

Facile Synthesis of Cu and Cu@Cu-Ni Nanocubes and Nanowires in Hydrophobic Solution in the Presence of Nickel and Chlorine Ions

Huizhang Guo, Yuanzhi Chen,* Hemei Ping, Jiarui Jin and Dong-Liang Peng*

Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, P. R. China

*Corresponding author: yuanzhi@xmu.edu.cn (Y. Chen); dlpeng@xmu.edu.cn (D. L. Peng)

Supplementary information

Experimental Section

Synthesis of Cu NCs using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as precursor. A mixture of 3 ml of oleylamine, 3 ml of dibenzyl ether and 0.5 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was decanted into a three-necked flask and kept under a flow of high-purity argon gas at 110 °C for 20 min with strong magnetic stirring. And then, different amounts of TOP (0.5 or 3 ml) were injected. After stirring for 5 min, the resulting solution was then slowly heated up to 280 °C directly and aged at this temperature for another 30 min and then cooled to room temperature. The products were separated from the solution by centrifugation, washed several times using the mixture of hexane and ethanol or acetone, and dried in a vacuum.

Synthesis of spherical Cu nanoparticles. A mixture of 7 ml of oleylamine, 0.5 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was decanted into a three-necked flask and kept under a flow of

high-purity argon gas at 110 °C for 20 min with strong magnetic stirring before 1 mmol of TOP was injected. After stirring for 5 min, the resulting solution was then slowly heated up to 280 °C directly and aged at this temperature for another 60 min and then cooled to room temperature. The products were separated from the solution by centrifugation, washed several times using the mixture of hexane and ethanol or acetone, and dried in a vacuum.

Ni seed-mediated growth of Cu NPs. In order to confirm the galvanic replacement between Ni and Cu²⁺, Ni NPs were synthesized and then served as seeds to induce the formation of Cu NCs. Specifically, a mixture of 7 ml of oleylamine, 0.4 mmol of Ni(acac)₂ was decanted into a three-necked flask and kept under a flow of high-purity argon gas at 80 °C for 20 min with strong magnetic stirring. And then, 0.3 ml of TOP was injected. After stirring for 5 min, the resulting solution was then slowly heated up to 200 °C directly and aged at this temperature for another 2 h and then cooled to room temperature. The products were separated from the solution by centrifugation. Then the products were mixed with 0.5 ml of oleylamine, 6.5 ml of dibenzyl ether and 0.8 mmol of CuCl₂·H₂O followed by a ultrasonic mixing. Then the mixture was heated up to 210 °C and kept at this temperature for 1h. After cooling down to room temperature naturally, similar cleaning steps as those for Cu nanocubes were applied.

Composition analyses of the time-dependent products. After the complete formation of Cu nanocubes or nanowires by aging at 180 °C for 4 h, the mixed solution was then heated up to 220 °C slowly (5 °C per min). The products aging at

220 °C for different time were taken out from the mixed solution and injected into hexane quickly. Then the compositions of the products were quantitatively analyzed by EDS in SEM.

