Materials Research Bulletin 47 (2012) 2460–2463

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Fast synthesis, formation mechanism, and control of shell thickness of CuS–polystyrene core–shell microspheres

Li-min Zhao *, Xin Shao, Yi-bin Yin, Wen-zhi Li

College of Materials Science and Engineering, Liaocheng University, Liaocheng 252059, China

ARTICLE INFO

Article history:
Received 2 March 2012
Accepted 17 May 2012
Available online 26 May 2012

Keywords:
A. Composites
B. Chemical synthesis
C. Thermogravimetric analysis
D. Optical properties

ABSTRACT

The silanol-modified polystyrene microspheres were prepared through dispersion polymerization. Then copper sulfide particles were grown on silanol-modified polystyrene through sonochemical deposition in an aqueous bath containing copper acetate and sulfide, released through the hydrolysis of thioacetamide. The resulting particles were continuous and uniform as characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fourier transform infrared, thermogravimetric analysis and UV–vis absorption spectroscopy were used to characterize the structure and properties of core–shell particles. The results showed the coating thickness of CuS shell can be controlled by the amount of silanol and the UV–vis absorption intensity of PSt/CuS composite also changed with the coating thickness of CuS.

1. Introduction

The core–shell colloids often display improved physical and chemical properties over their single-component counterparts and hence are very useful in a broader range of applications (e.g., electrical, magnetic, catalytic, mechanical, chemical, and optical) when compared with those of the core particles [1–3]. To prepare core–shell particles is also one of interests from fundamental and academic viewpoint, especially, in the area of colloid and interface science. Materials derived from core–shell particles are of extensive scientific and technological interest, due to their unique and tailored properties for various applications in material science [4–8]. Recently, there were many reports on fabricating core–shell particles, such as electrochemical method, electroless plating, layer-by-layer deposition, laser pulses, self-assembly, chemical reduction, microwave synthesis, sonochemical method, decomposition of organometallic precursors and photoreduction [9–14].

Copper sulfide (CuS) with various stoichiometry is an important p-type semiconductor and has been extensively used in solar cell, optical filter and super ionic materials, which show metallic conductivity and transform into a superconductor at 1.6 K [15]. CuS also exhibits fast ion conduction at high temperature and some other special properties [16]. In the last few years, the synthesis and characterization of CuS spheres has aroused much research interest. Zhu et al. [17] fabricated CuS spheres by thioglycolic acid assisted hydrothermal synthesis. However, most of them were broken hollow spheres. Ni et al. [18], Xu et al. [19] and Chen et al. [20], respectively, also reported CuS spheres synthesized by the aggregation of nano-sized spherical particles on CO_2, SO_2 or H_2S bubble surface. Shen et al. [21] reported CuS spheres were synthesized using styrene–acrylic acid copolymer (PSA) latex particles as template. However, this method showed a number of drawbacks such as the formation of irregular coatings, aggregation of the coated particles, and difficult control of coating thickness.

In this paper we describe a facile method to control the shell thickness of core–shell structure materials. Firstly, polystyrene microspheres were prepared through dispersion polymerization and were modified by 3-methacryloxypropyltrimethoxysilane as template. Then PSt/CuS composite particles were prepared through sonochemical deposition in an aqueous bath containing copper acetate and sulfide, released through the hydrolysis of thioacetamide. The coating thickness of CuS can be controlled by the amount of 3-methacryloxypropyltrimethoxysilane and the UV–vis absorption intensity of PSt/CuS composite also changed with the coating thickness of CuS. According to our knowledge, rather less research has been carried out in this respect.

2. Experimental

2.1. Materials and methods

Styrene, polyvinylpyrrolidone (MW, 30,000), 2,2-azobisisobutyronitrile and 3-methacryloxypropyltrimethoxysilane were supplied by Sinopharm Chemical Reagent Co. Ltd. Styrene was purified

---

* Corresponding author. Tel.: +86 635 8239863; fax: +86 635 8239863.
E-mail addresses: zhaolimin@lcu.ecu.cn, limin_zhao2008@hotmail.com (L.-m. Zhao).

0025-5408/$ – see front matter. Crown Copyright © 2012 Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2012.05.017

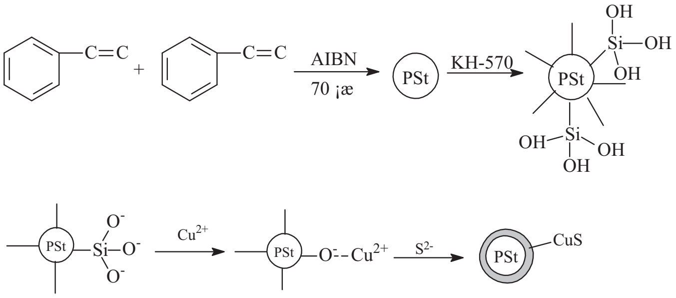

Fig. 1. Schematic illustration for the fabrication of PSt/CuS composite.

with vacuum distillation before use. Other starting reagents were used as received. All the chemicals were of analytical purity.

The morphology of the products was observed by scanning electron microscope (SEM, JSM-6380LV) and transmission electron microscopy (TEM, JEM-3010). Particle size distribution was recorded with Malvern Nano particle analyser series. FT-IR spectrometer (Nicolet IR100) with the KBr pellet technique was used to determine the structure of the PSt particles. TGA was performed using an STA 449C from the ambient temperature to 800 °C at a rate of 5 °C/min under oxygen purge. Ultraviolet absorption was recorded with an Agilent 8453 spectrophotometer.

