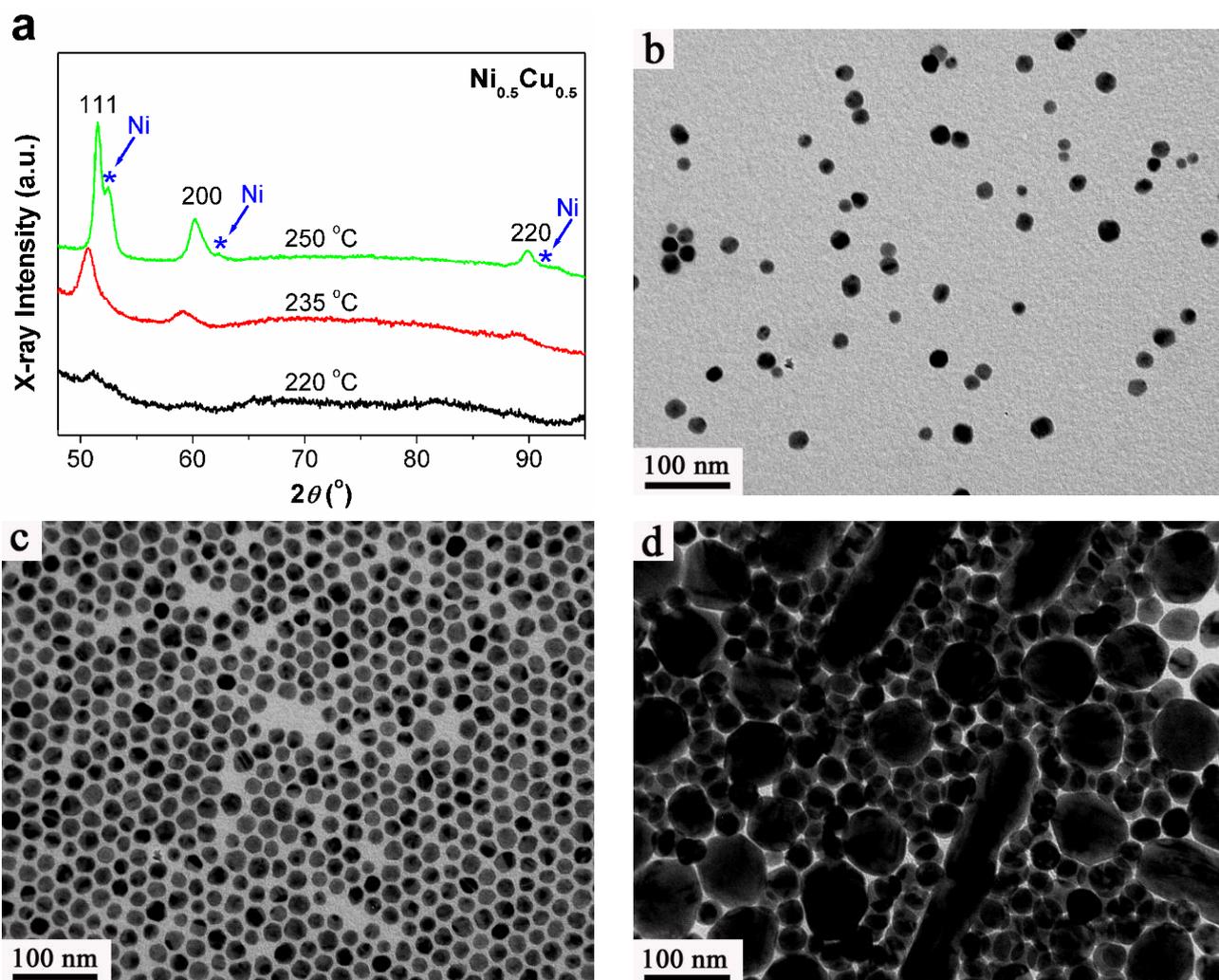
**Table S1: Lattice Constant and Crystallite Size of Ni<sub>1-x</sub>Cu<sub>x</sub> (x = 0-0.8) Nanocrystals Synthesized under Optimal Conditions in Oleylamine (OM)/1-Octadecene (ODE) (total volume: 20 ml).**

	Ni(acac) <sub>2</sub> [mmol]	Cu(acac) <sub>2</sub> [mmol]	ODE/OM	T [°C]	t [min]	a [nm]	Size [nm]
Ni	0.1	0	7.5:12.5	230	10	-	22.3±3.4 <sup>a</sup>
Ni <sub>0.8</sub> Cu <sub>0.2</sub>	0.16	0.04	10:10	230	10	0.3607(9)	27.3±2.4
Ni <sub>0.6</sub> Cu <sub>0.4</sub>	0.12	0.08	10:10	230	10	0.3609(9)	23.1±2.1
Ni <sub>0.5</sub> Cu <sub>0.5</sub>	0.1	0.1	10:10	230	10	0.3613(8)	22.7±1.7
Ni <sub>0.4</sub> Cu <sub>0.6</sub>	0.08	0.12	2.5:17.5	230	10	0.3614(8)	17.8±3.4
Ni <sub>0.2</sub> Cu <sub>0.8</sub>	0.04	0.16	2.5:17.5	230	10	0.3616(8)	19.3±4.4

<sup>a</sup> Standard deviation statistic from 50 nanocrystals.

