Spherical hollow assembly composed of Cu$_2$O nanoparticles

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Abstract

Hollow spheres of Cu$_2$O with an average diameter of 0.3–0.6 μm have been prepared by a simple reaction between CuO suspension and NH$_2$OH in the presence of deionized gelatin at room temperature. Gelatin played a decisive role as an inhibitor of the direct attack of NH$_2$OH to CuO surfaces and coagulation of the growing Cu$_2$O in producing the hollow spheres. The products were characterized by X-ray powder diffraction, transmission electron microscopy, X-ray photoelectron spectra techniques and UV-visible absorption spectroscopy. The band gap is estimated to be 2.60 eV according to the results of optical measurements of the hollow spheres.

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1. Introduction

Hollow spheres of nanometer to micrometer dimensions is being pursued with great interest because of several possible technical applications in catalysis, drug delivery systems, separation techniques, photonics as well as piezoelectric and other dielectric devices [1,2]. Cuprous oxide has attracted much current research interest since Cu$_2$O is a p-type semiconductor [3,4] with a direct band gap of 2 eV, which makes it a promising material for the conversion of solar energy into electrical or chemical energy [5]. Recently, it has been found that Cu$_2$O submicrospheres can be used as the negative electrode material for lithium ion batteries [6] and was reported to act as a stable catalyst for water splitting under visible light irradiation [7,8]. Cu$_2$O has been prepared by several different methods, such as electrodeposition [9–11], sonochemical method [12], thermal relaxation [13], liquid phase reduction [14] and vacuum evaporation [15]. In this paper, we report a method to synthesize Cu$_2$O at room temperature by a very simple reaction between Cu(CH$_3$COO)$_2$, NH$_2$OH·HCl and NaOH in the presence of deionized gelatin agents. Hollow spheres were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectra (XPS). The sizes of the subunits of the polycrystalline Cu$_2$O particles were

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estimated by Debye–Scherer formula according to XRD spectrum.

2. Experimental procedure

2.1. Materials

All the reagents used in the experiments were of the analytical purity. Cu(CH$_3$COO)$_2$, NaOH, NH$_2$OH·HCl and deionized gelatin were purchased from Shanghai Chemical Reagent Factory (China). Distilled water was used throughout.

2.2. Instruments

Powder XRD patterns were recorded on a Shimadzu X-ray diffractometer XD-3A (CuK$_\alpha$ radiation, $\lambda = 0.15418$ nm). TEM was performed using a JEOL-JEM 200CX instrument. XPS were recorded on ESCALAB MKII instrument. The samples used for TEM observations were prepared by dispersing some products in ethanol followed by ultrasonic vibration for 10 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. A shimadzu UV-3100 photospectrometer was used to record the UV-visible absorption spectra.

2.3. Standard procedure for the preparation of Cu$_2$O particles

The standard conditions for the synthesis of Cu$_2$O are as follows. First, CuO powder was prepared by adding 100 ml of 2.0 mol/l NaOH to the same volume of 1.0 mol/l Cu(CH$_3$COO)$_2$, aging the precipitated Cu(OH)$_2$ gel at 60°C for 2 days in a laboratory oven, thoroughly washing with doubly distilled water and freeze drying. Then 1.0 mol/l CuO suspension and 0.5 mol/l NH$_2$OH·HCl, were prepared, respectively, in which 2% deionized gelatin was contained. The same volume of the 1.0 mol/l CuO suspension stabilized, 0.5 mol/l NH$_2$OH·HCl and 0.5 mol/l NaOH were added rapidly with stirring for 2 h under agitation at room temperature. The products obtained were washed thoroughly with absolute ethanol in an inert glove box (O$_2$ < 2 ppm) and vacuum dried at room temperature overnight.

3. Results and discussion

3.1. XRD study

An XRD pattern of the hollow spheres was given in Fig. 1. The XRD spectrum contains five peaks that are clearly distinguishable. All of them can be perfectly indexed to crystalline Cu$_2$O, not only in peak position, but also in their relative intensity. The peak positions are in good agreement with those for Cu$_2$O powder obtained from the International Center of Diffraction Data card (ICDD, formerly JCPDS). The size of the subunits of the polycrystalline Cu$_2$O particles was calculated to be about 8 nm according to half width of the diffraction peaks using Debye–Scherer equation.

