Available online at www.sciencedirect.com
ScienceDirect
Journal of Colloid and Interface Science 306 (2007) 296–299
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

Novel Janus $Cu_2(OH)_2CO_3$/CuS microspheres prepared via a Pickering emulsion route

Yongjun He *, Kanshe Li

Department of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, Xi'an 710054, China

Received 13 September 2006; accepted 25 October 2006
Available online 28 November 2006

Abstract

Janus $Cu_2(OH)_2CO_3$/CuS microspheres were prepared via a Pickering emulsion route for the first time. By treating the Janus $Cu_2(OH)_2CO_3$/CuS microspheres with dilute hydrochloric acid, ringent $Cu_2(OH)_2CO_3$/CuS core/shell microspheres and ringent CuS shells were obtained. The hatch size of the ringent CuS shells increased with the increase of the hydrophobicity of the precursor $Cu_2(OH)_2CO_3$ microspheres. Scanning electron microscopy, X-ray diffraction, energy dispersion spectra, and particle size analysis were used to characterize the products thus formed.

Keywords: Janus particles; Core/shell structures; Cupric salts; Pickering emulsion

1. Introduction

In recent years, so-called "Janus particles" having asymmetrical surface regions have stimulated great interest because of their tunable surface properties and consequent wide potential applications in fields such as sensors, electronics, photonics, and drug delivery [1–6]. Various strategies for preparing Janus particles have been reported. These methods include the self-assembly of ABC triblock copolymers in solution or in bulk [3,4], vapor deposition of metals onto a surface-supported monolayer of colloids in a vacuum, and microcontact printing of molecules [5,6]. However, only limited kinds of Janus particles have been prepared till now. The development of new approaches to the synthesis of Janus particles remains a challenge.

About a century ago, Pickering found that when some fine solid powders were mixed with water and an oily solvent (for instance, toluene or kerosene), a solid-stabilized emulsion (often referred to as a Pickering emulsion) could be obtained even if no surfactants were used. The fine solid powders situated at the surface of the droplets formed a spherical shell and impeded the coalescence when two droplets approached [7]. Broad interest has recently been reawakened in the study of Pickering emulsions because of their potential use in the development of novel nano/microstructures. Polystyrene colloidsomes (capsules whose surfaces are composed of a close-packed layer of colloidal polystyrene particles), hairy SU-8 photoresist epoxy resin microspheres, polyaniline/nano-CeO_2 composites, and ZnO nanostructured microspheres have been prepared in Pickering emulsions [8–14]; however, most of the reported nano/microstructures synthesized by Pickering emulsions have symmetrical surface regions.

In this communication, we report the synthesis of Janus $Cu_2(OH)_2CO_3$/CuS microspheres via a Pickering emulsion route. This method was easy and straightforward; in addition, ringent $Cu_2(OH)_2CO_3$/CuS core/shell microspheres and ringent CuS shells could be obtained by simply treating the Janus microspheres with dilute hydrochloric acid.

2. Experimental

2.1. Materials

Cupric nitrate, sodium carbonate, ethyl alcohol, dichlorodimethylsilane, and hydrochloric acid (Tianjin Chemistry Reagent Co.) were of analytical grade and were used as received. Styrene of analytical grade (Beijing Chemicals Co.) was distilled under reduced pressure before use. Azobisisobutyronitrile

* Corresponding author. Fax: +86 29 85583182.
E-mail address: yongjhe@yahoo.com.cn (Y. He).

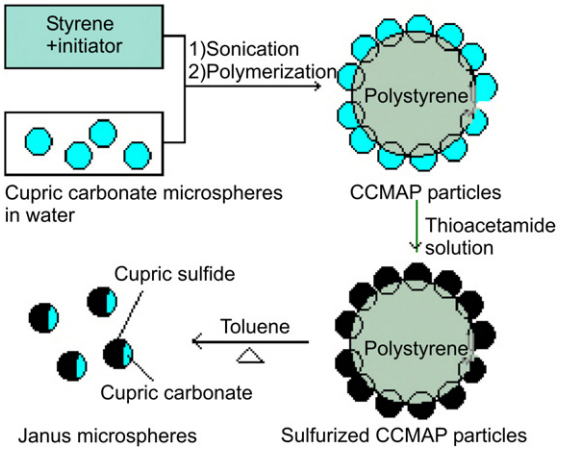
0021-9797/$ – see front matter
doi:10.1016/j.jcis.2006.10.070

of analytical grade (Beijing Chemicals Co.) was utilized without further purification. Deionized water was used throughout the experimental work.

2.2. Synthesis of Janus $Cu_2(OH)_2CO_3$/CuS microspheres

The precursor $Cu_2(OH)_2CO_3$ microspheres were prepared by a precipitation method, and had an average diameter of 4 μm (Figs. S1 and S2; see supporting materials).

