

Conversion of Cu₂O nanocrystals into hollow Cu_{2-x}Se nanocages with the preservation of morphologies†

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With the use of PVP (polyvinylpyrrolidone) as capping reagent, cubic, octahedral and spherical Cu₂O nanocrystals were obtained in aqueous media when different reducing agents were applied. After adding selenium sources at room temperature, these nanocrystals could be converted (based on the Kirkendall effect) into hollow Cu_{2-x}Se nanocages that keep their corresponding original morphologies.

The study of nano-/micro-semiconductors with shape- and size-controlled structure has attracted considerable interest due to their distinguished properties and applications in optical and electric areas.¹ Cuprous oxide and copper selenide are well-known p-type semiconductors that have potential applications in solar energy conversion,² catalysis,³ optical filter,⁴ supersonic material,⁵ and so on. Many methods have been developed for the synthesis of these two materials with nano/micro scale dimensions.^{6–13} In this communication, we reported a simple solution method to synthesize Cu₂O nano-/micro-materials with different shapes and to subsequently convert them into hollow Cu_{2-x}Se nanocages based on the Kirkendall effect at room temperature. Recently, the Kirkendall effect has been introduced for the formation of hollow nanostructured materials,¹⁴ where hollow structures are formed because of the difference in diffusion rates between two components. In our previous work, we employed the same idea to prepare 18-facet polyhedral Cu_xS nanocages using cubic Cu₂O nanocrystal as sacrificial template while altering the growth rates of different crystalline faces during the conversion process.¹⁵ As an extension of this, here we made use of different morphological Cu₂O precursors to investigate the validity of such effect in more complex systems.

The synthetic strategy included the fabrication of Cu₂O nanoparticle templates with different morphologies and followed by converting them into hollow Cu_{2-x}Se nanocages when appropriate selenium source was added under room temperature. Detailed experiments were described in the electronic supplementary information (ESI).†

Fig. 1 show the FESEM and TEM images of Cu₂O particles with different shapes obtained under different synthetic conditions as shown in the ESI.† Fig. 1A and B are the FESEM and TEM images of cubic-like Cu₂O particles prepared by using ascorbic acid as reducing agent. From the images, we can clearly find that cubic Cu₂O nanoparticles with average particle size ~200 nm are

exclusive products. The SAED pattern recorded from a single particle indicates that the particle is highly crystallized. We found that when ascorbic acid was replaced by hydroxylamine, octahedral Cu₂O nanocrystals were obtained, and the FESEM and TEM were shown in Fig. 1C and D. The SAED pattern (inset image of Fig. 1D), which can be indexed to the [111] zone axis, indicates that the octahedral Cu₂O is a single crystal. However, only spherical particles with porous structure could be yielded using the same chemicals as those of octahedral Cu₂O but with a different adding procedure (see detail in ESI†) as shown in Fig. 1E and F. The effects of chemical additives on the final morphology of Cu₂O have been clearly addressed in recent literature.⁷ In our case, we used the same chemical additive, PVP, but with different reducing agents. Ascorbic acid and hydroxylamine are chemical acid and base in nature, respectively, the synergetic effect between chemicals themselves and changes of alkalinity of the reaction systems might be responsible for the variation of morphology for the former two cases. However, we are not clear what makes the

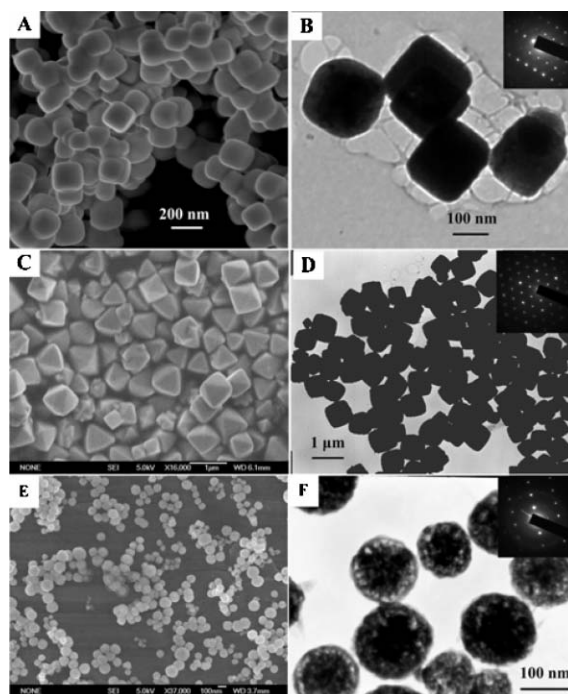


Fig. 1 FESEM and TEM images of Cu₂O particles with different shape. (A) and (B) cubic-like Cu₂O particles; (C) and (D) octahedral Cu₂O particles; (E) and (F) sphere-like Cu₂O particles. Inset images of (B), (D) and (F) are SAED patterns recorded from a single particle of a different shape, respectively.