2.2. Preparation of PSt particles

Preparation of PSt was schematically illustrated in Fig. 1. Styrene, polyvinylpyrrolidone, α-methylacrylic acid, 2,2-azobisisobutyronitrile, absolute ethanol, and doubly distilled water were charged into a 250 ml three-neck round-bottomed flask. The reaction solution was deoxygenated by bubbling nitrogen gas and then heated to 70 °C under stirred condition. After 5 h, 3-methacryloxypropyltrimethoxysilane (γ-MPS) was dispersed in absolute ethanol and then added into the reaction system. The reaction lasted for 6 h at 70 °C. The filtered white precipitate was air-dried for 12 h. The formulations used in this study were as follows: St 12.0 g, PVP 1.0 g, AA 0.45 g, AIBN 0.65 g, absolute ethanol 60.0 ml, doubly distilled water 25.0 ml, and γ-MPS 1.2 g (or 2.8 g). The products prepared with different γ-MPS were denoted as PSt 1 (1.2 g γ-MPS) and PSt 2 (2.8 g γ-MPS), respectively.

2.3. Core–shell particles

In a 100 ml flask, copper acetate (0.48 g) was dissolved into 50 ml ethanol. The suspended PSt microspheres (0.15 g) were added into copper acetate ethanol solution in a ultrasonic bath. After 30 min, it was centrifuged and washed with water several times and was added into ethanol solution in a ultrasonic bath again. Followed, thioacetamide (123 mg) in ethanol solution were added with stirring in ultrasonic bath and the mixture was left to react for 30 min. The final products were collected with centrifugation and washed several times with doubly distilled water, and then dried in the vacuum oven at 60 °C. The products prepared by PSt microspheres with different γ-MPS were denoted as PSt/CuS 1 (1.2 g γ-MPS) and PSt/CuS 2 (2.8 g γ-MPS), respectively.

3. Results and discussion

As mentioned in Section 2, the hybridization of polystyrene and γ-MPS could be received through a polycondensation reaction between the unsaturated double bonds of γ-MPS and styrene. The possible reaction model was illustrated in Fig. 1. In the process of polymerization, the terminal organicsilicone group of γ-MPS proceeded ethanolysis and formed terminal hydroxyl. In the self-assembly process, the PSt latex was considered as the template. The terminal hydroxyl on the PSt would strongly cooperate with Cu^{2+} ions during ultrasonic bath. During the coating procedure, thioacetamide gradually hydrolyzed to produce S^{2-}, which would react with Cu^{2+} ions to form CuS. As a result, PSt particles would be coated with CuS particles.

Fig. 2 displays the FT-IR data of the PSt particles with 1.2 g γ-MPS to further conform the reaction between the polystyrene and γ-MPS. The strong and broad band at about 698, 1453, 1494, 1613, 2920 and 3026 cm^{-1} correspond to the PSt standard. The strong and broad band at about 1086 cm^{-1} and 1676 cm^{-1} is owed to the emergence of C=O band, which means that γ-MPS has been successfully grafted on to polystyrene.

Fig. 3 shows SEM micrographs of PSt particles (A: PSt 1, B: PSt 2). From this figure, it can be seen that the obtained PSt has spherical morphology and good monodispersity with diameter about 700 nm. According to the results of particle size distribution, the average diameter of obtained PSt 2 was 686 nm and the average diameter of obtained PSt 1 was 667 nm. Fig. 4 is the SEM micrographs of PSt/CuS core–shell composite (A: PSt/CuS 1, B: PSt/CuS 2). The composite is as uniform and monodisperse as the original PSt particles. The shell of the single spheres is homogeneous and some nanoparticles can be seen on the surface. According to the results of particle size distribution, the average diameter of obtained PSt/CuS 1 was 1.13 μm and the average diameter of obtained PSt/CuS 2 was 1.28 μm. It can be deduced

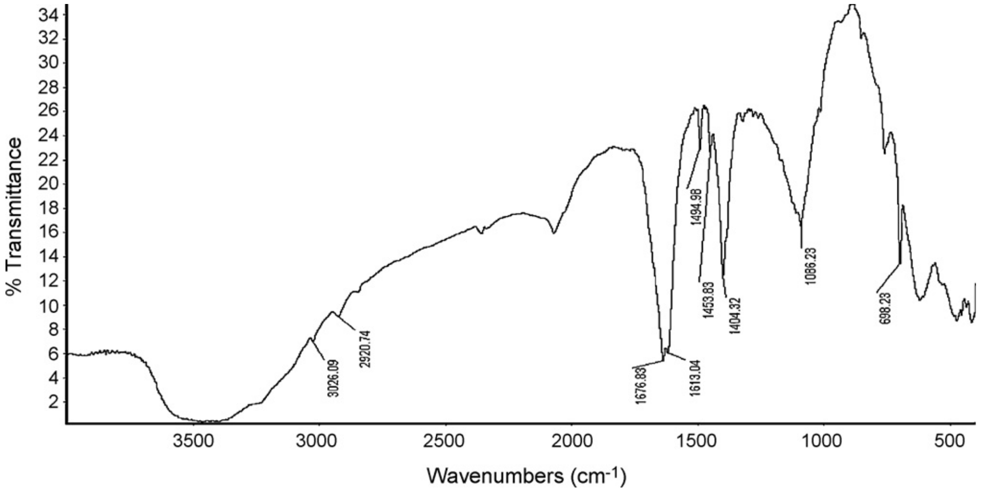

Fig. 2. FT-IR spectra of the PSt particles which modified by 1.2 g γ-MPS.