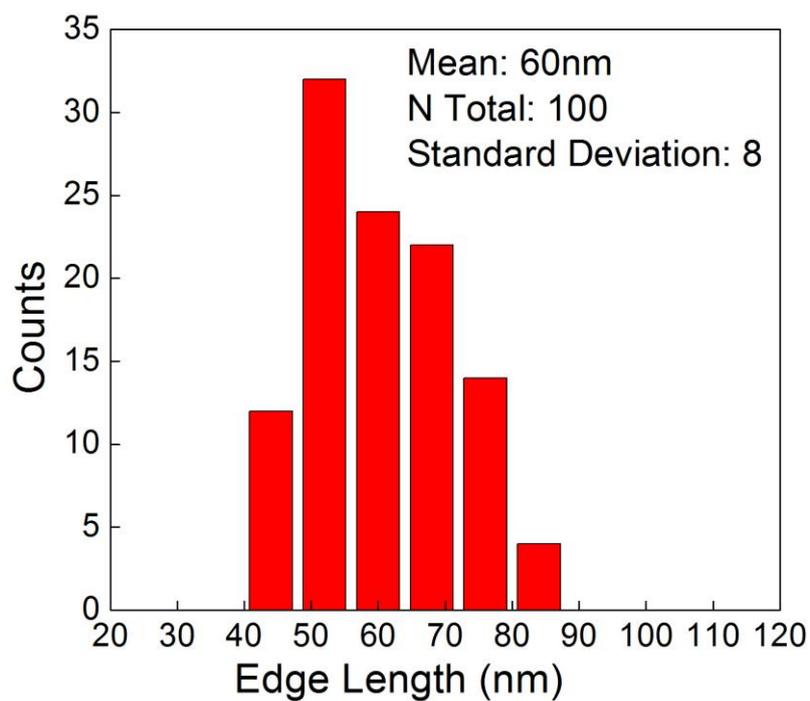


Fig. S1 Statistic result of edge length distribution determined from the typical Cu nanocubes.

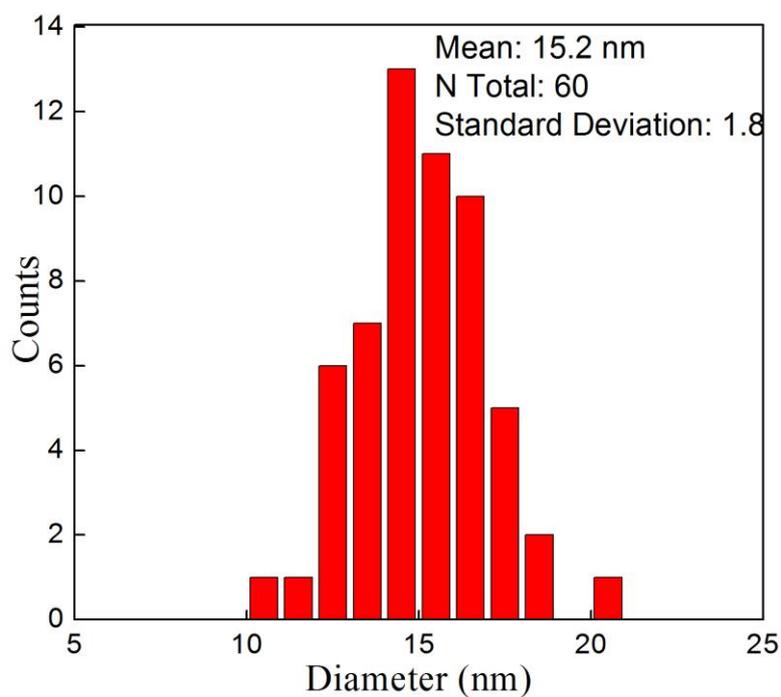


Fig. S2 Statistic result of diameter distribution determined from the Cu nanowires synthesized at 170 °C.

