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TEM study on hollow and porous Cu_2O nanoparticles prepared from solution phase*

Zhang Huai-Ruo(张怀若), Yu Hong-Chun(虞红春), Shen Cheng-Min(申承民),
Yang Huai-Xin(杨槐馨), and Li Jian-Qi(李建奇)†

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

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In this paper, hollow and porous Cu_2O nanoparticles were prepared by adjusting the cationic surfactant cetyltrimethylammonium (CTAB) concentration in the solution-phase reaction. Structural investigations reveal that Cu_2O nanoparticles can be either well-defined hollow nanoboxes or porous nanocubes depending on the synthesis conditions. The transmission electron microscopy (TEM) observations demonstrated that the nanoparticles in general are composed of small grains coherently growing along certain preferred orientations.

Keywords: nanostructures, chemical synthesis, oxides, electron microscopy
PACC: 6116D, 6146, 8110D

1. Introduction

The Cu_2O nanoparticles and related materials with a variety of microstructures have attracted much attention in recent studies due to their potential applications. Cu_2O is a p-type semiconductor with a direct band gap of 2.17 eV, which makes it a promising material for solar energy conversion,[1,2] photocatalysis,[3,4] negative-electrode for battery[5] and device applications.[6,7] Up to now, various interesting Cu_2O nanostructures have been synthesized by different methods,[8−14] among which nanostructures with hollow interiors are of great advantage in some specific areas including catalysis, drug delivery systems, molecular separation, chromatography, energy storage and microelectronics.[15−21] Although hollow Cu_2O spheres or boxes with submicrometre to micrometre dimensions prepared by different methods have been reported by several groups,[12−14] to our best knowledge, it is still a challenge to prepare well-defined hollow Cu_2O nanostructures. In previous publications, high concentration of CTAB was used to prepare Cu_2O nanocubes.[9] In this work, low concentration of CTAB was used as template to prepare a series of hollow and porous Cu_2O nanostructures, and structural analysis reveals the Cu_2O nanoparticles in the final products can be either well-defined hollow nanoboxes or porous nanocubes, depending on the synthesis conditions.

2. Experimental

Cu_2O nanostructures were prepared by reducing $CuSO_4$ with ascorbic acid in the presence of CTAB and NaOH solutions. As-prepared Cu_2O samples were checked using a Rigaku D/max 2500 diffractometer with Cu$K\alpha$ radiation and a graphite monochromator, then an FEI XL30 SEM and an FEI Tecnai F20 TEM were used to perform the microstructure analysis.

3. Results and discussion

Figure 1 shows a typical XRD data collected from an as-prepared sample: all shown peaks can be well indexed as the cubic Cu_2O with the lattice parameter of 4.27 Å. In present work, we have performed a series of experiments under different reaction times at low CTAB concentrations. Figures 2(a)–(c) show a series of SEM images for samples obtained respectively under the reaction time of 5, 10 and 30 min. All samples are synthesized with the CTAB concentration of 0.01 mol/L. The SEM images shown in Figs.2(a) and (b) reveal similar morphology and size distribu-

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†Corresponding author. E-mail: ljq@ssc.iphy.ac.cn

tion for these two samples. Most of the nanoparticles have the sizes ranging from 40 to 60 nm. According to our analysis, the Cu_2O nanoparticles tend to show up as cube-like shape for small particles and become corner rounded polyhedra with the increase of size. Careful analysis of the small grain from the broken nanoparticles reveals clear hollow features as illustrating in the inset of Fig.2(b), this cube-like particle has the hollow interior with the wall thickness of about 9 nm. Figure 2(c) shows a typical SEM image of samples prepared at the reaction time of 30 min, showing a relative uniform grain size of ~50 nm. Chemical composition of all samples have been checked by EDX observations. Figure 2(d) obtained from the nanoparticles indicates that the well-cleaned final products are mostly composed of Cu and O. Further experimental study indicates that the growth and morphology of Cu_2O nanoparticles can be greatly affected if the reaction time is as high as 60 min, and then, actually no perfect products could be obtained in the solution.

