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Research Article

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Synthesis of copper hollow nanospheres via a solvothermal reduction process

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ABSTRACT

Uniform copper hollow nanospheres with average diameters of ~500nm were synthesized through two stages. The first stage is the synthesis of copper hydroxide precursors and the second is the recrystallization stage by a simple surfactant-assisted solvothermal reduction method. These copper hollow nanospheres were formed through the reduction of copper hydroxide by the admixture of ethanol and ethylenediamine in the presence of surfactant sodium dodecyl benzenesulfonate (SDBS) at 180ºC. Influencing factors on the morphologies and components of the final products are discussed. The products were investigated in detail by X-ray powder diffraction (XRD), transmission electron microscope (TEM), the electron diffraction (ED) and UV-vis absorption spectrum.

Key words: Copper; Hollow nanosphere; Solvothermal method; Metal forming and shaping

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INTRODUCTION

The shape and size of nanostructures are two crucial factors in determining the properties of nanomaterials, and thus, the control of size and shape is great interest. Recently, controlling the shape and size of metal and semiconductor particles have been successfully achieved in solution phases by employing appropriate capping agents, such as surfactants [1, 2], polymers [3], and ligands [4]. These capping agents could kinetically control the relative growth rates of different crystal planes by chemically or physically adsorbing on the surfaces of the growing nanoparticles.

Monodispersenanospheres, core-shell nanostructure, and metal hollow nanospheres have received much attention because they have potential applications, such as photonic materials and microchip reactors [5-7]. Colvin et al. successfully developed a template method to produce macroporous metals such as three-dimensional nickel films with pore diameters between 200 and 1000nm [8]. C. Y. Wang et al. synthesized shell-core Cu2O-Cu nanocomposite particles in a microemulsion system [9]. Shuling Xu et al. Prepared Cu2O-Au core-shell nanospheres in aqueous medium at room temperature[10] .Among all metals, copper nanoparticles have attracted considerable attention because of their catalytic, optical, and conducting properties[11-13]. Here, we reported a simple surfactant-assisted solvothermal route to copper hollow nanospheres with average diameters of ~500nm based on the reduction of copper hydroxide powder by the admixture of ethanol and ethylenediamine (Here, the volume ratio of ethanol to ethylenediamine in the admixture is 16:5) in the presence of the surfactant SDBS at 180ºC for 24h.

EXPERIMENTAL SECTION

2.1 Synthesis of copper hydroxide precursors

All of the chemical reagents used in this experiment were analytical grade. There are three steps in our experiments to synthesize Cu hollow nanospheres. First, copper hydroxide precipitate was synthesized by the reaction of cupric chloride with sodium hydroxide in aqueous solution at room temperature. The precipitated copper hydroxide was filtered and washed, and finally dried in a vacuum at 60ºC for 3h.

2.2 Synthesis of copper hollow nanospheres

Second, 20mL ethanol, 6.25mL ethylenediamine and 0.1g SDBS were mixed under agitation. Finally, 26.25mL of the mixture solution and the appropriate amounts of pre-obtained copper hydroxide powder were transferred into a Teflon-lined autoclave of 35mL capacity. The autoclave was maintained at 180ºC for 24h and then cooled to room temperature naturally. The resulting solid products were filtered and washed, and finally dried in a vacuum at 60ºC for 5h.

2.3 Characterization

The phase and crystallographic structure of the obtained samples were characterized by X-ray powder diffraction (XRD), operating on a Japan Rigaku D/Max-γA X-ray diffractometer equipped with a graphite-monochromatized Cu Kα radiation source. The morphology and particle size of the product were determined by transmission electronic microscopy (TEM) and the electron diffraction (ED), which was carried out on a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200KV.

RESULTS AND DISCUSSION

3.1 Phase and Purity of the Products

The XRD pattern of the hollow nanospheres is shown in Figure 1. All the reflection peaks of Figure 1 can be indexed to the cubic (Face-centered) structured Cu with no impurities detected. The calculated cell constants, a=3.614Å, are very close to the reported values (a=3.615Å, JCPDS Card No.7440-50-8).

