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ScienceDirect
Journal of Colloid and Interface Science 301 (2006) 470–478
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

Preparation of uniform silica/polypyrrole core/shell microspheres and polypyrrole hollow microspheres by the template of modified silica particles using different modified agents

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Received 9 January 2006; accepted 10 May 2006
Available online 20 May 2006

Abstract

Silica/polypyrrole (PPY) core/shell microspheres and PPY hollow microspheres were prepared by the template of silica particles whose surface character was modified with different modified agents. The morphology and structure of the particles were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Elemental analysis and X-ray photoelectron spectroscopy (XPS) were carried out to characterize the structure of PPY hollow microspheres. We investigated the effect of different modified agents on the surface character of silica particles and the effect of surface character of silica particles on the morphology of PPY hollow microspheres. The effect of reaction conditions on the size of core/shell particles and hollow particles was also studied.

Keywords: Uniform; Core/shell microspheres; Hollow; Polypyrrole; Modified agents

1. Introduction

In recent years, polypyrrole (PPY) is regarded as one of the most prominent conductive polymers because of its electronic and photonic states as well as excellent conductivity and good environment stability [1–4]. However, like many other conductive polymers, PPY is insoluble in ordinary solvent and infusible because of decomposition before melting [3,4]. In order to improve the processability of PPY, lots of effort have been made to prepare the PPY hollow spheres. And also polymeric hollow spheres have recently been cited as novel types of carriers and nanoreactors with designed properties because they exhibit controllable permeability and surface functionality [5,6]. This should enable many applications such as the controlled release of drugs [7] or gene therapy [8].

Among many synthetic routes to hollow PPY spheres, template-directed synthesis, where polystyrene (PS) latex spheres [2,9,10], silica latex particles [11] are employed as removable templates by dissolution or calcination, has been demonstrated to be an effective approach. However, it is very difficult to enwrap the single template effectively by PPY to form core/shell particles and then obtain the PPY hollow spheres. At present, more attention has been focused on improving the surface character of PS spheres by adding some special substance and absorbing conducting polymers particles or their monomers on the surface of PS sphere, and then obtaining core-shell particles [9,12–15]. More recently, our groups have succeeded in improving the polarity of PS spheres surface simply through the sulfonation by concentrated sulfuric acid and then prepared conductive PS/polymers composite microspheres and polymer hollow spheres [2].

Compared to the template of PS spheres [2,9,12–15], using the silica template particles to prepare conducting polymers core-shell particles has some advantages. The synthesis condition and procedure of monodispersed silica spherical particles are very simple; the styrene monomer is noxious and the synthesis condition of PS spherical particles is complicated. However, so far, few literatures have been reported to

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0021-9797/$ – see front matter
doi:10.1016/j.jcis.2006.05.038

improve the surface character of silica particles and then prepare hollow conductive PPY spheres. Only Chen et al. used poly(*N*-vinylpyrrolidone) (PVP) to improve the silica surface character and prepared the PPY hollow capsules [11]. Nevertheless, it is still unclear whether other substances such as the silane coupling agent and kinds of surfactants could be used as the modified agents and then to prepare uniform silica/PPY composite microspheres and stable PPY hollow microspheres. Up to now, there is no report concerning how to choose different kinds of reagents with surface activity to improve the surface character of silica particles in order to obtain stable core/shell and hollow particles. In this paper, we first used different modified agents with surface activity to improve the surface character of silica particles and then obtained silica/PPY composite microspheres and PPY hollow microspheres. Here we used 3-(trimethoxysilyl) propyl methacrylate (MPS) and three kinds of surfactants, i.e., cetyltrimethylammonium bromide (CTAB), nonyl phenol polyethyleneoxy ether (ОП-10), and bis (2-ethylhexyl) sulfosuccinate (AOT) to improve the surface character of silica particles. The effect of modified agents on the surface character of silica particles and the effect of surface character of silica particles on the morphology of PPY hollow microspheres have been investigated. We also studied the effect of reaction conditions on the morphology of hollow microspheres.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%) as a silica source, ammonium hydroxide as a catalyst, ethanol as a solvent, 3-(trimethoxysilyl) propyl methacrylate (MPS), cetyltrimethylammonium bromide (CTAB), nonyl phenol polyethyleneoxy ether (ОП-10), and bis (2-ethylhexyl) sulfosuccinate (AOT) as modified agents. Pyrrole was freshly distilled under reduced pressure. All chemicals were used as received without further purification.