The synthesis of Janus $Cu_2(OH)_2CO_3$/CuS microspheres (see Scheme 1) involves three stages: (i) A quantity of 0.2 g of $Cu_2(OH)_2CO_3$ microspheres was dispersed in 10 ml of deionized water. A quantity of 0.03 g of azobis-isobutyronitrile was dissolved in 2 ml of styrene, and subsequently this was mixed with the $Cu_2(OH)_2CO_3$ dispersion. A stable styrene-in-water Pickering emulsion stabilized by $Cu_2(OH)_2CO_3$ microspheres was generated via sonication. The system was degassed by purging with nitrogen gas for 20 min and was subsequently polymerized at 70 °C for 8 h. After reaction, the mixture was centrifuged. The separated $Cu_2(OH)_2CO_3$ microsphere and armored polystyrene (CCMAP) particles were washed with water and ethyl alcohol, respectively, and dried under vacuum for 4 h. (ii) A quantity of 0.1 g of the CCMAP particles was dispersed in 10 ml of water under sonication. A quantity of 0.2 g of thioacetamide was dissolved in 5 ml of water, and this was mixed with the CCMAP dispersion. After reaction for 5 h, the mixture was filtrated. The obtained sulfurized CCMAP particles were washed with water and dried under vacuum. (iii) A quantity of 0.1 g of the sulfurized CCMAP particles was dispersed in 10 ml of toluene and heated at 70 °C for 3 h. The mixture was centrifuged and washed. Thus, Janus $Cu_2(OH)_2CO_3$/CuS microspheres were obtained.



Scheme 1. The synthesis procedure for Janus $Cu_2(OH)_2CO_3$/CuS microspheres.

The type of the Pickering emulsion was inferred by a dilution method, observing what happened when a drop of emulsion was added to a volume of either pure oil (styrene) or pure water. Water continuous (oil continuous) emulsions dispersed in water (oil) and remained as drops in oil (water) [15,16].

2.3. Synthesis of ringent $Cu_2(OH)_2CO_3$/CuS core/shell microspheres and ringent CuS shells

The obtained Janus $Cu_2(OH)_2CO_3$/CuS microspheres were dispersed in water. A suitable amount of 1 mol/L of hydrochloric acid was added to the dispersion. After reacting for 1 h and 4, respectively, the mixture was centrifuged, washed, and dried. Thus, $Cu_2(OH)_2CO_3$/CuS core/shell microspheres and ringent CuS shells were obtained, respectively.

2.4. Characterizations

The SEM images of the products were collected by a Hitachi S-2700 scanning electron microscope equipped with an energy dispersion spectrum (EDS) unit. XRD patterns were obtained by a Rigaku D/MAX-3C X-ray diffraction meter, using Cu$K\alpha$ radiation with 40 kV and 20 mA at a 0.2° scan rate (in 2θ). The size and size distribution of the products were also measured by a Brookhaven BI-90 particle size analyzer.

3. Results and discussion

3.1. Formation of $Cu_2(OH)_2CO_3$ microsphere-armored polystyrene (CCMAP) particles

Fig. 1a shows scanning electron microscope (SEM) images of the as-prepared $Cu_2(OH)_2CO_3$ microsphere-armored polystyrene (CCMAP) particles. Polystyrene spheres with a diameter of about 260 μm were enwrapped by a layer of $Cu_2(OH)_2CO_3$ microspheres. Some of the $Cu_2(OH)_2CO_3$ microspheres fell off, leaving behind coronal imprints at the surfaces of the polystyrene spheres (see Fig. 1b).

Provided that the coronal imprints of the $Cu_2(OH)_2CO_3$ microspheres on the polystyrene had a vertical depth of D and a

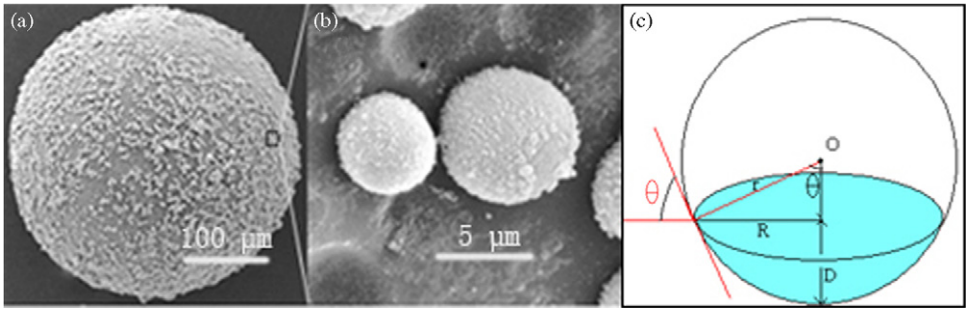


Fig. 1. SEM images of the CCMAP particle: (a) general view; (b) high-magnification picture; (c) illustration of the calculation of contact angles.