

Electronic Supplementary Information (ESI)

## Conversion of Cu<sub>2</sub>O Nanocrystals into Hollow Cu<sub>2-x</sub>Se Nanocages with the Preservation of Morphologies†

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### Details of experiments:

**Preparation of Cubic Cu<sub>2</sub>O:** Cubic Cu<sub>2</sub>O nanoparticles were prepared by adding weak reductive agent (ascorbic acid solution) into Cu<sup>2+</sup> and NaOH aqueous solution using PVP (polyvinylpyrrolidone) as capping agents, which was described in our previous report [1]. In a typical process, 0.20g PVP (polyvinylpyrrolidone) (K30) was dissolved into 100.0ml CuSO<sub>4</sub> (0.01M) aqueous solution under magnetic stirring at room temperature, followed by the addition of 25.0ml 1.50M NaOH aqueous solution. Upon the addition of NaOH, blue precipitates were formed. Then the mixture was kept under stirring for one to two minutes. Then 25.0ml 0.10 M ascorbic acid solution was added into the mixture and stirred for another 15 minutes at room temperature.

**Preparation of octahedral Cu<sub>2</sub>O:** Octahedral Cu<sub>2</sub>O nanoparticles were prepared using the same procedure except replacing ascorbic acid solution by 25ml hydroxylamine solution (0.1M).

**Preparation of spherical Cu<sub>2</sub>O:** Spherical nanoparticles were prepared using the same chemicals as those of octahedral Cu<sub>2</sub>O but with a different adding procedure. In a mixed solution containing 100ml 0.01M CuSO<sub>4</sub> and 0.2g PVP, a solution prepared from pre-mixing 25ml 0.1M hydroxylamine solution and 25ml 1.50M NaOH aqueous solution was added. Then the reaction system was stirred for 15 minutes still at room temperature.

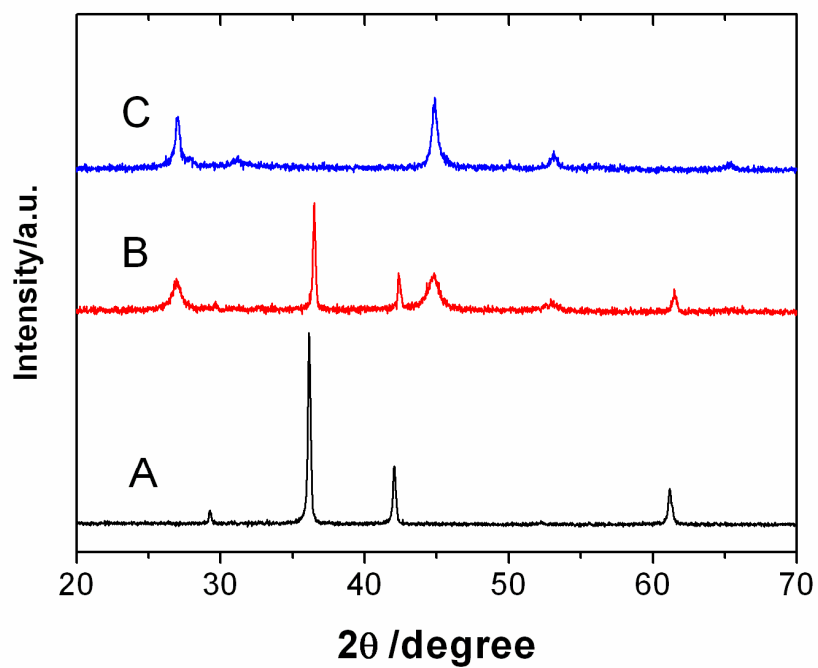
**Preparation of Selenium source:** Selenium source was prepared by mixing 0.1mmol Se powder with 0.1mmol KBH<sub>4</sub> in 10ml water under flowing N<sub>2</sub> gas at room temperature for 30min.

**Conversion Cu<sub>2</sub>O into Cu<sub>2-x</sub>Se:** For the formation of hollow Cu<sub>2-x</sub>Se cages, 10ml selenium source was injected into a dispersed Cu<sub>2</sub>O particles solution and the solution was stirred for 4 hours at room temperature. The non pure phase containing both Cu<sub>2</sub>O and Cu<sub>2-x</sub>Se was prepared by using 2.5ml selenium source instead of 10ml selenium source with other conditions kept same.

**Characterization:** Products were collected from the solution by centrifugation, washed by deionized water for several times, and then dried in a vacuum at 60°C. The as-prepared products were characterized by using powder X-ray diffraction (XRD, Shimadzu XRD-6000 with Cu K $\alpha$  radiation  $\lambda=1.5406\text{\AA}$ ), field-emission scanning electron microscopy (FESEM, FEI SIRION 200 and JEOL 7401) and transmission electron microscopy (TEM, JEM 100CX and JEOL 2010).

### Reference

1.H. L. Cao, X. F. Qian, C. Wang, X. D Ma, J. Yin and Z. K. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 16024.



**Figure S1.** XRD patterns of as-prepared products. (A) pure phase of  $\text{Cu}_2\text{O}$ ; (B)  $\text{Cu}_2\text{O}/\text{Cu}_{2-x}\text{Se}$  core/shell nanostructure, (C) pure phase of  $\text{Cu}_{2-x}\text{Se}$ .