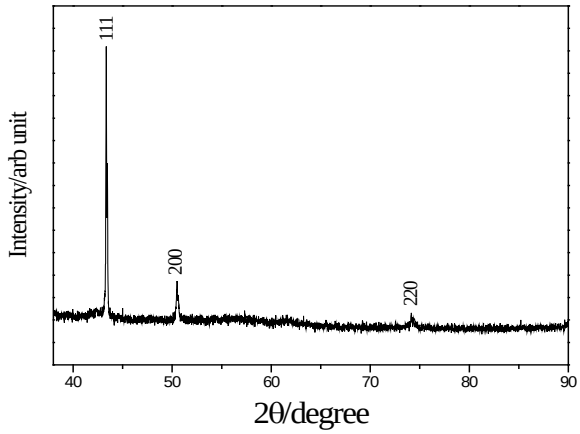

Fig. 1.XRD pattern of Cu hollow nanospheres obtained in the presence of SDBS

3.2 Morphology and Structure Characterization of the Products

Figure 2a and 2b are TEM images of Cu hollow nanospheres, which show that the product obtained in the presence of SDBS is predominated with uniform hollow nanospheres with diameters of ~500nm and no Cu nanoparticles are observed. From Figure 2b, we can observe that the surfaces of Cu hollow nanospheres are not smooth and the spheres seem to be composed by many smaller nanoparticles. Also, the electron diffraction (ED) pattern for the hollow nanospheres as shown in Figure 2d indicates that the nanospheres are polycrystalline nature. The ED image shows four main diffraction rings with the radii in the ratio of 错误!未定义书签。$\sqrt{3}:\sqrt{4}:\sqrt{8}:\sqrt{11}$. They relate to the (111), (200), (220), and (311) planes and reveal that the resultant hollow nanospheres are pure metallic copper with a face-centered cubic (fcc) structure, agreeing with the consequence from XRD pattern. To verify the proposed mechanism, we carried out the reaction in the absence of the surfactant SDBS while other conditions remained stable. It was found from this experiment that branch-like Cu microcrystals with diameters from several tens to several hundreds of nanometers formed after reaction. Figure 2c is the TEM image of these branch-like Cu microcrystals. Therefore, we suspected that the surfactant SDBS had significant influence on the shape and size of the products.

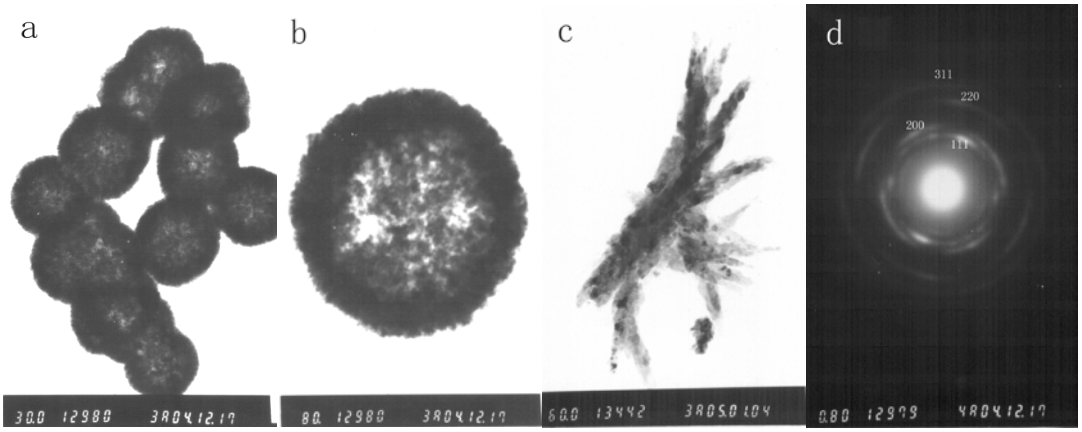

Fig.2. TEM and ED images of Cu hollow nanospheres (a,b) and branch-like Cu micropatterns (c)

3.3 Optical property of copper hollow nanospheres

Figure 3 shows the UV-vis absorption spectrum taken from the as-synthesized copper nanospheres dipersed in ethanol. The absorption maxima at 590 nm were in good agreement with the reported values for copper nanoparticles [12], and attributable to the plasma excitation in copper hollow nanospheres.

