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ScienceDirect
Ceramics International 35 (2009) 905–907
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Preparation and characterization of CuS hollow spheres

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Received 18 December 2007; received in revised form 30 December 2007; accepted 4 February 2008
Available online 4 June 2008

Abstract

CuS hollow spheres have been successfully prepared using styrene–acrylic acid copolymer (PSA) latex particles as template. The process involved the deposition of inorganic coatings on the surface of PSA latex particles and subsequent removal of the latex particles by dispersing in toluene. The synthesized products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) and UV–vis absorption spectroscopy. The results showed the wall thickness of CuS shell to be about 20 nm and the pore diameter to be about 150 nm. The possible formation mechanism of CuS hollow spheres has been proposed.

Keywords: CuS; Hollow spheres; Characterization

1. Introduction

Hollow spheres with nanometer or micrometer dimensions are attracting considerable attention because of their specific structure and potential applications as photonic crystals, fillers, vehicle systems, and catalysts [1,2]. Efforts have therefore been made to prepare inorganic hollow spheres because of their excellent physical and chemical properties being different from the bulk materials [3].

Copper sulfide (CuS) with various stoichiometry is an important p-type semiconductor and has been extensively used in solar cell, optical filter and superionic materials, which show metallic conductivity and transform into a superconductor at 1.6 K [4]. CuS also exhibits fast-ion conduction at high temperature and some other special properties [5]. In the last few years, the synthesis and characterization of CuS hollow spheres has aroused much research interest. Zhu et al. [6] fabricated CuS hollow spheres by thioglycolic acid (TGA) assisted hydrothermal synthesis. However, most of them were broken hollow spheres. Ni et al. [7], Xu et al. [8] and Chen et al. [9], respectively, also reported CuS hollow spheres synthesized by the aggregation of nano-sized spherical particles on CO_2, SO_2 or H_2S bubble surface. However, this method based on vesicles as templates showed a number of drawbacks such as the formation of irregular coatings, aggregation of the coated particles, and difficult control of coating thickness.

Poly-(styrene–acrylic acid) (PSA) latex particles have been widely used as template for the fabrication of hollow spheres of magnetic, ceramic, metallic, and composite materials [10]. Moreover, PSA latex spheres can be synthesized simply. In this paper, we report the coating CuS on PSA spheres using a layer-by-layer self-assembly technique to create core–shell composite and subsequent removal of the core template by dispersing in toluene.

2. Experimental

All of the chemicals were of analytical purity, and used without further purification. PSA latex particles, used as core materials, were prepared by radical co-polymerization of styrene and acrylic acid using ammonium persulfate as the initiator [11].

To prepare PSA/CuS core/shell composite structure, a mixture containing PSA latex, $CuSO_4$, thiourea, urea and polyvinylpyrrolidone (PVP) was dispersed in deionized water in an ultrasonic bath, then aged in a 50 ml Teflon-lined stainless steel autoclave at 85 for 8 h. After that, the suspension was cooled to room temperature, centrifuged and washed with water. The

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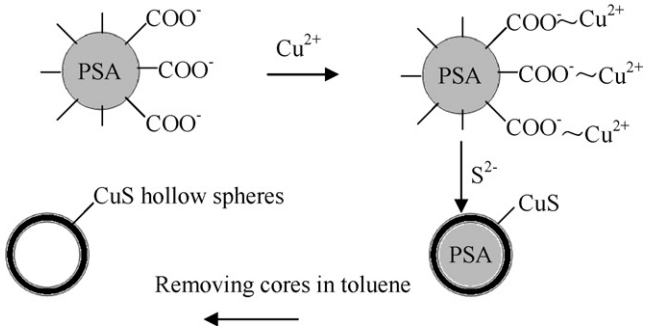
0272-8842/$34.00
doi:10.1016/j.ceramint.2008.02.003



Scheme 1. Schematic illustration for the fabrication of PSA/CuS core–shell and hollow CuS spheres.

coating procedure was repeated for three times to increase the thickness of the coatings. The final suspension was washed with deionized water and absolute ethanol for several times.

To prepare CuS hollow spheres, the composite particles were dispersed in toluene to dissolve the PSA cores, then, centrifuged and resuspended in solvent. This process was repeated several times, and then the purified hollow spheres were dried in vacuum before characterization.

The morphology of the products was observed by transmission electron microscope (TEM, JEM-3010). The phase identification of the samples was carried out on X-ray powder diffraction (XRD, Rigaku Damax-2200). FT-IR spectrometer (Rayleigh WQF-410) with the KBr pellet technique was used to determine the structure of the powders. UV–vis spectra were recorded on a Hitachi U-3010 spectrophotometer.

