Supporting Information

Controllable synthesis of Cu-based nanocrystals in ODA solvent

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Experimental Details

Chemicals: All the reagents used in this work, including $Cu(NO_3)_2 \cdot 3H_2O$, $CuSO_4 \cdot 5H_2O$, $Cu(Ac)_2 \cdot H_2O$, $CuCl_2 \cdot 2H_2O$, ODA, ethanol, and cyclohexane were of analytical grade from the Beijing Chemical Factory of China and were used without further purification.

Synthesis: In a typical synthesis of Cu_3N nanocubes, 0.3 g of $Cu(NO_3)_2 \cdot 3H_2O$ was added into 10 ml of ODA at 240 °C. After 10 min of magnetically stirring, the system was allowed to cool to 80 °C and the final products were collected at the bottom of the beaker. We washed Cu_3N nanocubes with ethanol several times, and then dispersed them in non-polar solvent such as cyclohexane. Cu and Cu_2O nanocrystals were synthesized when 0.1 g and 1 g of $Cu(NO_3)_2 \cdot 3H_2O$ were used as reactants respectively. Cu_2S nanocrystals were synthesized when 0.3 g of $CuSO_4 \cdot 5H_2O$ was used as reactant. The other procedure was the same as that for Cu_3N nanocubes.

Characterization: The powder XRD patterns were recorded with a Bruker D8-advance X-ray powder diffractometer with CuKα radiation (λ = 1.5406 Å). The specimen was prepared as follows: a small amount of product was dispersed in cyclohexane. Then, we dripped one drop of the resulting suspension onto a glass substrate. After it was dried at room temperature in air, we continued to drip another one until the final product fully covered the substrate. The 2θ range used in the measurement was from 10° to 80° in steps of 0.02° with a count time of 1 s. The size and morphology of as-synthesized samples were determined by using Hitachi model H-800 transmission electron microscope and JEOL-2010F high-resolution transmission electron microscope. The specimen was prepared as follows: a small amount of product was dispersed in cyclohexane; then, one drop of the resulting suspension was transferred onto a standard holey carbon-covered copper (or molybdenum) microgrid and dried at room temperature in air. Energy dispersive spectroscopy was recorded to determine the composition of the products. The visible absorption spectra of as-obtained samples were performed on Shimadzu UV-2100S from 400 to 800 nm.

Supplementary Figures

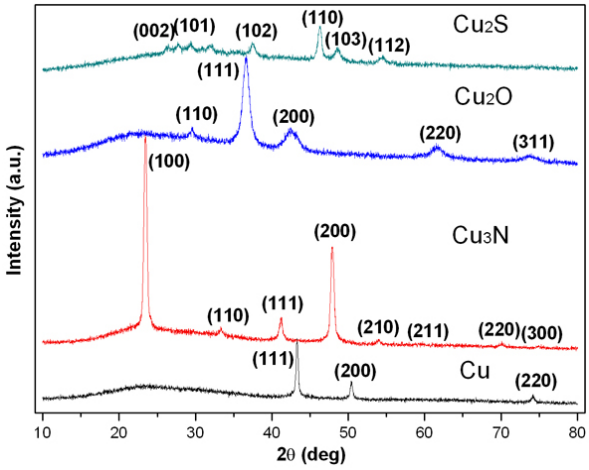

Figure S1. XRD patterns of Cu, Cu_3N, Cu_2O, and Cu_2S nanocrystals.

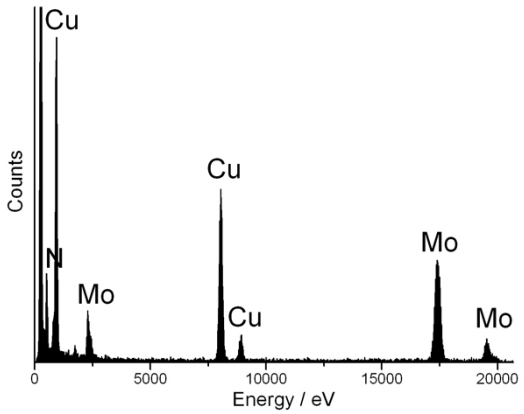

Figure S2. EDS pattern of Cu_3N sample.