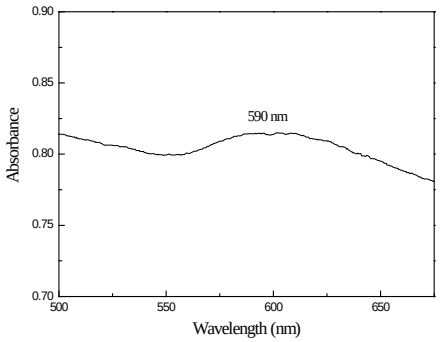

Fig.3. UV-vis spectra of the as-synthesized copper nanospheres

3.4 Influences of the Admixture of Ethanol and Ethylenediamine

In the solvothermal process, the admixture of ethanol and ethylenediamine acts as reducing agent. We found that the admixture of ethanol and ethylenediamine was unique for the synthesis of Cu hollow nanospheres in the present synthesis. When other reducing agent, such as ammonia, ethanol, ethylenediamine, and hydrazine were used instead of the admixture of ethanol and ethylenediamine, no Cu nanoparticles were produced. Using ethylenediamine as reducing agent, almost no solid products were synthesized because Cu2+ ions tended to bond with ethylenediamine to form complex Cu (en)22+ in the solution of ethylenediamine with high density. Using ethanol as reducing agent, the compound of CuO and Cu2O formed, which indicated that the reducing intensity of ethanol was not enough for formation of metal copper. So, we attempted to mix ethanol and ethylenediamine in order to decrease the density of ethylenediamine and increase the reducing intensity of ethanol. Finally, single-phase of Cu were successfully synthesized via the reduction of copper hydroxide by the admixture of 20mL ethanol and 6.25mL ethylenediamine.

3.5 Effect of SDBS on the Nanospheres Growth

There are many studies concerning the effects of surfactants on crystal growth and habit modification [14-16].It is believed that the adsorption of surface active species decreases the surface energy of the 3D or 2D nuclei by saturation of dangling bonds on the crystal surface. This leads to smaller nuclei, less energy for nucleus formation and a high nucleation rate, and thus promotes the reaction [15].

According to the above theories, we speculated that SDBS was the important factor in the present procedure for the synthesis of Cu hollow nanospheres. It could be believed that the surfactant SDBS might play roles on at least two aspects: controlling the size and morphology of the final products. As shown in Figure 2c, only branch-like copper microcrystals with dissimilar diameters were obtained when SDBS was not used in the experiment. This indicates that the initial formed copper nanoparticles had a strong tendency to adsorb as larger ones when no protective agents were added. When SDBS was introduced in appropriate amounts, the initially formed nanoparticles were relatively

small in dimension, and well dispersed in the solution because these SDBS molecules would strongly and rapidly adsorb on the surfaces of these nascent nanoparticles. But the exact roles of SDBS on the formation of the hollow nanospheres are still unclear. A further study of this issue is under way.

CONCLUSION

In summary, copper hollow nanospheres with a uniform diameter have been prepared in high yield via a surfactant-assisted solvothermal reduction process at 180ºC. There are two key points for the preparation of Cu hollow nanospheres: the presence of the surfactant SDBS and the selective use of the reducing agent (the admixture of 20mL ethanol and 6.25mL ethylenediamine). SDBS played a crucial role on the shape of the final products. The admixture of 20mL ethanol and 6.25mL ethylenediamine was the important factor in determining the components of the final product. We believe that such a rational synthetic route is versatile and can be adapted for the fabrication of 3D nanostructures of various transition metals and their alloys by choosing the suitable capping agents and the reaction parameters.

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