3. Results and discussion

Fig. 1 shows TEM micrographs of PSA latex, PSA/CuS core/shell coated particles and the obtained CuS hollow spheres. PSA has spherical morphology and good monodispersity with diameter about 150 nm. The structure of PSA/CuS core/shell composite is as uniform and monodisperse as the original PSA particles. The shell of the single nanospheres is smooth and homogeneous, and only some little nanoparticles can be seen on the surface. When the composite particles were dispersed in toluene to dissolve the PSA cores, CuS hollow spheres were obtained (Fig. 1c). The contrast between the dark edge and pale center is the evidence for its hollow nature. Moreover, the hollow CuS spheres are still retained in spherical symmetry without agglomeration and collapse. The diameters of hollow CuS spheres are very close to the PSA diameter, and the wall thickness of CuS shell is about 20 nm and the pore diameter is about 150 nm, indicating a relative narrow size distribution of the products.

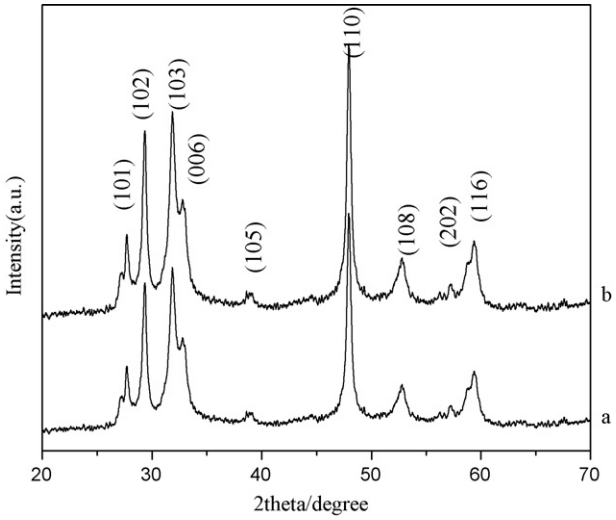


Fig. 2. XRD patterns of coated particles (a) and CuS hollow spheres (b).

Fig. 2 displays the XRD patterns of coated particles and CuS hollow spheres. The XRD pattern of PSA/CuS core–shell spheres is similar to that of CuS hollow spheres except for lower intensity of the diffraction peaks. The diffraction patterns of the two samples are very agreement with the hexagonal CuS (JCPDS No. 06-0464). No obvious impurity peaks are observed. The broadening of these diffraction peaks indicates that coated particles and CuS hollow spheres may be constructed from CuS particles.

Fig. 3 compares the FT-IR data of the coated particles and CuS hollow spheres to further confirm the formation of the inorganic shells and the complete removal of organic components. Well-defined bands of the phenyl group (700, 756 and 1400 cm^{-1}) in polystyrene, bands of O–H group (3518 and 3601 cm^{-1}) and bands of C–O group (2850 and 2940 cm^{-1}) in polyacrylic acid in Fig. 3a correspond to the PSA standard. When the core template is removed, the band

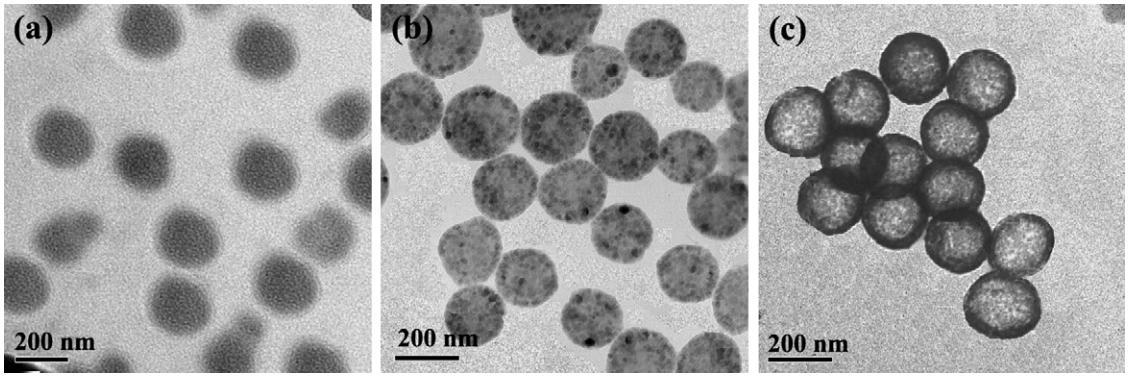


Fig. 1. Typical TEM images of PSA latex (a), coated particles (b) and CuS hollow spheres (c).