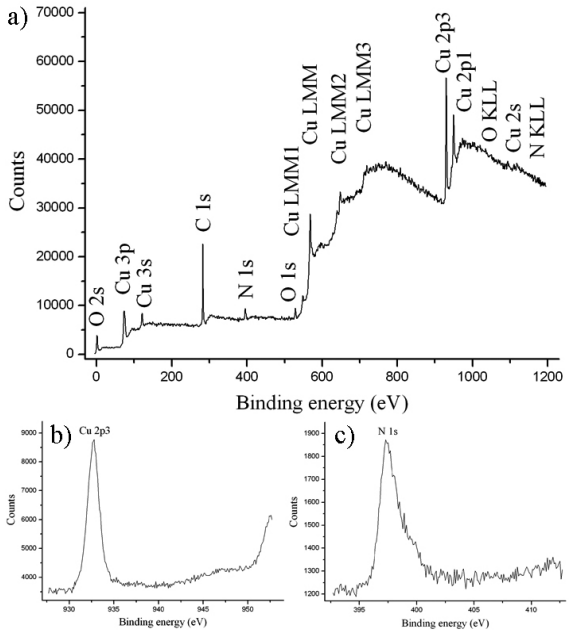

Figure S3. XPS spectra of Cu_3N nanocubes: a) survey spectrum; b) Cu 2p spectrum; c) N 1s spectrum.

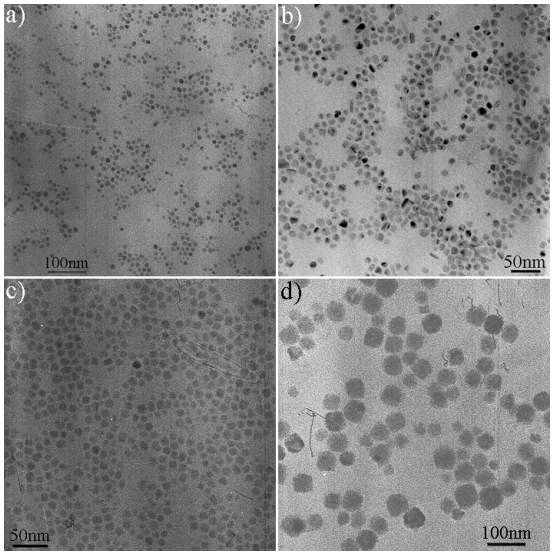

Figure S4. TEM images of Cu_3N nanocrystals with different size and morphology obtained under controlled conditions: a) Cu_3N nanoparticles with average size of 10 nm (In 10 ml of ODA, 0.3 g of $Cu(NO_3)_2{\cdot}3H_2O$ reacted at 280 °C for 5 min); b) Cu_3N nanopolyhedrons with average size of 15 nm (In 10 ml of ODA, 0.3 g of $Cu(NO_3)_2{\cdot}3H_2O$ reacted first at 260 °C for 5 min and then at 240 °C for another 5 min); c) Cu_3N nanoparticles with average size of 15 nm (In 10 ml of ODA, 0.3 g of $Cu(NO_3)_2{\cdot}3H_2O$ reacted first at 220 °C for 5 min and then at 240 °C for another 5 min); d) Cu_3N nanospheres with average size of 50 nm (In 10 ml of ODA, 0.3 g of $Cu(NO_3)_2{\cdot}3H_2O$ reacted at 220 °C for 20 min).

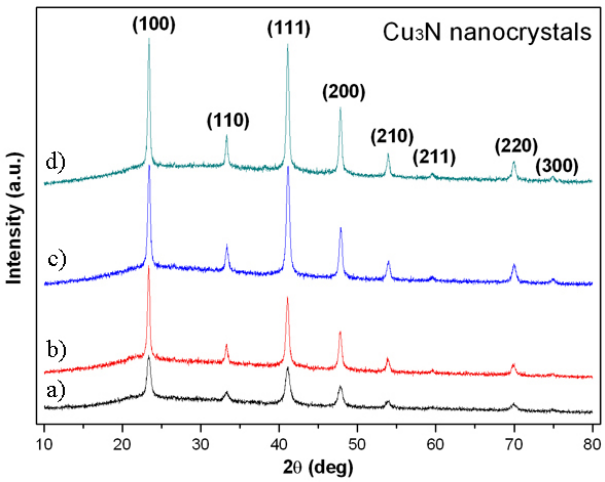

Figure S5. XRD patterns of Cu_3N nanocrystals with different size and morphology obtained under controlled conditions: a) Cu_3N nanoparticles with average size of 10 nm; b) Cu_3N nanopolyhedrons with average size of 15 nm; c) Cu_3N nanoparticles with average size of 15 nm; d) Cu_3N nanospheres with average size of 50 nm.

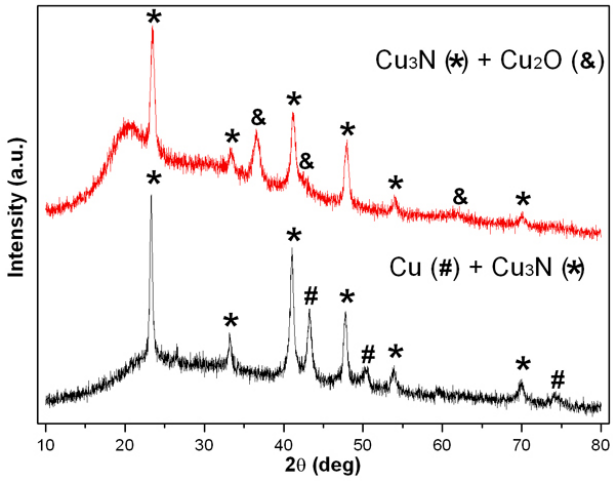

Figure S6. XRD patterns of products obtained via thermal decomposition of 0.2 g and 0.6 g of $Cu(NO_3)_2$ in 10 ml of ODA solvent respectively.

