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Preparation of Cu_2O Hollow Nanospheres Assisted by Tween-60 by a Simple Liquid Method

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In this paper, cuprous oxide (Cu_2O) hollow nanospheres have been synthesized by reducing copper sulphate with ascorbic acid in the presence of Tween-60 at room temperature. The method is simple and productive. The sample is characterized by X-ray powder diffraction, field-emission scanning electron microscopy, transmission electron microscopy and ultraviolet-vis light (UV-vis) absorption spectra. A possible formation mechanism of Cu_2O hollow nanospheres is discussed.

Key Words: Nanosphere, Chemical synthesis, Transmission electron microscopy. X-ray diffraction.

INTRODUCTION

The shape and size of nanoparticles have important influence on material physical and chemical properties, such as electronic, optical, thermal and catalytic properties. The synthesis of nanoparticles with well-controlled shape and size has become a focus for material researches[1].

In recent years, much attention has been paid to architecture fabrication of hollow spheres with nano- and micro-sizes. Due to some unique properties including low density, high specific surface area and good permeation, hollow spheres have potential applications in artificial cells, catalysts, fillers, coatings, pigments and the protection of light-sensitive components, especially in delivery vehicle systems for the controlled release of drugs, cosmetics, inks and dyes[2-6].

Due to smaller band gap, Cu_2O has potential applications in solar energy conversion[7], photocatalyst[8], lithium ion batteries[9] and gas sensors[10]. Hence, more efforts have been devoted to shape controlled synthesis of Cu_2O hollow spheres. Chen and co-workers used gelatin as a softtemplate to synthesize Cu_2O hollow spheres with an average size of about 150 nm[11]. Xu and co-workers designed a multiple emulsion (O/W/O) system to prepare submicron Cu_2O hollow spheres with diameters ranging from 600-1200 nm[12]. Zeng and co-workers used a solvothermal method to prepare hollow Cu_2O nanospheres with outer diameters of 100-200 nm in N,N-dimethylformamide (DMF) at 150-180 ºC for 20-40 h[13]. However, the synthesis of Cu_2O hollow sphere assisted by Tween-60 (polyoxyethylene sorbitan monostearate) is rarely reported.

Here, we describe a simple liquid reduction route to fabricate cuprous oxide hollow naosphere with narrow size distribution. These spheres were obtained by reducing $Cu(SO_4)_3 \cdot 5H_2O$ with ascorbic acid in the presence of Tween-60 at room temperature.

EXPERIMENTAL

All of the chemical reagents used in this experiment were analytical grade. Cu_2O nanospheres were synthesized as follows: 4 mL of Tween-60 and 0.375 g of $CuSO_4 \cdot 5H_2O$ were completely dissolved in 100 mL of deionized water and magnetic stirred for 20 min. Then, 30 mL of 0.05 M NaOH was added in dropwise manner into the above solution and a blue precipitate of $Cu(OH)_2$ was soon produced. After stirring for 0.5 h, 30 mL of 0.05 M ascorbic acid solution was dropped into the $Cu(OH)_2$ solution, the colour of $Cu(OH)_2$ precipitates gradually changed from blue to brick red. The resulting solution was stirred for about 50 min until the $Cu(OH)_2$ precipitates were completely reduced by ascorbic acid. When the reaction was finished. The brick red precipitates was separated from the solution by centrifugation and washed by alcohol several times, then dried at 60 ºC for 8 h in a vacuum oven for further characterization.

The phase structure and phase purity of the as-synthesized powders were examined using a D/MAX-500 X-ray powder diffractometer with Cu K_α radiation (λ = 1.5418 Å) and the operation voltage and current were maintained at 40 kV and 70 mA, respectively. The morphologies and sizes of the products were further observed by field-emission scanning electron microscopy (JSM-6700F) operated at 5 kV. Transmission electron microscopy (TEM) observations were carried out on a Jeol JEM-2010 instrument in bright field (operated at 200 kV). Room-temperature UV-vis absorption spectrum was recorded on a UV-2550 spectrophotometer in the wavelength range of 300-600 nm.

RESULTS AND DISCUSSION

The XRD pattern of obtained sample is shown in Fig. 1 and all the peaks of the pattern are labeled and can be indexed to the cubic phase of Cu_2O crystals (JCPDS 74-1230). No peaks of impurity are detected in the XRD pattern, indicating the formation of pure crystalline Cu_2O through the presented procedure.