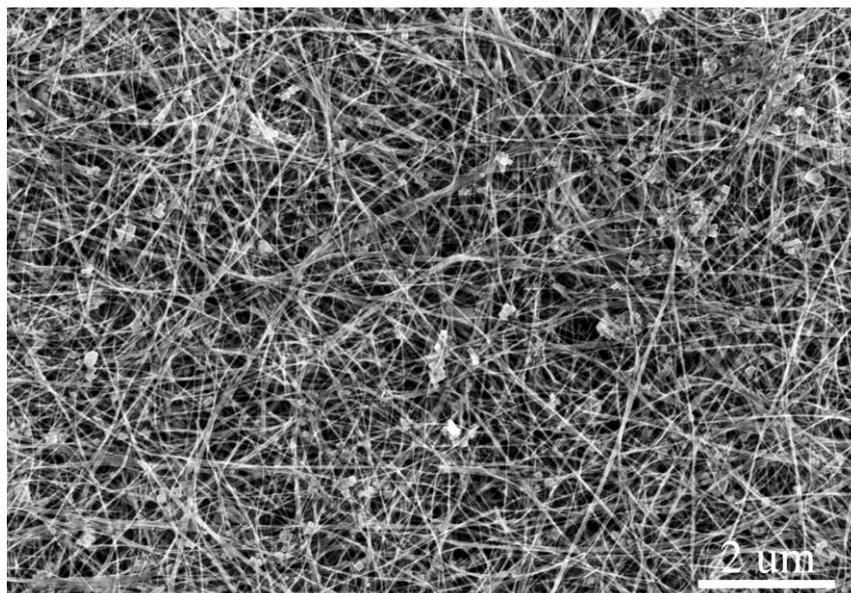


Fig. S3 Low-magnification SEM image of the Cu nanowires synthesized at 170 °C.

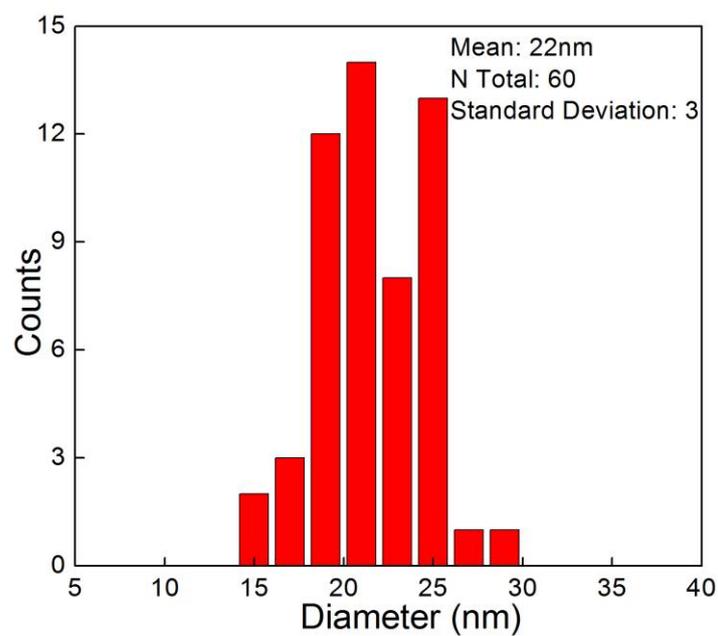


Fig. S4 Statistic result of diameter distribution determined from the Cu nanowires synthesized at 180 °C.

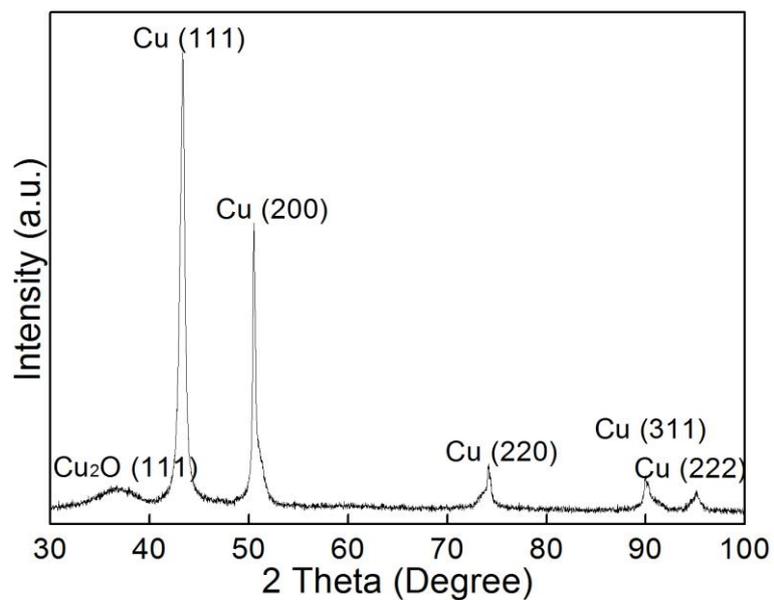


Fig. S5 XRD pattern of the Cu nanowires without dense coating of TOPs.

