Available online at www.sciencedirect.com

ScienceDirect

Colloids and Surfaces A: Physicochem. Eng. Aspects 295 (2007) 233–238

COLLOIDS AND SURFACES A

www.elsevier.com/locate/colsurfa

Selective removal of particle cores to fabricate manganese carbonate hollow spheres and composite microcapsules

Weijun Tong, Changyou Gao [*]

Department of Polymer Science and Engineering, Zhejiang University, and Key Laboratory of Macromolecule Synthesis and Functionalization, Ministry of Education, Hangzhou 310027, China

Received 1 August 2006; received in revised form 3 September 2006; accepted 5 September 2006
Available online 9 September 2006

Abstract

We report here the finding of different dissolution rate between the core and shell of a manganese carbonate particle, which was prepared by mixing NH_4HCO_3 and $MnSO_4$ at room temperature. Based on the results of X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), we believe that the denser crystallites in the shells have a stronger stability against acid decomposition compared with the randomly and loosely assembled crystallites in the particle cores. Hollow spheres were then fabricated by utilizing the difference of decomposition rate between the particle shells and the cores in acidic solution at room temperature. Furthermore, by incorporating polyelectrolyte multilayers onto the particles prior to core decomposition, hybrid organic/inorganic hollow spheres were successfully produced.

Keywords: Manganese carbonate; Colloids; Hollow spheres; Hybrid materials; Layer-by-layer

1. Introduction

Hollow spheres in the dimension from nanometer to micrometer constitute an important class of materials. They have attracted increasing interest because of their potential applications in encapsulation and controlled release for drugs, cosmetics, dyes and inks, in catalysis and acoustic insulation, in the development of piezoelectric transducers and low dielectric constant materials, and for the manufacture of advanced materials [1]. Various substances have been used for the preparation of hollow spheres, usually being polymers and inorganic materials [1]. The methods currently used to fabricate a wide range of stable hollow spheres include nozzle reactor processes, emulsion/phase separation, sol–gel processing, and sacrificial core techniques [2].

Another class of mineralization methods has also been introduced to produce inorganic hollow spheres. For instance, the double-hydrophilic block copolymers (DHBCs) can effectively tune the morphologies of inorganic colloidal particles, thus in some cases producing hollow spheres [3,4]. Hollow $CaCO_3$ spheres as well as hollow Ag spheres are also fabricated by using complex micelle templates of block copolymers and surfactants [5,6]. Recently, Xu et al. reported the synthesis of stable amorphous $CaCO_3$ hollow spheres in the presence of phytic acid [7]. These methods usually need careful adjustment of the concentrations of the additives, the pattern of their functional groups and the ratio of additives to reaction components because the particle morphologies are very sensitive to these parameters.

Moreover, template assisted assembly has demonstrated its great success in fabricating hollow capsules, typically exemplified by the layer-by-layer (LbL) assembly on colloidal particles followed by core removal [8–10]. The LbL assembly technique has been diversely applied to fabricate ultrathin organic multilayers or hybrid films with various properties since it was introduced by Decher [11]. By incorporating pre-formed inorganic nanoparticles or inorganic molecular precursors during the process of multilayer film construction on the colloidal particles and subsequently removing the cores, organic/inorganic hybrid hollow spheres have been fabricated. Inorganic hollow spheres could be further obtained by calcination of the cores and bridging polymers [2,8]. As an extension of incorporation of charged macromolecules in the pre-formed microcapsules, nanoparticles such as Fe_3O_4, YF_3, and hydroxyapatite have been formed in situ exclusively inside the microcapsules, thus inorganic/organic

---

[*] Corresponding author. Tel.: +86 571 87951108; fax: +86 571 87951948.
E-mail address: cygao@zju.edu.cn (C. Gao).

0927-7757/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2006.09.005

nanocomposite hollow microcapsules were obtained [12]. The advantages are that important parameters such as size, geometry, composition, wall thickness and uniformity, as well as the diameter-to-wall thickness ratio of the hollow spheres can be readily controlled. Yet very high temperature, usually being several hundreds centigrade degrees, is basically required to fabricate the inorganic hollow spheres in the calcination procedure.

Carbonate microparticles such as $CdCO_3$, $CaCO_3$ and $MnCO_3$ have been widely used for the fabrication of clean multilayer capsules, because they can be easily and completely removed [13–14]. In this work, we shall report our recent finding on the dissolution rate difference of $MnCO_3$ microparticles in acid solution. Different with many of their counterparts, the $MnCO_3$ microparticles obtained in this research have a unique feature of faster core dissolution than their shells. Characterizations on the microparticle structure were made to explain the mechanism. Utilizing this feature, hollow $MnCO_3$ spheres were obtained by controlling the dissolution time. Furthermore, by coating the $MnCO_3$ spheres prior to acid-treatment with polyelectrolyte multilayers, inorganic/organic hybrid microcapsules with enhanced stability were fabricated. This has provided an easy and effective pathway to produce hollow spheres and composite microcapsules that may find wide applications in the future.