The morphology of as-prepared Cu_2O powers was studied with SEM, as shown in Fig. 2(a-b), which reveals that the sample consists of many spheres with the average diameter of about 500 mm. The low-magnification SEM image (Fig. 2a) shows that Cu_2O was formed in a sphere-like morphology and the spheres covered a large area of the copper substrate uniformly and compactly. However, the SEM image at a higher magnification (Fig. 2b) reveals that the nanospheres are formed by mean of self-assembling nanoparticles.

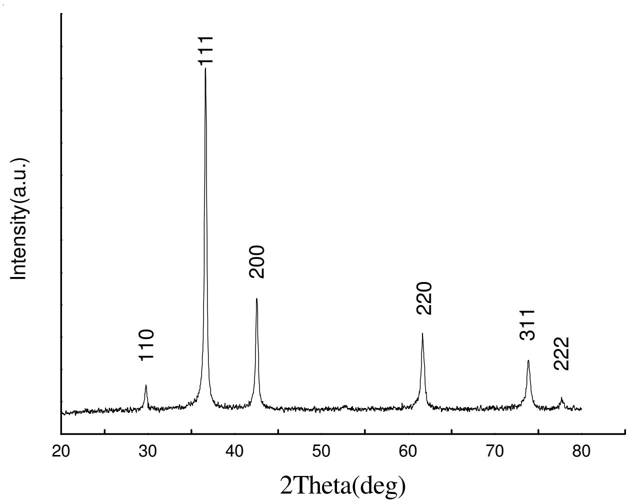

Fig. 1. XRD pattern of cuprous oxide powders as-prepared

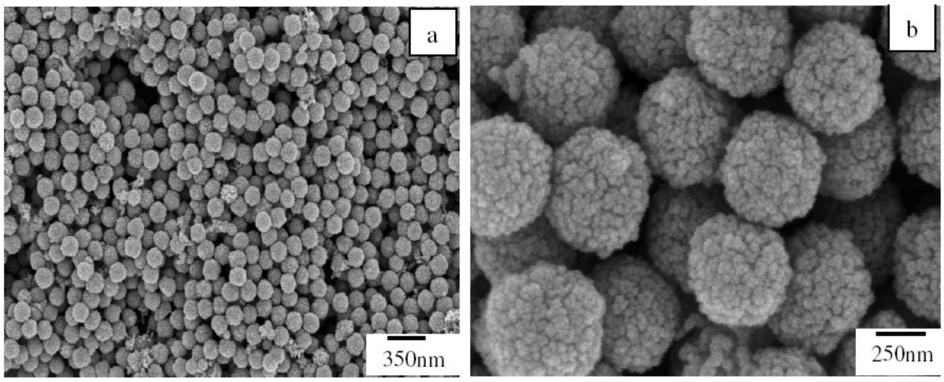

Fig. 2. SEM Images of cuprous oxide powder (a-b)

It is obvious to check whether the nanospheres are hollow from Fig. 2, since broken hollow spheres in the product are not found in the SEM images [Fig. 2(a-b)], but the corresponding TEM [Fig. 3(a-b)] images indicate that the powders consists of many hollow nanospheres. Fig. 3a is the TEM image of the obtained Cu_2O powder, showing that it exists in a large quantity of Cu_2O hollow spheres with an average diameter of 500 nm, which is consistant with the SEM image. The higher magnification TEM image shown in Fig. 3b indicates that the walls of Cu_2O hollow nanospheres are rough and composed of many nanocrystallites, which is consistent with the result in Fig. 2b. From Fig. 3b, we can see the wall of hollow spheres is about 20 nm. The corresponding selected area electron diffraction (SAED) pattern (the inset in Fig. 3b) on a single hollow sphere reveals that cuprous oxide particles are polycrystalline. The discontinuous fringes reveal that there exist many tiny crystallites on the hollow sphere wall.