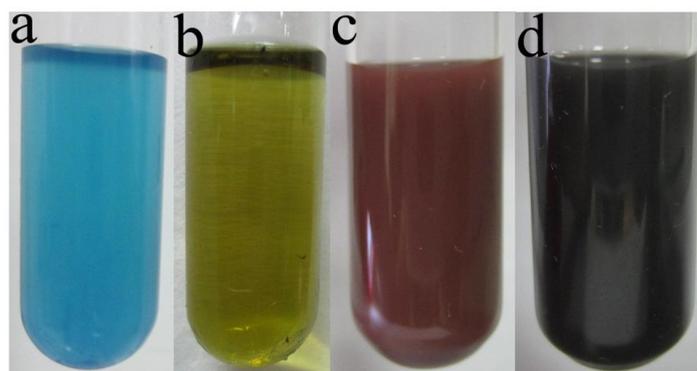


Fig. S6 Photographs of the reaction solutions at different stages: (a) and (b) are the solutions at 80 and 160 °C, respectively. (c) is the colloidal suspension of Cu nanocubes after reacting at 180 °C for 4 h. (d) is the colloidal suspension of Cu@Cu-Ni nanocubes after reacting at 230 °C for 2 h.

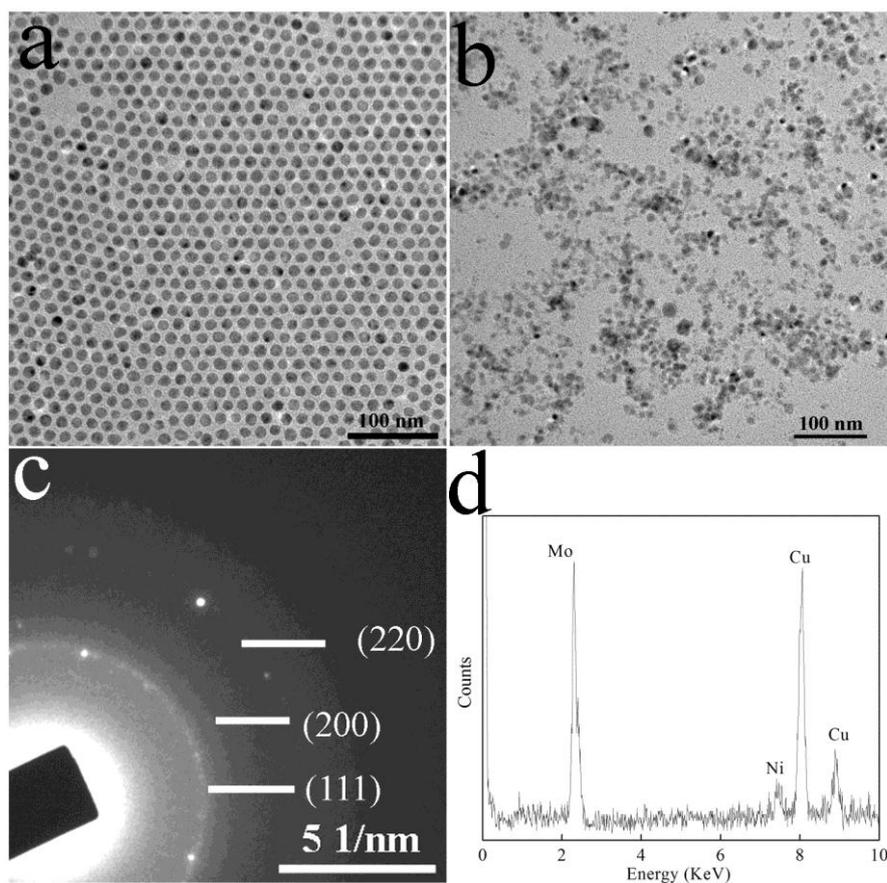


Fig. S7 (a) and (b) are TEM images of Ni nanoparticle seeds and Cu NCs prepared using nanoparticle seeds, respectively. (c) and (d) are SAED pattern and EDS spectrum of the Cu NCs shown in (b) (Mo signal is from the Mo TEM grid).