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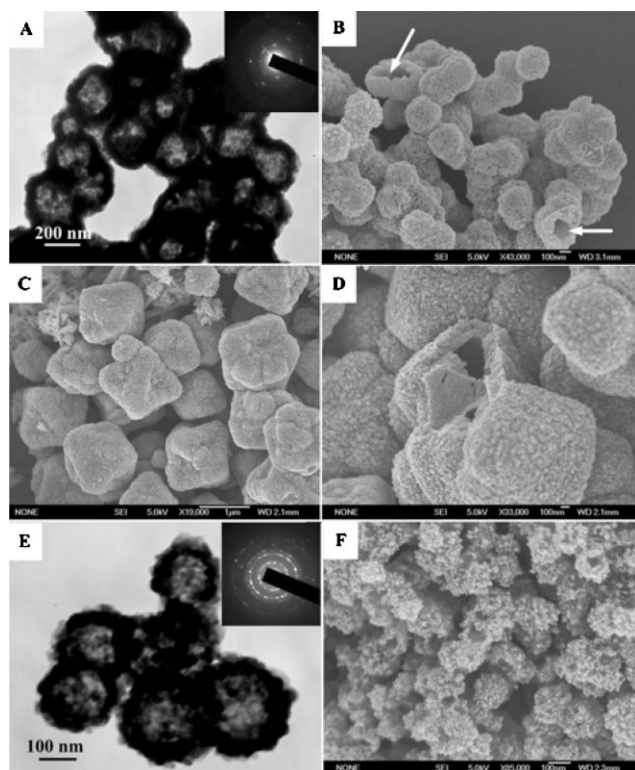


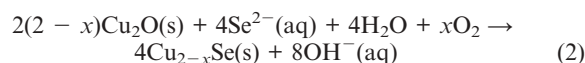
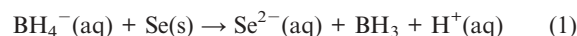
Fig. 2 Sections (A) and (B) are the TEM and FESEM images of Cu_{2-x}Se hollow cages obtained from cubic-like Cu_2O template, Inset image of (A) is SAED pattern recorded from a single particle; (C) and (D) are the FESEM images of Cu_{2-x}Se hollow cages obtained from octahedral Cu_2O template; (E) and (F) are the TEM and FESEM images of Cu_{2-x}Se obtained from sphere-like Cu_2O template, Inset image of (E) is the SAED pattern recorded from a single particle.

morphology difference when only adding orders were changed for octahedral and spherical Cu_2O particles.

Since Cu_{2-x}Se has much lower solubility (K_{sp}) than Cu_2O in aqueous alkaline solutions, it could be formed when Se^{2-} ions were added to the mixture containing Cu_2O precipitates *via* a dissolution process. Redox reactions were also involved as the valence of copper ions changed during such transformation procedure. Fig. 2A shows the TEM image of Cu_{2-x}Se prepared by using cubic-like Cu_2O nanoparticles as template (Fig. 1A and B). From that we find out that cube-like particles with rough surface are the exclusive products. The strong contrast difference between their edges (dark) and centers (bright) indicates cube-like nanocages with a ~ 180 nm hollow interior and ~ 50 nm thickness wall. Homocentric spotty cirques of SAED pattern (Fig 2A, inset image) recorded from an individual particle imply that the cage might be constructed from fine small crystalline particles. As TEM does not offer clear 3-D images of the obtained Cu_{2-x}Se nanoparticles, FESEM was utilized to investigate the overall appearance of such products. It shows that cube-like or quasi-spherical morphologies, similar to those of original Cu_2O cubic nanoparticles but with a slight growth of particle size, are obtained. Furthermore, broken particles clearly show the existence of hollow interior (arrows in Fig. 2B) and the walls of the cubic-like particles are constructed with many small particles (about 5–20 nm). Such observations are consistent with the TEM

results. Octahedral and spherical Cu_{2-x}Se particles with hollow interior can also be fabricated from corresponding octahedral or spherical Cu_2O templating particles, as shown in Fig. 2C to 2F. Meanwhile, these particles have voids inside and are rough in surfaces as they are composed of small particles, which are close to the case for cubic-like structure. Besides difference in morphologies, the grain size is much larger for octahedral particles.

