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Synthesis and characterization of Cu_3P hollow spheres by a facile soft-template process

Xinjun Wang*, Fuquan Wan, Juan Liu, Youjun Gao, Kai Jiang*

College of Chemistry and Environmental Science, Henan Normal University, 46# East of Construction Road, Xinxiang, Henan 453007, PR China

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ABSTRACT

Hollow Cu_3P microspheres have been successfully synthesized by a facile ethylenediamine tetraacetic acid (EDTA) mediated solvothermal route using $CuSO_4{\cdot}5H_2O$ and yellow phosphorus as starting materials in a mixture solution of ethylene glycol (EG), ethanol and water. The formation of these hollow spheres is attributed to the oriented aggregation of Cu_3P nanocrystals around the gas–liquid interface between PH_3 and the mixture solution. The possible growth mechanism is proposed.

1. Introduction

The morphology of inorganic solid materials is an important factor to their properties, thus, the preparation of inorganic compounds with special morphologies has attracted a great deal of interest [1]. Up to now, a number of novel nano/microstructures have been prepared with different morphologies. Among these novel nano/microstructures, inorganic hollow sphere have received considerable attention because of their diverse applications, such as in drug delivery [2], heterogeneous catalysis [3], nanostructured composites [4], and the protection of enzymes and proteins [5], bioencapsulation [6]. Various methods have been developed for preparing hollow spheres. For example, hollow polymer, oxide, and glass composite microspheres with diameters generally in the micrometer-size range can be produced by spray drying techniques, which use nozzle systems to dispense individual liquid droplets of uniform size [7]. Another method for obtaining hollow spheres is involved with the direct synthesis of intact inorganic shells around various sacrificial templates, such as polystyrene latex spheres [8,9], vesicles [10], liquid droplets [11], latex templates [12], microemulsion droplets [13], silica spheres [14]. However, in most cases, the pure product was obtained only after the complete removal of the templates, which makes the experiments become more complicated. However, it still remains a challenge to develop simple methods for the fabrication of hollow nano- and microspheres of solid material. Recently, a lot of inorganic hollow spheres have been prepared via a bubble template route. The use of gas bubbles produced during the reaction to provide aggregation centers is a novel and effective method to fabricate hollow microspheres. Compared to the other template-synthetic methods, this soft-template method is very simple, convenient and avoids the introduction of impurities, and is therefore suitable for modern chemical synthesis. For example, Li and co-workers [15] prepared ZnSe hollow sphere by using N_2 bubbles as soft template. Lu and co-workers [16] synthesized ZnS hollow sphere by taking H_2S bubbles as the aggregation centers. Han et al. [17] obtained $CaCO_3$ hollow spheres by the aggregation of nano-sized spherical particles on CO_2/N_2 bubble surface.

Due to their excellent properties and potential application, transition metal phosphides have attracted more and more attention. Among these metal phosphides, Cu_3P is widely used as a potential electrode material in lithium batteries [18,19], a kind of fine solder and important alloying addition [20], a reinforcing agent in high speed steel (HSS) composite materials [21] and it can enhance the sintering behavior of 316L stainless steel [22].

In this paper, we report a facile one-pot soft-template method for the synthesis of hollow Cu_3P microspheres. In our experiment, copper sulfate ($CuSO_4 \cdot 5H_2O$) and yellow phosphorus were used as Cu source and P source, respectively, and the desired samples were obtained in a mixed solvent (EG, ethanol and water) at relatively low temperature (200 °C). EDTA is used to regulate the pH values

* Corresponding authors. Tel.: +86 373 3326336; fax: +86 373 3326336.
E-mail address: wxjtg2006@126.com (X. Wang).

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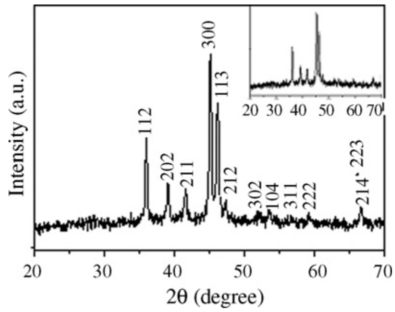

Fig. 1. Typical XRD pattern of the obtained sample.

and the rate of releasing of Cu^{2+} ions for the formation of Cu_3P hollow spheres.

2. Experimental

In a typical experiment, the desired amount of copper sulfate ($CuSO_4{\cdot}5H_2O$, 0.517 g) and 0.748 g EDTA were dissolved in 20 ml deionized water under stirring. After the solution became transparent, a mixture of 10 ml EG and 10 ml ethanol was added to the above solution. Several minutes later, the mixed solution was transferred to a 50 ml Telfon-lined stainless steel autoclave and appropriate amount of yellow phosphorus (0.45 g) was added to the above system. Then the autoclave was sealed and maintained at 200 °C for 17 h and then cooled to room temperature naturally. The resulting black precipitate was separated by centrifugation and washed respectively with distilled water, carbon disulfide (CS_2) and absolute ethanol to remove the residual reactants, excess yellow phosphorous and by-products. After that, the obtained sample was dried in vacuum at 60 °C for 6 h.