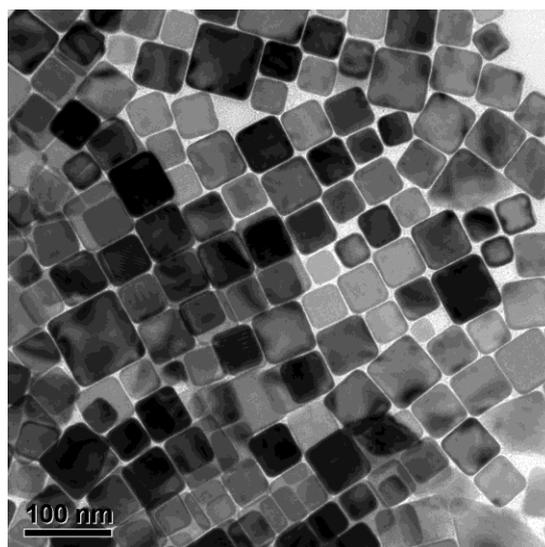


Fig. S8 TEM image of the products obtained at 180 °C for 120 min following the synthetic scheme for Cu nanocubes.

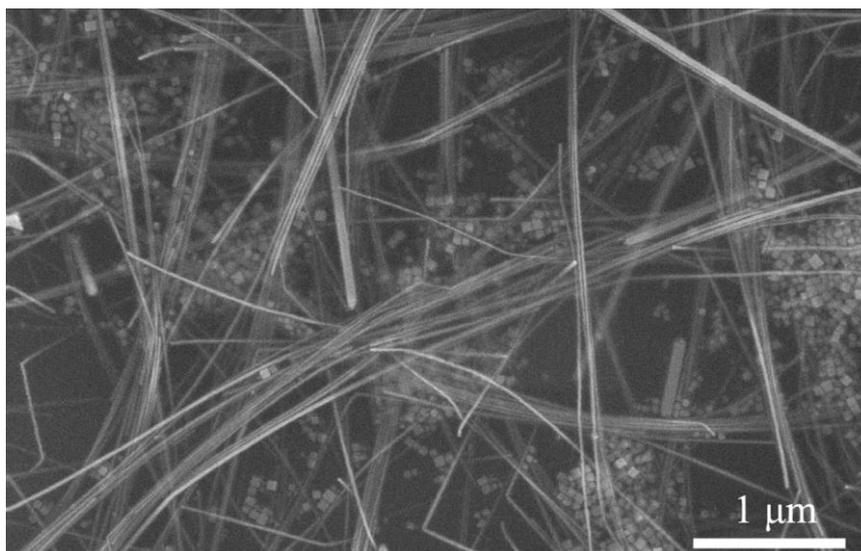


Fig. S9 SEM image of the products synthesized in the presence of 0.1 mmol TOPO rather than TOP. Other reaction conditions were the same as those of the products shown in Figure 1.