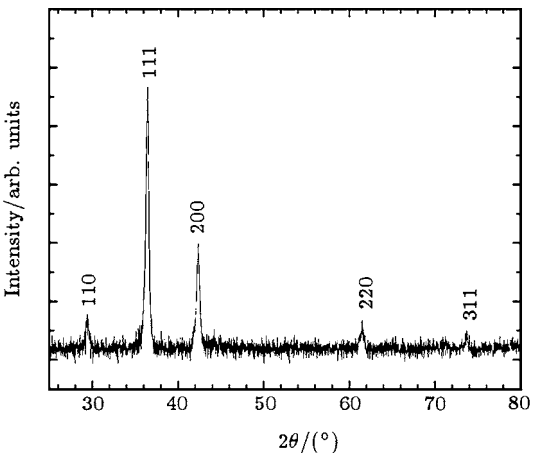


Fig.1. Typical XRD pattern of an as-prepared product. All peaks can be well assigned to the known cubic Cu_2O structure, in consistency with the data of JCPDS card No: 05-0667.

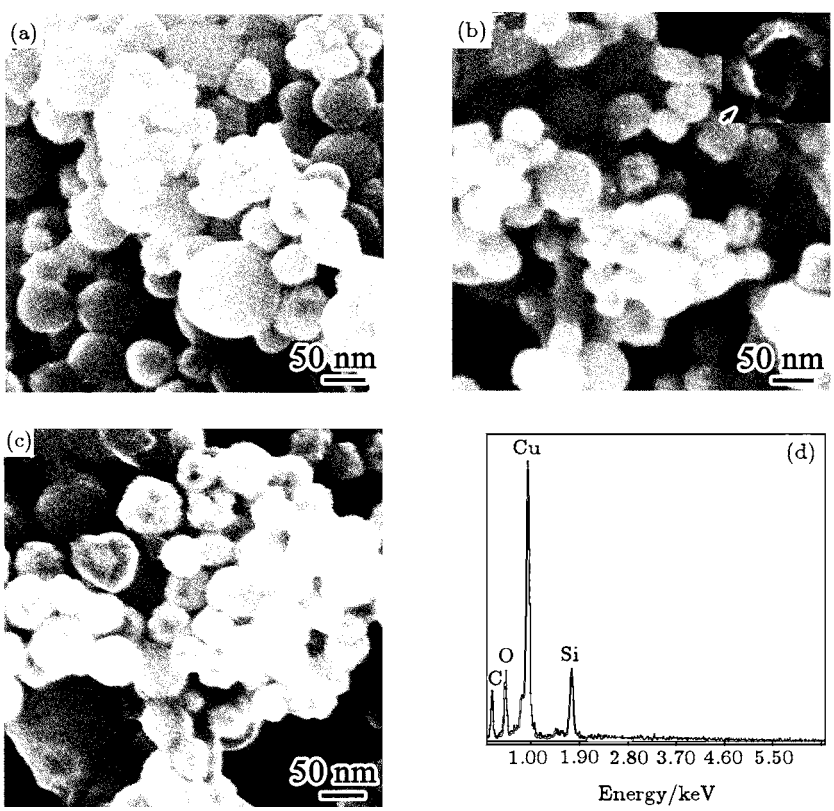


Fig.2. SEM images of samples prepared under different reaction time in 0.01mol/L CTAB solution. (a) 5 min, (b) 10 min, (c) 30 min, (d) Typical EDX data obtained from the nanoparticles (deposited on Si wafer).