3.2. TEM measurements

The morphology of the as prepared Cu$_2$O was studied by TEM. Fig. 2 shows the as prepared Cu$_2$O with hollow spheres and the average diameter is about 0.3–0.6 μm. In TEM images containing the hollow spheres, we can clearly observe single particle with 5–10 nm size. This result is in good agreement with XRD result.

3.3. XPS measurements

The wide XPS picture of the product is shown in Fig. 3. Fig. 4a shows the photoelectron spectrum of Cu$_{2p}$, The peak at 932.55 eV, which was corrected with reference to C$_{1s}$ (284.6 eV), corresponding to the binding energy of Cu$_{2p}$, is in good agreement with data observed for Cu$_2$O [16]. As shown in Fig. 4b, the O$_{1s}$ core-level spectrum is broad, and has two O$_{1s}$ peaks (marked as a and b). Peak (a) at the lower energy of 530.3 eV is in good agreement with O$^{2-}$ in Cu$_2$O [16]. Peak (b) at the higher energy of 531.7 eV, is attributed to O adsorbed on the surface of Cu$_2$O hollow spheres.
Thus, the XPS results prove that the sample is composed of Cu$_2$O.

3.4. Proposed reaction path

Based on the investigation on the formation of Cu$_2$O hollow spheres, the possible mechanism may be summarized as follows:

\[
\text{Cu(CH}_3\text{COO)}_2 + 2\text{NaOH} \rightarrow \text{Cu(OH)}_2 + 2\text{NaCH}_3\text{COO},
\]

\[
\text{Cu(OH)}_2 \rightarrow \text{CuO} + \text{H}_2\text{O},
\]

\[
\text{NH}_2\text{OH} \cdot \text{HCl} + \text{NaOH} \rightarrow \text{NH}_2\text{OH} + \text{NaCl} + \text{H}_2\text{O}.
\]

\[
4\text{CuO} + 2\text{NH}_2\text{OH} \rightarrow 2\text{Cu}_2\text{O} + \text{N}_2\text{O} + 3\text{H}_2\text{O}.
\]
In the experiment, we employed hydroxylamine hydrochloride as the reducing agent. The gelation works as an inhibitor of both the direct reaction of NH₂OH with CuO and coagulation of the produced Cu₂O particles.

3.5. Optical properties

We have carried out the UV-Visible absorption spectrum of the product in order to resolve the excitonic or interband transitions of Cu₂O particles. UV-Visible absorption spectrum (Fig. 5a) of the as-prepared Cu₂O particles dispersed in ethanol solution shows a broad absorption peak whose center is at about 505 nm. The Cu₂O particles were well dispersed in ethanol to form a transparent solution by ultrasonic vibration for 10 min. An estimate of the optical band gap is obtained using the following equation for a semiconductor:

\[ \alpha(v) = A(\frac{hv}{2 - E_g})^{m/2} \]

where \( A \) is a constant, \( \alpha \) is the absorption coefficient and \( m \) equals 1 for a direct transition. The energy intercept of a plot of \((\alpha E_{\text{ photons}})^2 \) vs. \( E_{\text{ photons}} \) yields \( E_g \) for a direct transition (Fig. 5b) [17]. The band gap of the as-prepared Cu₂O particles is calculated to be 2.60 eV from the UV-Visible absorption spectrum, which is larger than the reported value for the bulk Cu₂O (\( E_g = 2.17 \) eV) [18].

3.6. Roles of gelatin

The gelatin in the bulk and on the surfaces of CuO particles in the form of an adsorption layer may control the diffusion of NH₂OH molecules. As a result, the reaction may occur mainly in a balanced region of the reagent flux and counter flux of the released metal ions, more or less away from the surface of each solid precursor particle. In the absence of gelatin, the reaction may take place on the surfaces of the solid precursor, because of the too rapid diffusion of the reagent. The gelation works as an inhibitor of both the direct reaction of NH₂OH with CuO and coagulation of the produced Cu₂O particles.

4. Conclusion

Cu₂O hollow spheres with size of 0.3–0.6 μm have been successfully prepared by a sol–gel/emulsion technique at room temperature. The role of gelatin in the growing Cu₂O hollow spheres was discussed. The band gap is estimated to be 2.60 eV according to the results of optical measurements of the hollow spheres of Cu₂O. It is expected that the method can be extended to prepare other submicrometer hollow sphere materials.
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