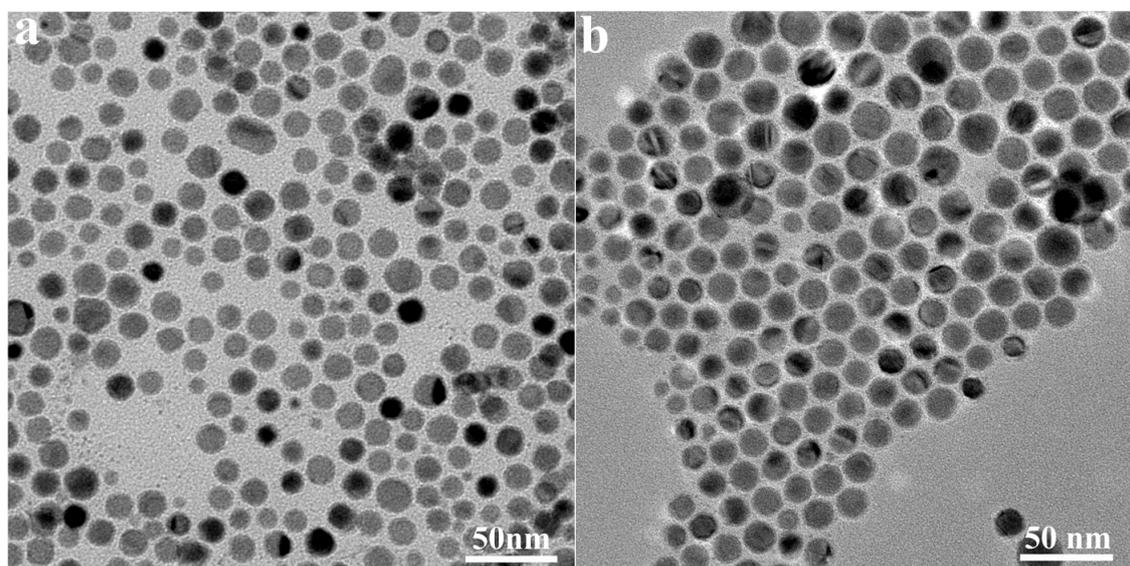


Fig. S10 TEM images of spherical Cu NCs synthesized using copper (II) nitrate as precursor compound with different amount of TOPs: (a) 0.5 ml TOP, (b) 3 ml TOP.

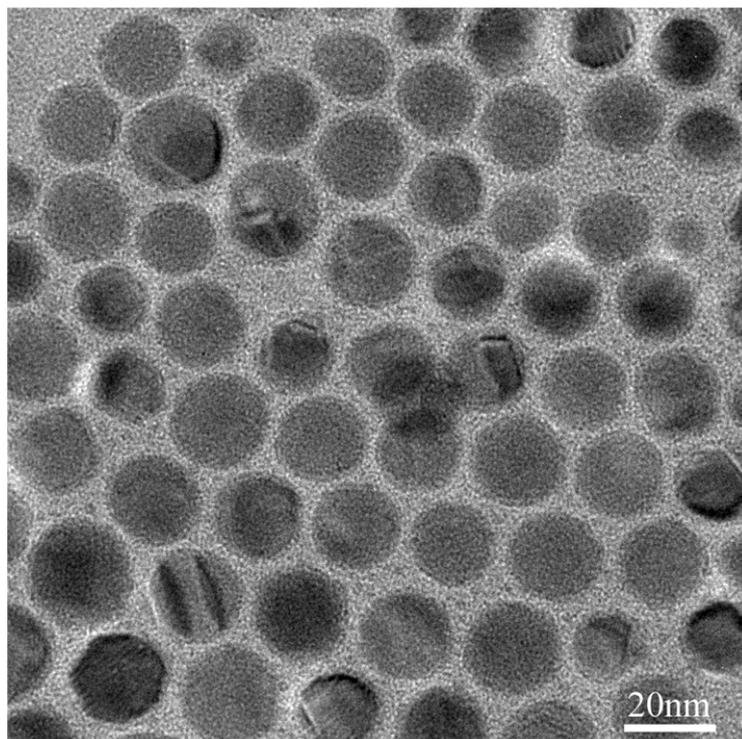


Fig. S11 TEM image of spherical Cu NCs synthesized using copper (II) nitrate as precursor compound.