The formation of hollow Cu_{2-x}Se nanocages based on Cu_2O templates can be formulated as following reaction equations:



The XRD patterns clearly show the phase transformation from Cu_2O to copper selenide (Fig. S1, ESI†) and all peaks in Fig. S1A match well with cubic Cu_2O (JCPDS NO. 05-0667). All three systems gave the same transformation trend, which means that pure Cu_2O with different morphologies was the only template in forming copper selenide. The completeness of conversion from Cu_2O to Cu_{2-x}Se depends mainly on the adding amount of selenium source although reaction time should be taken into consideration as well. When the amount of Se^{2-} is higher than stoichiometric composition, pure cubic-phase Cu_{2-x}Se (JCPDS NO. 06-0680) was obtained (Fig. S1C, ESI†). While the mixture of Cu_2O and Cu_{2-x}Se was produced when less amount of Se^{2-} was used (Fig. S1B, ESI†). Surprisingly, such mixture took a form similar to core/shell structure.

The formation process of Cu_{2-x}Se cube-like nanocage could be described as a two-step procedure as depicted by FESEM images (Fig. 3). In the first step, when Cu_2O template was mixed with Se^{2-} in appropriate reaction condition, the Cu_{2-x}Se forming reaction occurred and a thin layer of Cu_{2-x}Se was formed on the surface of Cu_2O particles. This thin layer consisted of many small Cu_{2-x}Se nuclei, which were formed directly by the reaction between copper ions produced from dissolution–precipitation process of Cu_2O on the particle surface and selenium ions provided by selenium source. This step was terminated due to the depletion of free copper ions from the dissolution–precipitation process. During the second step, deposited Cu_{2-x}Se nuclei on the surface tend to grow through “Ostwald ripening” process in the conversion courses. The supply of copper ions can be viewed as copper ions migration from particle interior as a result of the Kirkendall effect.¹⁴ With the reaction proceeding, copper ions were further moved outward and water in reverse through the rough selenium shell, in which Cu_2O templates were converted to Cu_{2-x}Se and OH^- in the presence of water. The movements of

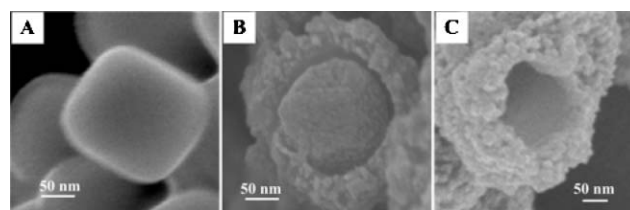


Fig. 3 FESEM images of as-prepared products. (A) Cubic Cu_2O particle; (B) $\text{Cu}_2\text{O}/\text{Cu}_{2-x}\text{Se}$ core/shell structure from a broken particle; (C) a broken particle of hollow Cu_{2-x}Se cage.

copper ions and water lead to the formation of core/shell structure of $\text{Cu}_2\text{O}/\text{Cu}_{2-x}\text{Se}$ (Fig. 3B and Fig. S1B, ESI†) when insufficient selenium ions was provided. To our surprise, an obvious gap between Cu_2O and Cu_{2-x}Se could be observed due to the incomplete reaction, as shown in Fig. 3B. Finally, hollow Cu_{2-x}Se nanocages were obtained after Cu_2O was exhausted when plenty of Se^{2-} ions were added.

In summary, cubic-like, octahedral-like and sphere-like Cu_{2-x}Se hollow cages were successfully fabricated from shape-controlled Cu_2O as sacrificial cores, precursors or templates by a single technique at room temperature. A plausible formation mechanism of these structures could be based on the Kirkendall effect followed by the Ostwald riping process. Such process and mechanism might be extended to other systems for the synthesis of hollow cages.

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