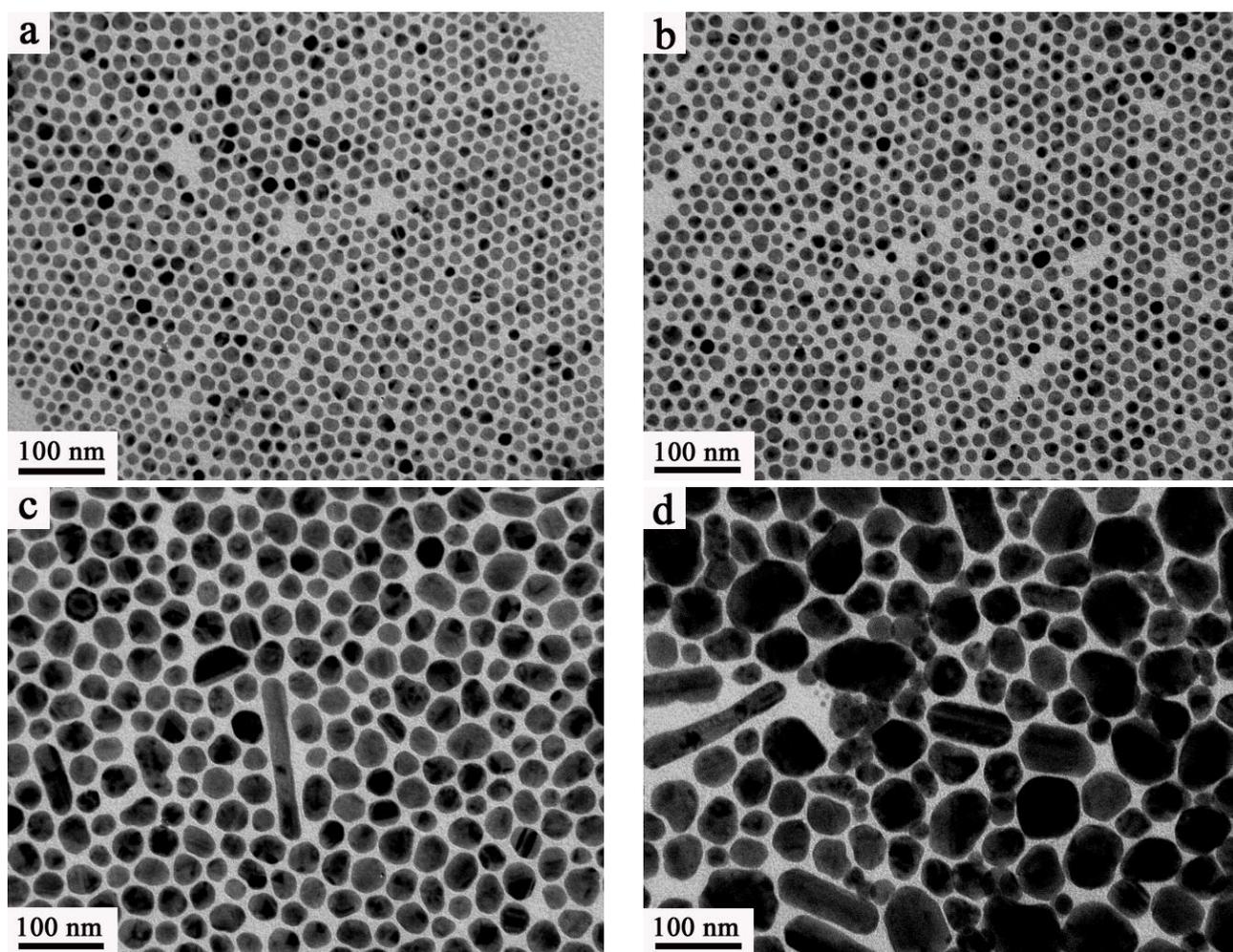


**Figure S1.** Low magnification TEM image of  $\text{Ni}_{0.5}\text{Cu}_{0.5}$  nanocrystals synthesized at 230 °C for 10 min in oleylamine (OM)/1-octadecene (ODE) (total volume: 20 ml) under an Ar atmosphere, using a mix of 0.1 mmol  $\text{Ni}(\text{acac})_2$  and 0.1 mmol  $\text{Cu}(\text{acac})_2$  as precursors (ODE:OM = 10:10).



**Figure S2.** (a) XRD patterns of  $\text{Ni}_{0.5}\text{Cu}_{0.5}$  nanocrystals synthesized at different temperatures for 30 min in 20 ml of oleylamine under an Ar atmosphere, using a mix of 0.1 mmol  $\text{Ni}(\text{acac})_2$  and 0.1 mmol  $\text{Cu}(\text{acac})_2$  as precursors. TEM images of as-synthesized  $\text{Ni}_{0.5}\text{Cu}_{0.5}$  nanocrystals at different temperatures: (b) 220 °C; (c) 235

°C; (d) 250 °C.



**Figure S3.** TEM images of  $\text{Ni}_{0.5}\text{Cu}_{0.5}$  nanocrystals synthesized at 230 °C for 10 min in oleylamine (OM)/1-octadecene (ODE) (total volume: 20 ml) under an Ar atmosphere, using a mix of 0.1 mmol  $\text{Ni}(\text{acac})_2$  and 0.1 mmol  $\text{Cu}(\text{acac})_2$  as precursors: (a) ODE/OM = 0:20; (b) ODE/OM = 5:15; (c) ODE/OM = 12.5:7.5; (d) ODE/OM = 15:5.