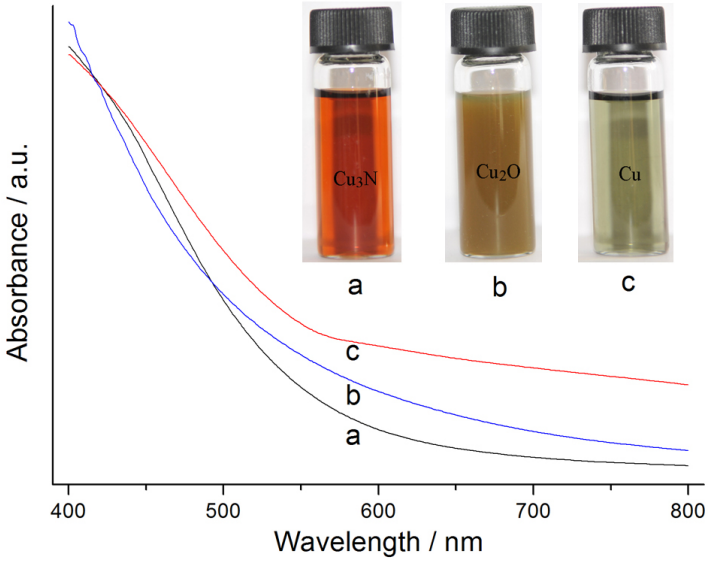

Figure S7. Visible absorption spectra and visual images (insets) of as-prepared samples dispersed in cyclohexane: a) Cu_3N; b) Cu_2O; c) Cu.

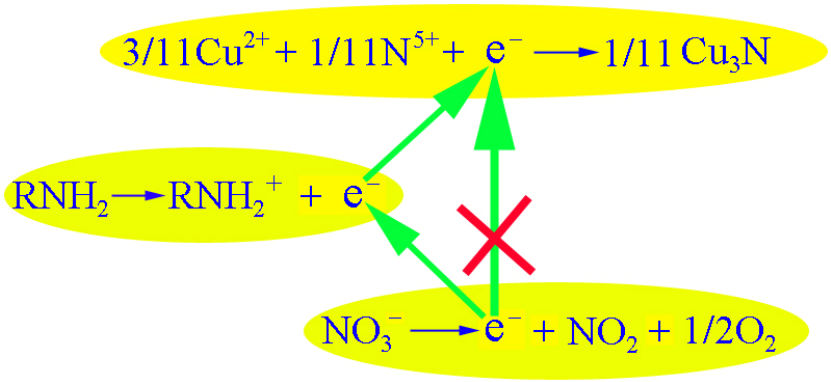

Figure S8. Scheme of Cu_3N formation process in ODA solvent.

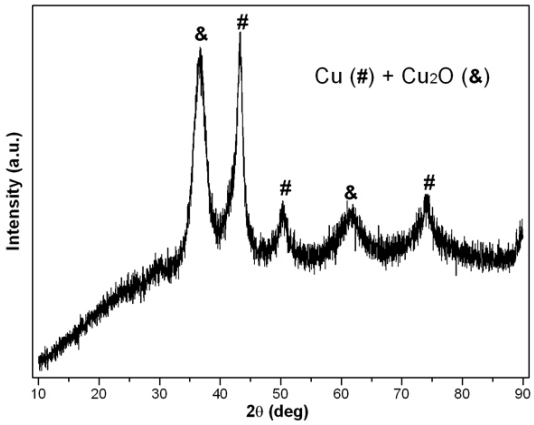

Figure S9. XRD pattern of products obtained via thermal decomposition of 0.3 g of $Cu(Ac)_2$ in ODA solvent.

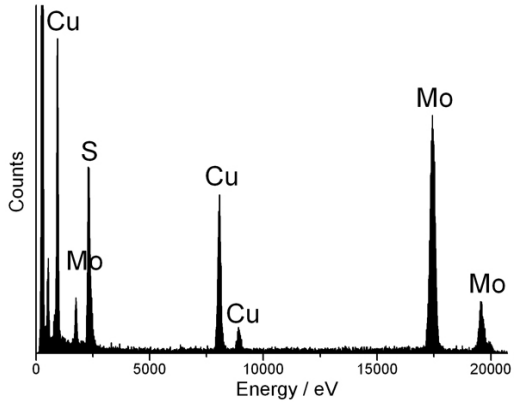

Figure S10. EDS pattern of Cu_2S sample.