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# Synthesis and characterization of hollow spherical copper phosphide ($Cu_3P$) nanopowders

Shuling Liu [a], Yitai Qian [b,c], Liqiang Xu [b,*]

[a] College of Chemistry and Chemical Engineering, Shaanxi University of Science & Technology, Xi'an 710021, PR China

[b] College of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, PR China

[c] Department of Chemistry and Structure Research Laboratory, University of Science and Technology of China, Hefei, 230026, PR China

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ABSTRACT

In this paper, hollow spherical $Cu_3P$ nanopowders were synthesized by using copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and yellow phosphorus in a mixed solvent of glycol, ethanol and water at 140–180 °C for 12 h. X-ray powder diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), electron diffraction pattern (ED) and transmission electronic microscopy (TEM) studies show that the as-synthesized nanocrystal is pure hexagonal phase $Cu_3P$ with a hollow spherical morphology. Based on the TEM observations, a possible aggregation growth mechanism was proposed for the formation of $Cu_3P$ hollow structures. Meanwhile, the effects of some key factors such as solvents, reaction temperature and reaction time on the final formation of the $Cu_3P$ hollow structure were also discussed.



## 1. Introduction

Copper phosphides have attracted much attention due to their extant and potential technological properties. When focusing on the Cu–P system, we find that among all the reported copper phosphides ($Cu_3P$ [1], $CuP_2$, and $Cu_2P_7$ [2]), only $Cu_3P$ is air stable and already possesses the industrial applications as a kind of fine solder and as an important alloying addition [3]. Very recently, it is reported that $Cu_3P$ has good qualities as negative electrode material in lithium batteries, its gravimetric capacity is close to that of graphite, but its volumetric capacity is almost four times higher than that of graphite [4].

Traditionally, $Cu_3P$ has been prepared via many routes. For example, $Cu_3P$ was synthesized on an industrial scale by a direct solid-state reaction at temperatures higher than 800 °C [4], electrochemical method by reaction of metal sulfate solution with phosphorus shines, etc [5–7]. Parkin et al. also reported an exothermic, self-propagating reaction between sodium phosphide ($Na_3P$) and anhydrous copper halides in evacuated sealed Pyrex or quartz ampules [8]. Recently, solvothermal methods [9,10] have also been reported to prepare $Cu_3P$, but only $Cu_3P$ solid nanoparticles with irregular morphology were obtained.

## 2. Experiment

All the chemical reagents were analytical pure grade and were used without further treatment. In this report, hollow spherical $Cu_3P$ nanopowders were synthesized via a solvothermal process. In a typical experimental procedure, copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 2 mmol) and a mixed solvent (10 mL glycol, 24 mL ethanol and 12 mL water) were mixed with stirring and were transferred into a Teflon lined autoclave of 50 mL capacity. When the solution was transparent, yellow phosphorus (5 mmol) was added. Then, the autoclave was sealed, heated from room temperature to 180 °C, and held for 12 h. Subsequently, the autoclave was allowed to cool down to room temperature naturally. After that, the precipitates were dispersed in benzene by stirring and the suspension was left for a while to dissolve unreacted yellow phosphorus; then, they were filtered and washed successively with absolute ethanol and distilled water to remove the residual reactants. Finally, the obtained black sample was dried in vacuum at 50 °C for 4 h and collected for characterization.

* Corresponding author. Tel.: +86 531 8836 4543; fax: +86 531 8836 6280.
*E-mail address:* xulq@sdu.edu.cn (L. Xu).

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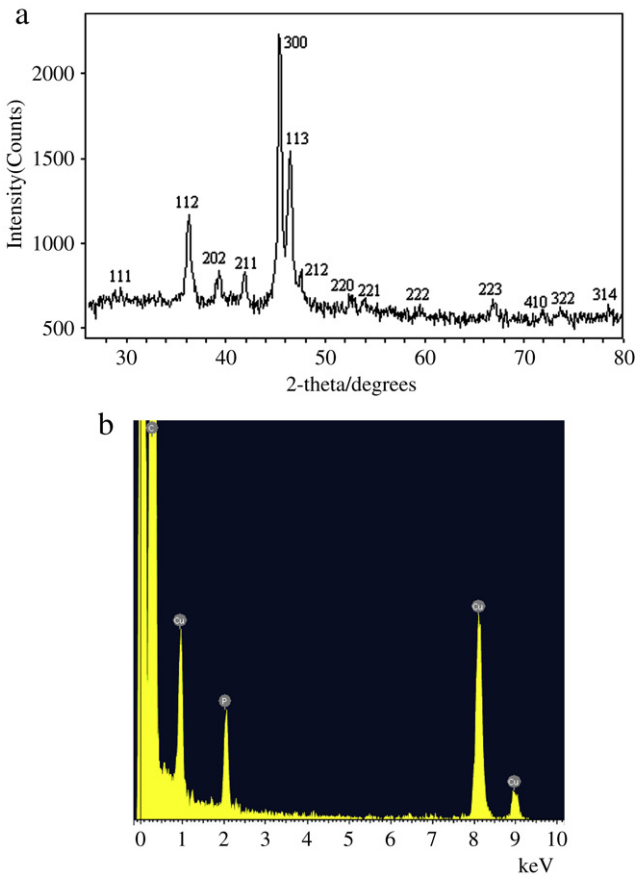