Systematic TEM analyses have been performed on samples prepared at various concentrations of CTAB solution. Figures 3(a) and (b) show typical bright field TEM images obtained from samples prepared at CTAB concentration of 0.005 mol/L and 0.01 mol/L, respectively, which reveal that the Cu_2O

nanoparticles have well-defined hollow interiors. Observation with large tilting angle ($\pm 60°$) shows that the hollow profiles change from square (or circular) to elliptic. We call this kind of nanoparticles as nanoboxes. As shown by our systematic investigation, the average sizes of the nanoboxes ranging from 20 nm to 100 nm are monotonically increased with the increasing of CTAB concentration. Electron diffraction observations on individual nanobox show that majority of nanoboxes exhibit the preferred [111] orientation. Figure 3(c) shows an electron diffraction pattern from a nanobox showing the texture structure with the common $< 111 >$ preferential directions. Some nanoboxes have the well-defined single crystal structure as shown in Fig.3(d); in this pattern all main diffraction spots can be indexed by the cubic Cu_2O structure. Superfluous weak diffraction spots as indicated by arrows arise from small particles absorbed on the surface which were not well incorporated into the nanobox. The TEM dark-field image in Fig.3(e) clearly reveals that the Cu_2O nanobox was composed of small grains with the average size of around 8 nm, this result is in good agreement with that calculated from XRD pattern using Scherrer's formula. We also find a number of small polyhedral grains in the region near the nanobox as shown in Fig.3(f) (indicated by an arrow). It has been documented that Cu_2O crystallite can form cubic, cuboctahedral or octahedral shapes under different conditions.[10,22] In our system, the octahedral and cuboctahedral Cu_2O nanocrystal grains have been observed. In the point of view of geometry and energy, the {111} based octahedra or {111}+{100} based cuboctahedra can be assembled into an perfect integer with similar faces touching each other face-to-face.[23] As a result, the Cu_2O nanoboxes' outer surfaces were highly oriented with 4 {111} faces and 2 {100}+{111} faces, and could easily give rise to the [111] zone-axis diffraction.