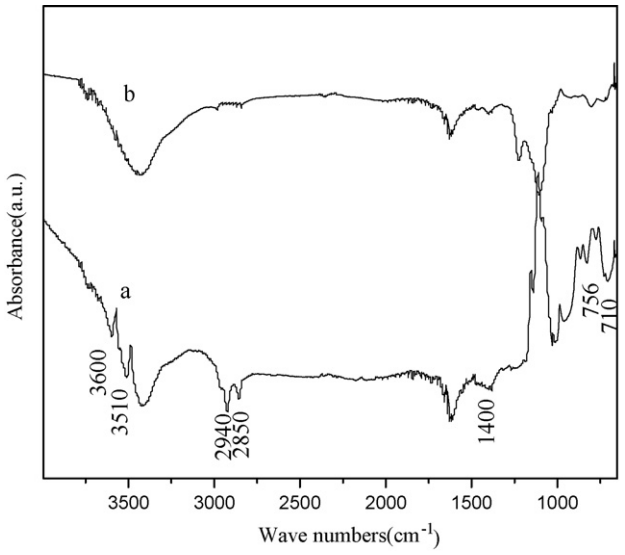


Fig. 3. FT-IR spectra of coated particles (a) and CuS hollow spheres (b).

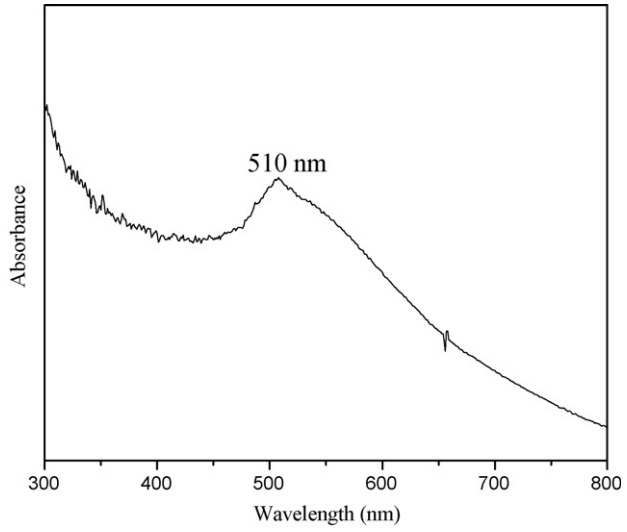


Fig. 4. UV–vis absorption spectrum of CuS hollow spheres.

characteristic of the PSA latex disappears or sharply weakens. Some weak bands characteristic of PSA still remain in Fig. 3b, indicating that there is strong interaction between the PSA and CuS hollow spheres.

The UV–vis absorption spectrum of obtained hollow CuS spheres is shown in Fig. 4. The UV–vis absorption peak locates near 510 nm, which is a typical characteristic of CuS.

Based on the experimental process and results, the following growth mechanism of CuS hollow spheres could be clearly derived (Scheme 1). Firstly, it was necessary to add PVP as a protective agent in the system to prevent the aggregation of core particles and the coated particles. Urea was used to adjust the pH of the reaction mixture. In the self-assembly process, the PSA latex was considered as the template. The carboxyl on the PSA would strongly cooperate with Cu^{2+} ions during ultrasonic bath. During the coating procedure, thiourea gradually hydrolyzed to produce S^{2-}, which would react with Cu^{2+} ions to form CuS. As a result, PSA particles would be coated with CuS particles. As the solubility product of CuS was extremely small (6.3×10^{-36}), the nucleation behavior of CuS was sensitive to the saturation degree. Too high Cu^{2+} ions concentration would lead to the rapid deposition of CuS. To ensure particles coated with smooth shells, it was necessary to repeat the process for three times to increase the coating thickness. It was found that PSA/CuS coated particles could be successfully fabricated. After the core was removed in toluene, CuS hollow spheres were obtained.

4. Conclusions

CuS hollow spheres with a wall thickness about 20 nm and a pore diameter about 150 nm have been successfully prepared using the PSA latex template approach. High qualitative intact CuS hollow spheres could be synthesized by this process. The possible formation mechanism of CuS hollow spheres has also been proposed. It is expected that the synthesis strategy can be extended to other inorganic semiconductor compound hollow spheres under mild conditions.

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