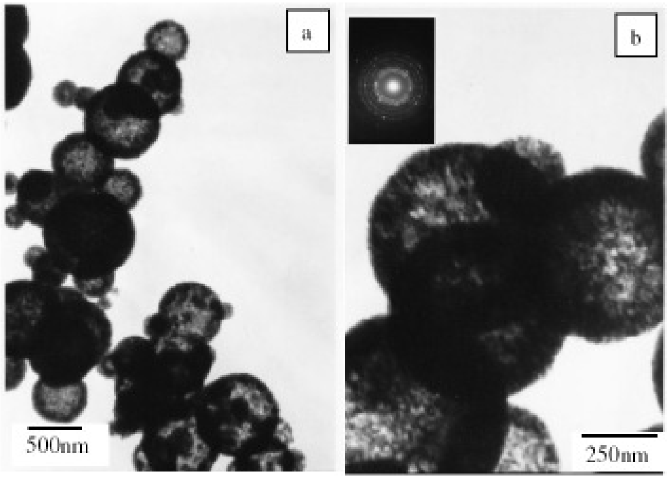

Fig. 3. TEM images of cuprous oxide hollow nanosphere (a-b)

The UV-vis absorption spectra of the Cu_2O hollow sphere powder is measured and is shown in Fig. 4. It shows broad absorption peak at 486 nm. In connection with the quantum-confined effect arising from the low dimensional nanocrystals comprising Cu_2O spheres, hollow spheres show blue shift effect comparing to bulk Cu_2O (Eg = 2.17 eV)[14,15].

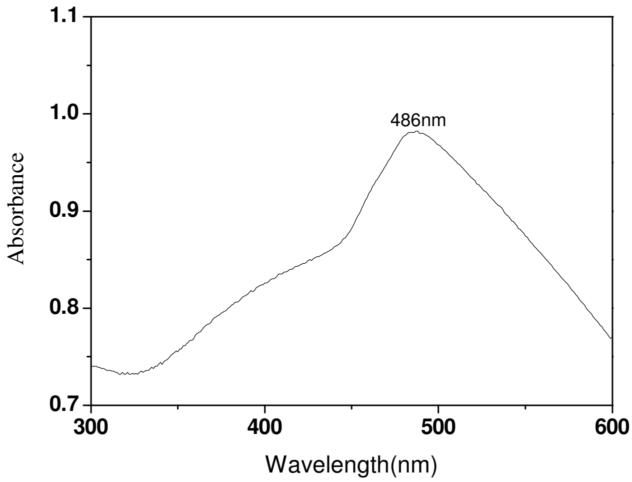

Fig. 4. UV-Vis absorption spectra of Cu_2O hollow powder

The reactions processes for synthesis of Cu_2O hollow spheres in this experiment can be described as follows:

$$Cu^{2+} + OH^{-} \longrightarrow Cu(OH)_2$$

$$C_6H_8O_6\,(\text{ascorbic acid}) + 2Cu(OH)_2 \longrightarrow C_6H_6O_6 + Cu_2O\downarrow + 3H_2O$$

The effect of Tween-60 on the morphology of the cuprous oxide can be explained by the selective adsorption of Tween-60 on the surfaces of the cuprous oxide. It is believed that Tween-60 kinetically controlled the growth rates of various faces of Cu_2O through adsorption on these surfaces. Chemical interaction might also be involved because there seemed to exist in selectivity for the functional group on the capping reagent. Tween-60 macromole molecules could selectively interact with different faces of Cu_2O nanostructures. Due to Tween-60, the equaxial growth occurs, so spherical cuprous oxide particles were obtained.

Here the formation mechanism of Cu_2O hollow spheres is similar to the Kirkendall effect[16], in which pores form because of the difference in diffusion rates between two components in adiffusion couple. On one hand, ascorbic acid can permeate through the Cu_2O layers and continue to react with the inner $Cu(OH)_2$, while the by-products $C_6H_6O_6$ and H_2O can get out of the Cu_2O layers. On the other hand, the outward diffusion of $Cu(OH)_2$ cores is possible. Alivisatos *et al*.[17] believe that placing solid nanocrystals containing one reactant in a comparatively dilute solution creates an additional asymmetry that may favour the creation of hollow structures. With the reaction going on, Cu_2O hollow structures yield.

Conclusion

In this work, Cu_2O hollow nanosphere is successfully prepared with Tween-60 as surfactant and ascorbic acid as the reductant at room temperature through a simple liquid reduction method. The diameter of Cu_2O hollow nanosphere is about 500 mm. UV-Vis absorption test indicates that Cu_2O hollow nanosphere powder shows blue shift effect comparing to bulk Cu_2O.

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