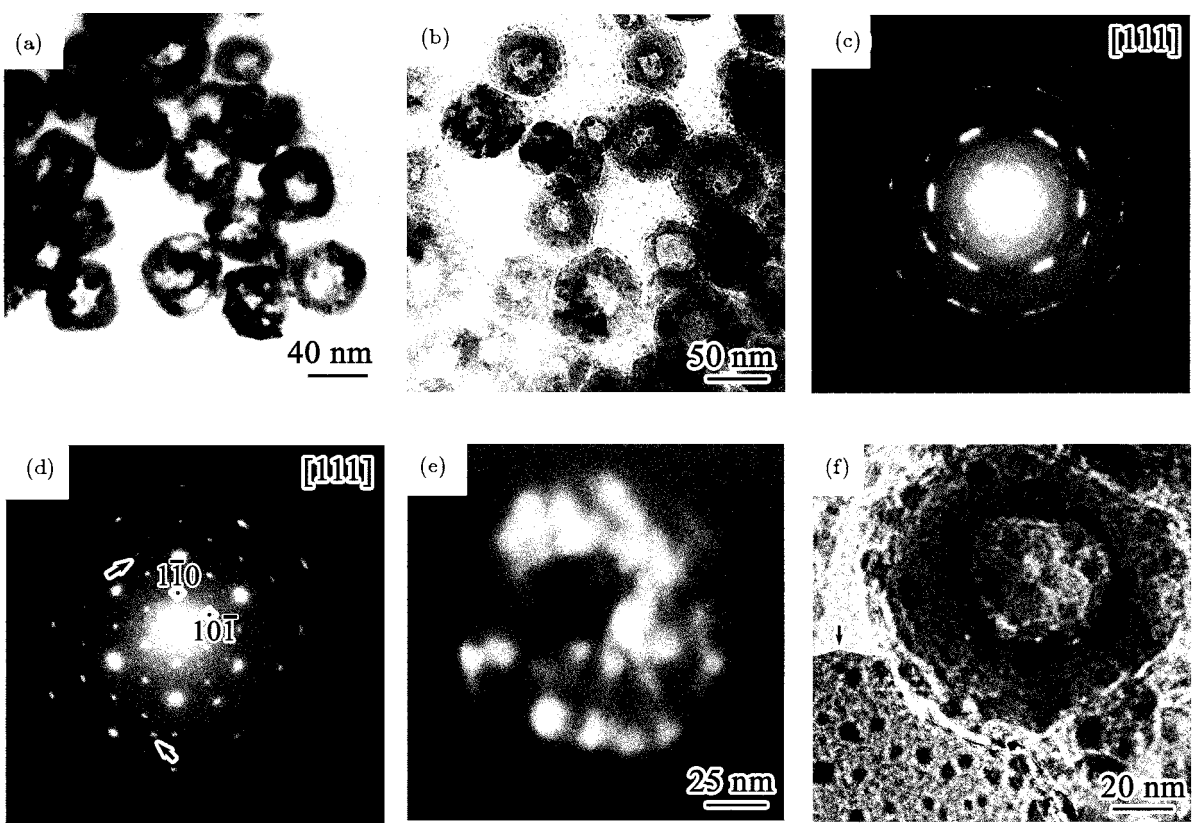


Fig.3. TEM results for the nanoboxes prepared in low CTAB concentration. (a, b) Typical bright field TEM images of Cu_2O nanoboxes prepared in 0.005 mol/L and 0.01 mol/L CTAB solution, respectively. (c, d) Typical electron diffraction patterns taken along [111] zone axis. (e) Dark field TEM image of a nanobox. (f) Bright field TEM image showing the small grains with different shapes.

Further TEM examination of the products prepared at higher CTAB concentration ($\geq$0.03 mol/L) reveals that the nanoparticles have remarkable change in the microstructure. Figures 4(a) and (b) show the bright field TEM images illustrating the microstructure of Cu_2O samples prepared under the CTAB concentration of 0.03 mol/L. The particles are nanocubes ranging from 120 nm to 220 nm. The hollow feature remarkably diminishes with the increase of the size, which is mostly because the wall thickness of the nanocubes are increased and becomes too thick to be penetrated by the electron beam. Instead, porous structural features can be clearly recognized in most nanocubes. The growth terraces (indicated by arrow) in Fig.4(b) suggest the nanocube was assembled by regular smaller grains layer-by-layer along the relevant direction. Figure 4(c) shows a dark-field TEM image, indicating the presence of remarkable porous structure in Cu_2O nanoparticles, the pore sizes in general are as small as 5–8 nm. As the CTAB concentration is increased to 0.05–0.07 mol/L, very well crystallized nanocubes can be obtained with sizes ranging mostly from 150 to 200 nm (as shown in Fig.4(d). Electron diffraction reveals that all these cubes prepared under high CTAB concentration grow along $< 100 >$ directions instead of the preferred $< 111 >$ directions of the nanoboxes prepared under low CTAB concentration, which suggests that the nanocrystal grains prepared under high CTAB concentration were cubes with 6 {100} faces instead of the cuboctahedra prepared under low CTAB concentration. Micro-diffraction patterns in Figs.4(e) and (f) taken along [001] and [011] zone axes respectively indicate perfect crystal structure of these nanocubes. Double diffraction spots also emerged due to too large thickness of the nanocubes.