2.2. Preparation of silica particles

Silica particles were synthesized by base-catalyzed hydrolysis of TEOS, as described by Stöber et al. [16]. Briefly, 12.22 ml of aqueous ammonia (25 wt%) was added into a solution containing 30 ml of ethanol and 2.22 ml of deionized water. Separately, 4.02 ml of TEOS was mixed with 25.4 ml of ethanol. The two solutions were rapidly mixed under vigorous stirring. The reaction mixture was kept stirring for 8 h to yield uniform silica particles. Then, the resulting silica particles were separated by centrifugation at 3000 rpm for 15 min and washed four times with water. Finally, the silica particles were dried at 50 °C for 24 h in vacuum oven.

2.3. Preparation of modified silica particles using different modified agents

0.5 g of silica particles was dispersed in 15 ml of ethanol by sonication for 15 min. Then 10 ml of ethanol solution containing 2 ml of MPS was added into the above solution. The suspension was stirred for 24 h, and then separated by centrifugation. The deposits were collected and washed with ethanol and water several times, then the modified silica particles were obtained.

The modified silica particles using the ОП-10 were prepared by the same method but ОП-10 instead of MPS used.

0.5 g of silica particles was dispersed in 20 ml of 0.1 M CTAB aqueous solution by sonication for 15 min. The suspension was stirred for 24 h, and then separated by centrifugation. The deposits were collected and washed with ethanol and water several times, then the CTAB modified silica particles were obtained.

The modified silica particles using the AOT were prepared by the same method but AOT instead of CTAB used.

2.4. Preparation of silica/PPY core/shell particles

0.2 g of modified silica was dispersed in 15 ml of ethanol, and then 0.1 ml of pyrrole monomer was added into above solution. After sonication for 20 min, 15 ml of aqueous solution containing 0.9 g of $FeCl_3$ was added into the suspension. The reaction mixture was kept stirring for 12 h to yield uniform silica/PPY core/shell particles. Then, the resulting composite particles were separated by centrifugation at 4000 rpm for 15 min and washed four times with water. Finally, the composite particles were dried at 50 °C for 24 h in vacuum oven.

2.5. Preparation of PPY hollow spheres

The composite particles were soaked in an aqueous solution of 20 wt% HF for 24 h to remove the silica cores. And then the sample was separated by centrifugation at 4000 rpm for 15 min and washed four times with water. Finally, the sample was dried at 50 °C for 24 h in vacuum oven.

2.6. Characterization

The sizes and morphologies of the products were examined by transmission electron microscopy (TEM; Hitachi H-600) and scanning electron microscopy (SEM; JEOL JEM 200CX). Infrared spectra of the samples were measured on KBr pellets on a MAGNA560 Fourier transform IR spectrophotometer. The conductivity of product was measured by a four-probe conductivity instrument with an ADVANTEST R6551 DIGITAL multimeter and an ADVANTEST PROGRAMMABLE DC voltage/current generator as a current source. Elemental analysis and X-ray photoelectron spectroscopy (XPS) measurements were employed to characterize the structure of the hollow PPY microspheres.

3. Results and discussion

3.1. The formation mechanism of silica/PPY core/shell particles and PPY hollow spheres

Scheme 1 shows the formation mechanism of silica/PPY core/shell particles and PPY hollow spheres. The silica parti-