3. Results and discussion

Fig. 1 shows the XRD pattern of the obtained sample synthesized at 200 °C for 17 h and 6 h. All the diffraction peaks can be readily indexed as the hexagonal phase Cu_3P with lattice constants of a = 6.9595 Å and c = 7.1467 Å, which are close to the literature values (JPCDS Card No. 71-2261). No peaks of impurities were detected, indicating the high purity of the products.

Fig. 2 shows the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the products obtained at 200 °C for 17 h in presence of EDTA in the mixture solution of water, EG and ethanol. Fig. 2a is a representative TEM image of the Cu_3P hollow spheres. The contrast between the dark edge and pale inner part provides a direct proof for its hollow nature. The size and wall thickness of these hollow spheres are calculated to be approximately 0.8–1.0 μm and 50–80 nm, respectively. Fig. 2b shows a SEM image at low magnification of the as-prepared Cu_3P microspheres. It was clearly demonstrated that the majority of the products exhibited spherical morphology. The average diameter of Cu_3P spheres is about 0.8–1.0 μm. The broken shells observed on some of the spheres indicate the hollow structure of them, and a magnified image of one hollow sphere with the broken part is shown in Fig. 2c, confirming the hollow structure of these Cu_3P microspheres. From Fig. 2c, the wall thickness of the microspheres is estimated to be approximately 50–80 nm, which is consistent with the TEM observation. The agglomerates structure maybe result from the high surface energies of Cu_3P hollow spheres.

In our prior works [23], our group have successfully fabricated Cu_3P hollow sphere by a two-step solvent-assisted coordination and reduction process, in which EG serves not only as a reducing reagent, but also as a complexing solvent. This process can be described as follows:

$$Cu(OH)_2 \xrightarrow[\text{coordination}\ (1)]{EG} [Cu(EG)_x]^{2+} \xrightarrow[\text{reduction}\ (2)]{} Cu \xrightarrow[\text{redox}\ (3)]{P_4} Cu_3P$$

However, we have not exactly understood how on earth to form the hollow spherical structure so far. The possible formation process may be due to the Kirkendall effect.

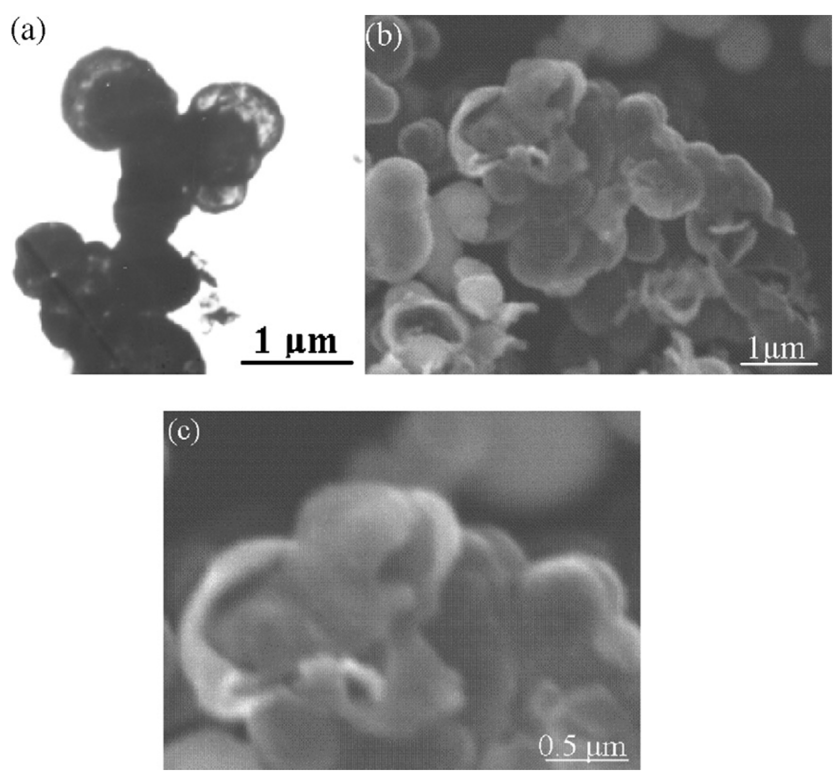

Fig. 2. TEM and SEM images of the as-obtained sample at 200 °C for 17 h.