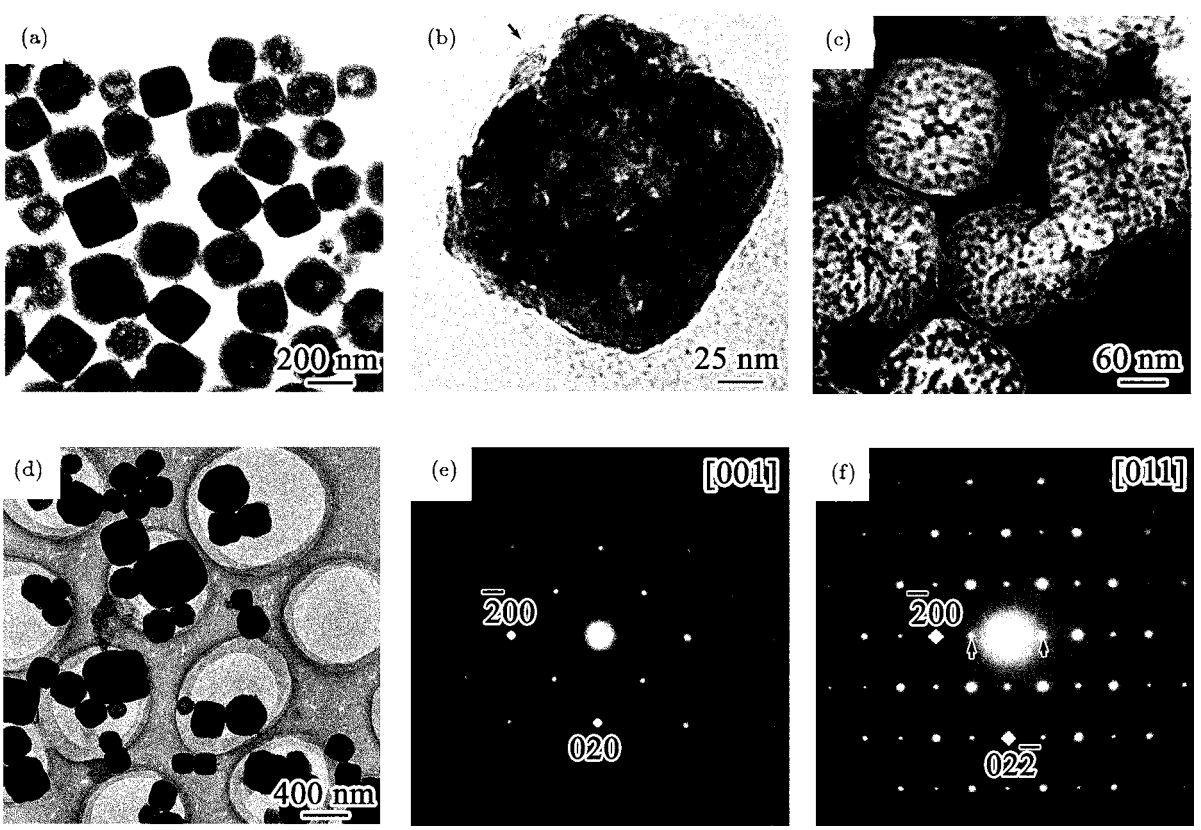


Fig.4. (a, b) TEM images of porous nanocubes prepared in 0.03 mol/L CTAB solution. (c) Dark field TEM image of nanocubes, showing the notable porous structural feature. (d) Typical TEM image of nanocubes prepared in the 0.05–0.07 mol/L CTAB solution. (e, f) Electron diffraction patterns of nanocubes taken along [001] and [011] zone-axes, the spots indicated by arrows are double diffractions that should be forbidden following extinction conditions for crystals of Pn-3m.

High-resolution transmission electron microscopy (HRTEM) was used to investigate the crystal structure, microstructures, and defects in the Cu_2O nanoparticles prepared under different conditions. Figure 5(a) is an HRTEM image from a small particle, indicating the cubic crystal structure projected