2. Experimental

2.1. Materials

Sodium poly(styrene sulfonate) (PSS, Mw ~70 kDa), poly(allylamine hydrochloride) (PAH, Mw ~70 kDa), tetramethylrhodamine isothiocyanate labeled dextran (TRITC-dextran, Mw ~65 kDa) and rhodamine 6G (Rd6G) were purchased from Sigma–Aldrich. All other chemicals are of analytical grade and were used as received. The water in all the experiments was triple-distilled.

2.2. Methods

2.2.1. Manganese carbonate particle preparation

Equal volume of 0.16 M NH_4HCO_3 was added into a mixture of 0.016 M $MnSO_4$ and ethanol under vigorous agitation with a final ethanol concentration of 5% (v/v) [13,15]. The system was then incubated at 50 °C for 1 h to yield $MnCO_3$ microparticles. At the end of the reaction, the precipitated $MnCO_3$ particles were separated and washed using membrane filtration apparatus with a filter of pore size 0.45 μm.

2.2.2. LbL coating and hollow capsule fabrication

The stepwise assembly of PSS/PAH multilayers on the $MnCO_3$ microparticles was conducted via a centrifugation protocol. The adsorption of polyelectrolytes (2 mg/mL) was conducted in 0.2 M NaCl solution for 10 min followed by three washings in H_2O. Then the respective oppositely charged polyelectrolyte species were adsorbed. After five bilayers were adsorbed the coated particles were subjected to 0.1 M HCl solution to decompose the $MnCO_3$ particle cores partially to get the hybrid hollow spheres. The hollow $MnCO_3$ spheres on a glass slide were prepared by incubating the particle-containing slide in 0.1 M HCl solution for 1 min, followed by sequential rinsing with a large amount of water.

2.2.3. Instrumental characterizations

Confocal laser scanning microscopy (CLSM) images were taken with a Bio-Rad Radiance 2100 confocal system equipped with a 100× oil immersion objective and a 40LD× objective. To follow the dynamic dissolution process, a drop of the $MnCO_3$ particle suspension was put onto a glass slide. After the water had been evaporated, a drop of 0.01 M HCl solution was applied to the particles. The images in transmission mode were taken in a time course method. Confocal fluorescent images were taken after staining the hollow $MnCO_3$ spheres with Rd6G, or after labeling the hybrid spheres with TRITC-dextran.

Scanning electron microscopy (SEM) images were taken with a HITACHI S-520 scanning electron microscope. The samples were prepared by directly drying a drop of suspension on glass slides. Transmission electron microscopy (TEM) images were obtained with a JEM-1230 electron microscope (JEOL, Japan). The samples were embedded in polymerized epoxy resin and ultramicrotomed. Powder X-ray diffraction (XRD) studies were performed on a D8-Advance X-Ray Diffractometer (Bruker, Germany).

3. Results and discussion

$MnCO_3$ microparticles were prepared by mixing $MnSO_4$ and NH_4HCO_3 solutions. Ethanol was added to decrease the dielectric constant of the system and the solubility of the inorganic salts. The supersaturation of the inorganic salts accelerated by the ethanol addition drives the nucleation and growth of the solid-phase, yielding finally the $MnCO_3$ spherical particles (Fig. 1a) with an average diameter of 5.5 ± 0.5 μm. A magnified image (Fig. 1b) shows that the surface morphology of the particles is rather rough.

Using the $MnCO_3$ microparticles as templates, five bilayers of poly(styrene sulfonate) and poly(allylamine hydrochloride) were assembled. It was found that after incubation in 0.1 M HCl for 10 min, the hollow multilayer capsules were obtained with collapse morphology as a result of drying (Fig. 2a). This phenomenon and the resulting morphology with folds and creases (Fig. 2a, unmarked microcapsules) are quite normal for hollow microcapsules with ultrathin wall thickness, which may due to the capillary force acting upon drying.

We noticed in Fig. 2a that part of the capsules (marked with asterisks) show a slight different morphology with those completely collapsed ones. This would mean that the template $MnCO_3$ cores may have different dissolution rate. To examine the difference, we shortened the etching time to 1 min. While a few collapsed capsules were formed, most of the composite particles kept their spherical topology after drying (Fig. 2b). No obvious change of the particle size was found either. This observation indeed demonstrates the inhomogeneity between the particles. To our surprise, some hollow hemispheres (Fig. 2b, especially the inset image) as indicated by the arrows were