**Fig. 1.** Typical XRD pattern (a) and EDX (b) of as-prepared sample prepared at 180 °C for 12 h.

X-ray powder diffraction (XRD) patterns were carried out on a Bruker D8 Advanced X-ray diffractmeter with Cu Ka radiation ($\lambda = 1.5418$ Å). The morphologies of the as-prepared samples were observed by an H-600 transmission electron microscope (TEM) and a JEM-2100 high-resolution transmission electron microscope (HRTEM).

## 3. Results and discussion

Fig. 1(a) shows the typical XRD pattern of the as-prepared samples at 180 °C for 12 h. All the diffraction peaks in this pattern can be indexed to hexagonal $Cu_3P$ phase with lattice constants $a = 6.947$ Å, $c = 7.066$ Å, which are close to those of the reported values (JCPDS card No. 02-1263). No other peaks that belong to impurities such as P or Cu could be detected. The purity of the sample is also determined by EDX (Fig. 1(b)). The result shows that only Cu and P exist in the product. The fact that $Cu_3P$ is only air stable phosphide among all the copper phosphides [3] further proves the high purity of the as-obtained sample.

The TEM image of the as-prepared $Cu_3P$ sample obtained at 180 °C for 12 h is shown in Fig. 2. It is observed that the sample consists of a large quantity of nearly spherical hollow nanoparticles. Their average diameters are in the range of 200–300 nm. These results reveal that small particles might aggregate into hollow nanoparticles. The content of these hollow spherical materials is estimated to be above 90% through the TEM observations. The three obvious diffraction rings in the ED pattern (inset in Fig. 2) recorded from the hollow spheres can be indexed as the (300), (222) and (322) planes of hexagonal $Cu_3P$ nanocrystals.

In the present route, the synthesis of $Cu_3P$ is based on the reaction of $Cu^{2+}$ with $PH_3$. $PH_3$ was produced by the reaction of P and the solvents (see Eqs. (1) and (2) [11–13]). Once $PH_3$ gases were generated, copper ions will immediately react with them to form $Cu_3P$. The produced $H_3PO_3$ and $H_3PO_4$ undergo successive reactions shown in Eqs. (3) and (4), which increases the amount of $PH_3$ and accelerates the reaction of $PH_3$ with the copper ion until one of the raw materials runs out [14,15].

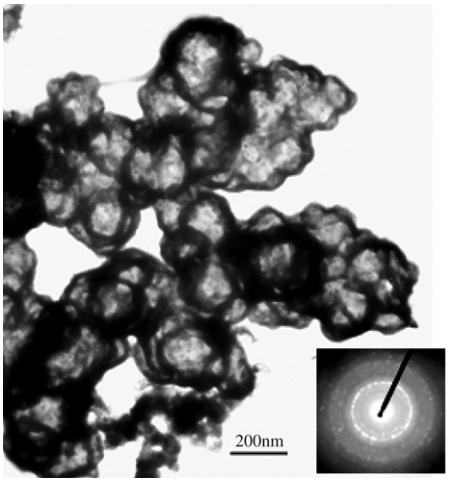


**Fig. 2.** Typical TEM image, ED pattern (the inset) of the as-prepared $Cu_3P$ sample.

$$2P_4 + 12H_2O \rightarrow 3H_3PO_4 + 5PH_3 \quad (1)$$

$$P_4 + 6C_2H_5OH \rightarrow 2H_3PO_3 + 2PH_3 + 6C_2H_4 \quad (2)$$

$$4H_3PO_3 \rightarrow PH_3 + 3H_3PO_4 \quad (3)$$

$$P_4 + 6H_3PO_4 + 6H_2O \rightarrow 10H_3PO_3. \quad (4)$$

In order to investigate the formation process, the TEM images of the $Cu_3P$ nanoparticles at different reaction time were obtained. When the reaction time was prolonged from 3 to 9 h, the amount of solid particles decreased dramatically and the amount of hollow spheres increased correspondingly (Fig. 3(a)–(c)). When the reaction time was extended to 10 h, hollow spherical $Cu_3P$ nanoparticles became the majority product (Fig. 3(d)). When the reaction time was further extended, these hollow spheres were attached and congregated together and only a dim borderline could be detected (Fig. 3(e)–(f)).