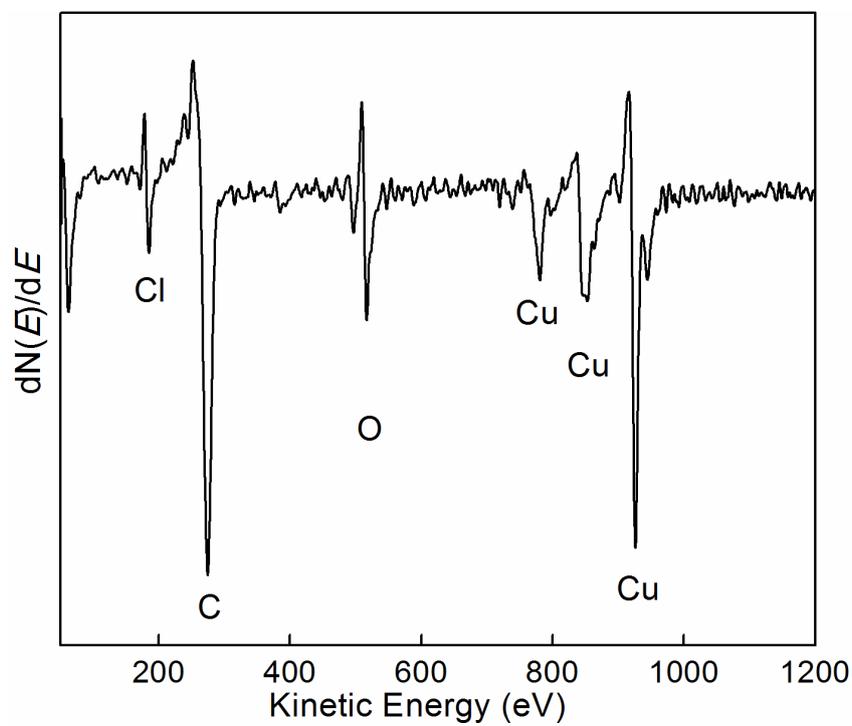


Fig. S12 Auger spectrum in derivative mode ($dN(E)/dE$) obtained from the surface of the as-synthesized Cu nanowires.

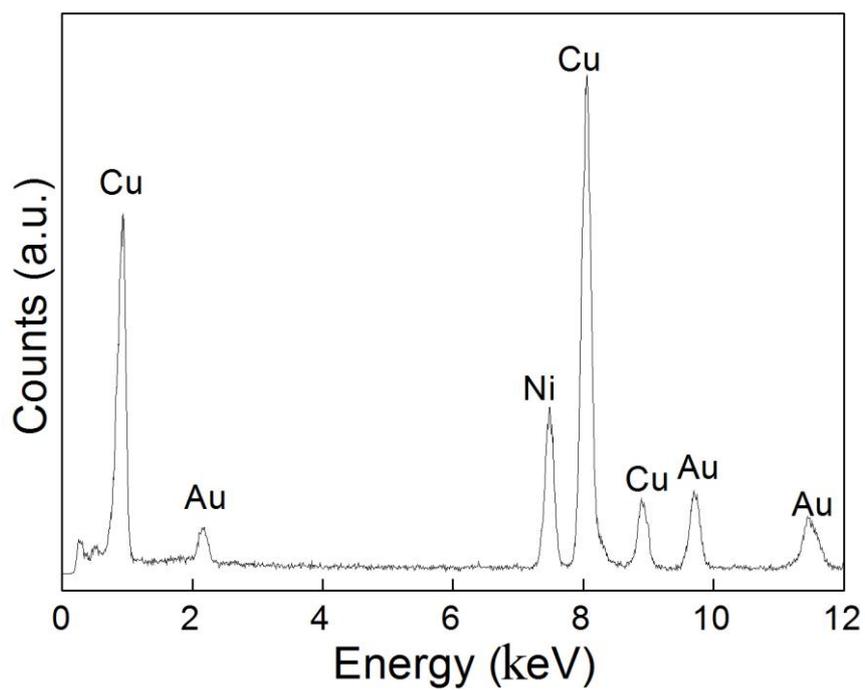


Fig. S13 EDS spectrum of the as-synthesized Cu@Ni-Cu nanocubes.