along < 001 > direction. The HRTEM image can be well simulated using multislice method as shown in the inset, and this theoretical TEM image for the thickness of 9 nm and the defocus value around 84 nm with a 5 nm defocus step is in good agreement with the experimental one. The Cu atoms in the present HRTEM image can be recognized as bright dots. Figure 5(b) presents an HRTEM image of lower magnification from a hollow nanobox, the lattice fringes along the interior edge indicate the assembled nanoparticles are highly orientated along the same direction, an arrow indicates the Moiré fringes originating from superposition of small particles with little inclination to each other. Figure 5(c) is taken from the wall part of a nanobox, the small polyhedral nanoparticles have coalescenced together with clearly visible boundaries and an empty pore in the sample, and, as a result, most surfactant can be easily removed by the deionized water washing. Figure 5(d) is an HRTEM image of a nanocube's edge. The straight steps can be traced back to the incorporating of small nanocubes. The gap denoted by an arrow suggests that pores can be created in the incorporation process. It can also be recognized that the nanocube grows along < 100 > and < 010 > directions.

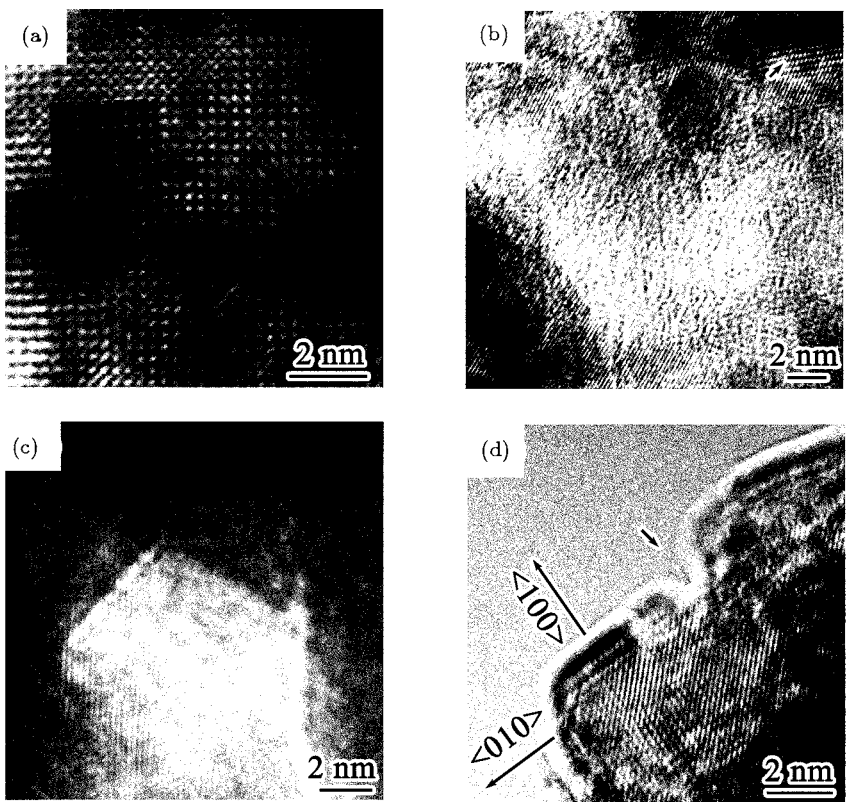


Fig.5. (a) HRTEM image from a small particle showing the perfect lattice structure of Cu_2O projected along [001] zone-axis. The inset image is a simulated HRTEM. (b, c) Typical HRTEM images of nanobox centre region and wall, showing the coherent growth of small particles and grain boundaries. (d) A typical HRTEM image of a nanocube's edge, illustrating the nanocube grows along < 100 > and < 010 > directions.

4. Conclusions

A series of Cu_2O nanoparticles have been synthesized successfully by reducing $CuSO_4$ with ascorbic acid in the presence of CTAB and NaOH solutions. At low CTAB concentration, CTAB acts as templates to direct the growth of hollow Cu_2O nanoboxes. The average sizes of the nanoparticles are increased with the increasing of the CTAB concentration. At high concentration ($\geq$ 0.03 mol/L), the final products are porous Cu_2O nanocubes. XRD, SEM, and TEM investigations suggest that the nanoparticles are composed of small highly orientation coherent grains.

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