Based on the results of our TEM observations and the hollow spherical structure of the product, the possible growth process of these hollow spherical $Cu_3P$ nanoparticles is proposed, which is similar to the reported formation processes of $Co_2P$ hollow tubes and ZnSe microspheres [16,17]. After the initial nucleation, the newly formed $Cu_3P$ nuclei will grow into nanoparticles and then quickly aggregate into bigger solid particles. Therefore, when the reaction time was 3 h, only these larger particles were observed (see Fig. 3(a)). With the increment of the reaction time, abundant gas bubbles (such as $PH_3$ and $C_2H_4$ et al.) were produced. The smaller nanoparticles might break away from the initial solid and large aggregated ones under the circumambience of abundant bubbles, super-saturation and the pressure of solvothermal conditions, and self-assemble around the surfaces of these hollow spheres to reduce their surface energy [18]. Moreover, the dissolution process is temperature dependent, e.g. it can only take place at high temperatures. A further temperature-dependent study suggests this point. The product obtained at 140 °C for 6–9 h is composed of almost 80% solid spheres. Therefore, we obtain hollow spherical $Cu_3P$ nanoparticles with a high yield when the reaction temperature is raised or the reaction time is prolonged to a certain reaction stage (see Fig. 3(e)–(f)). The appearance many small nanoparticles with a size of 20–30 nm near the aggregated solid and hollow spheres

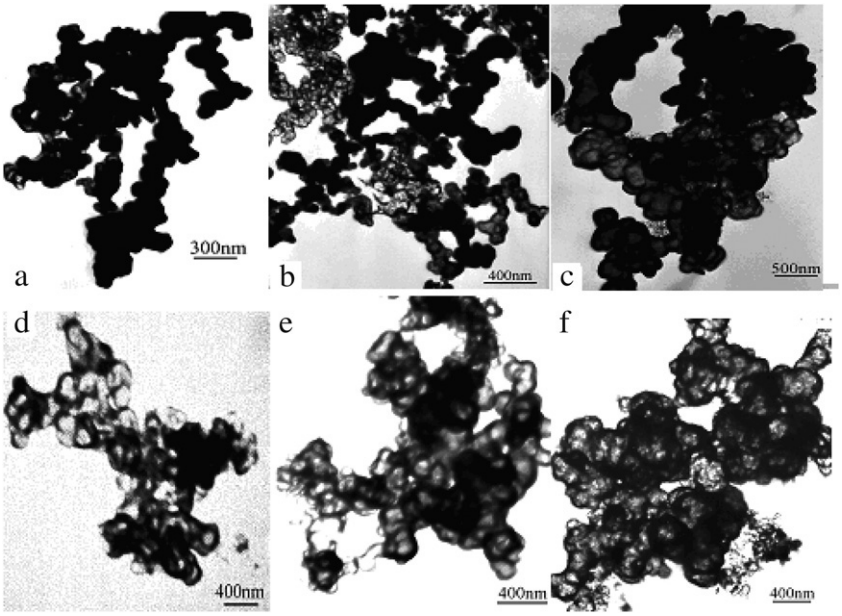


**Fig. 3.** Typical TEM images of $Cu_3P$ nanocrystals obtained at (a) 3 h, (b) 6 h, (c) 9 h, (d) 10 h, (e) 11 h, (f) 12 h, respectively.

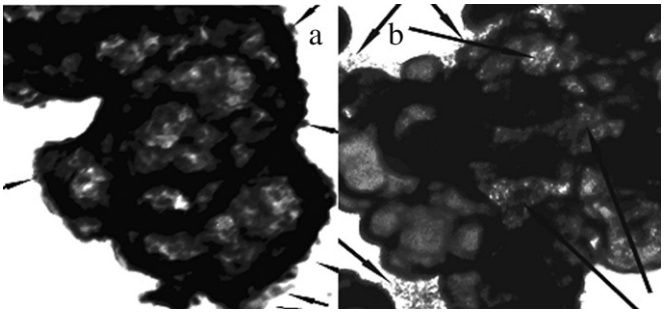


**Fig. 4.** The magnified TEM images of some small nanoparticles (as arrowed) near the solid and hollow spheres prepared at (a) 6 h, (b) 9 h.

(as arrowed in Fig. 4(a) and Fig. 4(b)) during the reactions might further prove the above process. However, due to the relative complex and fast velocities of the reaction system involved in this experiment, the exact formation mechanism of the hollow spherical $Cu_3P$ nanoparticles still needs further research.

As the experimental system we designed here is rather complex, many contrasting experiments have been carried out in order to find the influencing factors on the final morphology and phase of the products. The results indicate that the solvents, reaction temperature play important roles in the experiment.

When different kinds or ratios of solvents were used while keeping other conditions unchanged, it was found that the optimal solvent was the mixture of glycol, ethanol, and water. Other solvents lead to incomplete reaction or lower production of hollow spheres. When the temperature was increased from 140 to 180 °C, the yield of hollow spheres gradually increased, which indicates that a higher reaction temperature is favorable for the formation of hollow spherical $Cu_3P$ powders.

## 4. Conclusion

In conclusion, we report a simple and mild solvothermal route to synthesize $Cu_3P$ hollow spherical nanoparticles with a yield of about 90%. The as-obtained hollow spherical nature of the $Cu_3P$ nanoparticles with other species or surface modification might present an interest in potential technological properties such as alternative devices as anode materials for lithium ion batteries, where special issues are required [4].

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