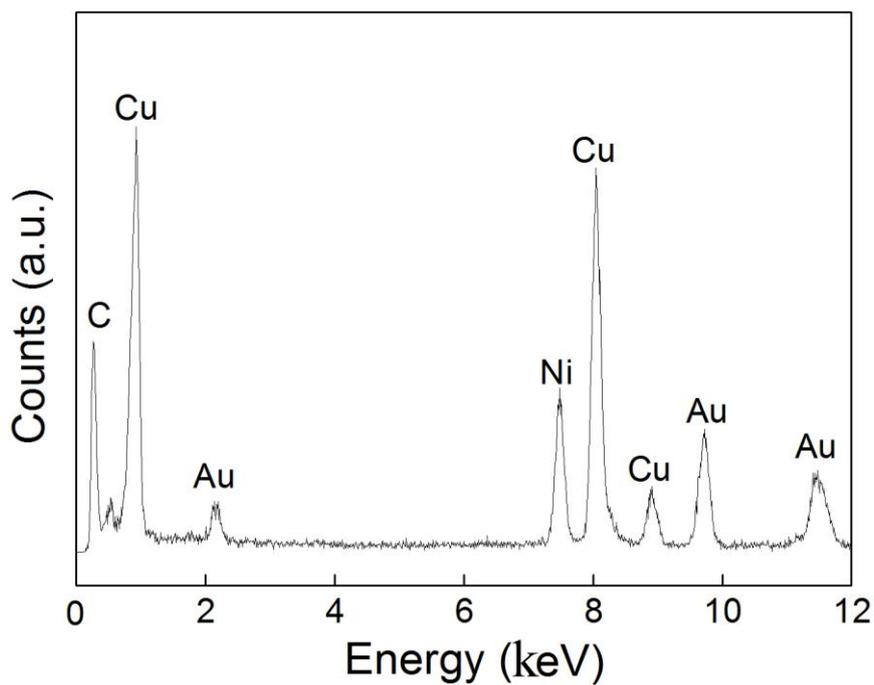


Fig. S14 EDS spectrum of the as-synthesized Cu@Ni-Cu nanowires.



Fig. S15 Photographs illustrate the magnetic response of the Cu@Cu-Ni nanocube suspensions to an external field. Left: without an external magnetic field; Right: in the presence of a magnetic bar.

Table S1 Atomic Ratio (%) (Cu vs. Ni) of the time-dependent products in the typical syntheses of Cu@Ni-Cu core-shell nanostructures (see experimental section)

Synthetic Conditions				Atomic Ratio (%)	
No.	Aging time t (min)	T (°C)	Cu	Ni	
Cube	1	240	180	100	0
	2	0	220	93.1	6.9
	3	20	220	72.0	28.0
	4	40	220	63.7	36.3
	5	60	220	62.8	37.2
	6	60	210	77.0	23.0
Wire	7	240	180	100	0
	8	0	220	100	0
	9	20	220	97.2	2.8
	10	40	220	79.0	21.0
	11	60	220	72.4	27.6
	12	60	210	72.0	28.0

Table S2 Analytical results of magnetic properties of Cu@Cu-Ni NCs

	<i>T</i>	<i>M</i>	<i>H_c</i>	<i>M_r</i>
Cu@Cu-Ni nanocubes	5	2.9	12	0.25
	300	0.8	0	0
Cu@Cu-Ni nanowires	5	3.0	70	0.75
	300	0.4	21	0.01

T= temperature (K); *M*= magnetization at 50 kOe (emu/g);

H_c= coercivity (Oe); *M_r*= remanence (emu/g).