

Fabrication of silica hollow spheres using a sacrificial template method assisted with spray drying process

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Abstract. Core-shell composites of silica-coated MF microspheres were prepared by the hard template of MF microspheres whose surface were clad with silica colloid in a spray drying induced in-situ coating process. Furthermore, silica hollow spheres were obtained by removal of MF cores at calcinations in air. The influence of the concentration of the SiO₂ colloid and the ratio of MF microspheres to the core/shell composites and the hollow spheres on the composition, the morphology and size were studied with fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) .

Introduction

Preparation of inorganic hollow spheres has attracted increasing research interest because of their important applications in different fields such as magnetism, drug storage and release, energy storage, chromatography and catalysis. Recently, lots of efforts have been developed to prepare inorganic hollow spheres by a variety of chemical and physicochemical methods, including sol-gel method, layer-by-layer self-assembly, sacrificial template method and the Kirkendall effect^[1-2]. Presently, sacrificial template method has been considered to be the most effective and multifunctional strategy to fabricate various types of hollow materials with homogeneous, dense layers. In a typical procedure, core-shell composites can be synthesized by template particles coated in solution by inorganic molecule precursors, inorganic hollow spheres were obtained in a subsequent step by selective dissolution in an appropriate solvent or by calcination at elevated temperatures in air. However, in the formation process of core-shell structure requires template particles should be carried with certain charge or be modified with specific functional groups in surface sedimentary processes^[3]. Here, spray drying technology with evaporation-induced self-assembly process of aerosols is introduced to solve this problem^[4]. In this work, we described the fabrication of core-shell composites using melamine formaldehyde (MF) microspheres as hard templates and silica colloid as shell precursors via spray drying induced in-situ coating process, in subsequent calcination stage, removal of the MF core by a sacrificial template route forms silica hollow spheres. The composition, the morphology and the size of the core-shell composite microspheres and the hollow spheres were investigated and compared.

Experimental Section

Materials. Formaldehyde (37%), melamine, polyvinyl alcohol (PVA), acetic acid, colloidal silica (LUDOX AS-40, GRACE Davison). All the chemicals were of AR grade and used without further purification. Distilled water was used in the experiments.

Synthesis of SiO₂ Hollow Spheres. MF microspheres were synthesized according to previous work^[5]. First, core-shell composites of silica-coated MF microspheres (the core-shell structures was labeled as MF@SiO₂) were obtained based on the spray drying process. 0.2 g of MF microspheres and various volume of silica colloid were dispersed into distilled water (300 ml) with the assistance of magnetic stirring for several hours. Then MF@SiO₂ microspheres were prepared by inhaling the above suspension containing MF microspheres and silica nanoparticles into a spraying dryer, where silica colloid was dried transiently and deposited onto the surface of MF microspheres. Finally, SiO₂ hollow spheres were obtained by calcining in a tube furnace at 550 °C for 5 h in air to burn out the MF

cores. Different hollow spheres were obtained by tuning the ratio of MF microspheres to the silica colloid in the synthesis of the core-shell intermediates.

Characterization. The morphologies of the samples were examined by a JEOL JSM-6390LV scanning electron microscopy (SEM) and a JEM-2010F transmission electron microscopy (TEM). Fourier transformation infrared (FTIR) spectra were recorded with a Nicolet 5700 FTIR spectrometer on KBr pellets.

Results and Discussion

Fig. 1 displays the SEM images of the five samples obtained from different conditions. The monodisperse MF template particles with a mean diameter around $1.2\mu\text{m}$ were showed in Fig. 1a. Fig. 1b shows SiO_2 particles with a doughnut shaped that the particles of SiO_2 prepared using 1mL SiO_2 colloid, which was diluted with 100mL deionized water, as precursor by the same procedure been described for the preparation of the composites. When silica-coated MF microspheres mixture were obtained from 0.2 mL, 0.4 mL and 0.6 mL SiO_2 colloids used as precursors, the morphology of MF@ SiO_2 composites turns to a bit of irregular after the spraying dry process (see Fig. 1c-1e).

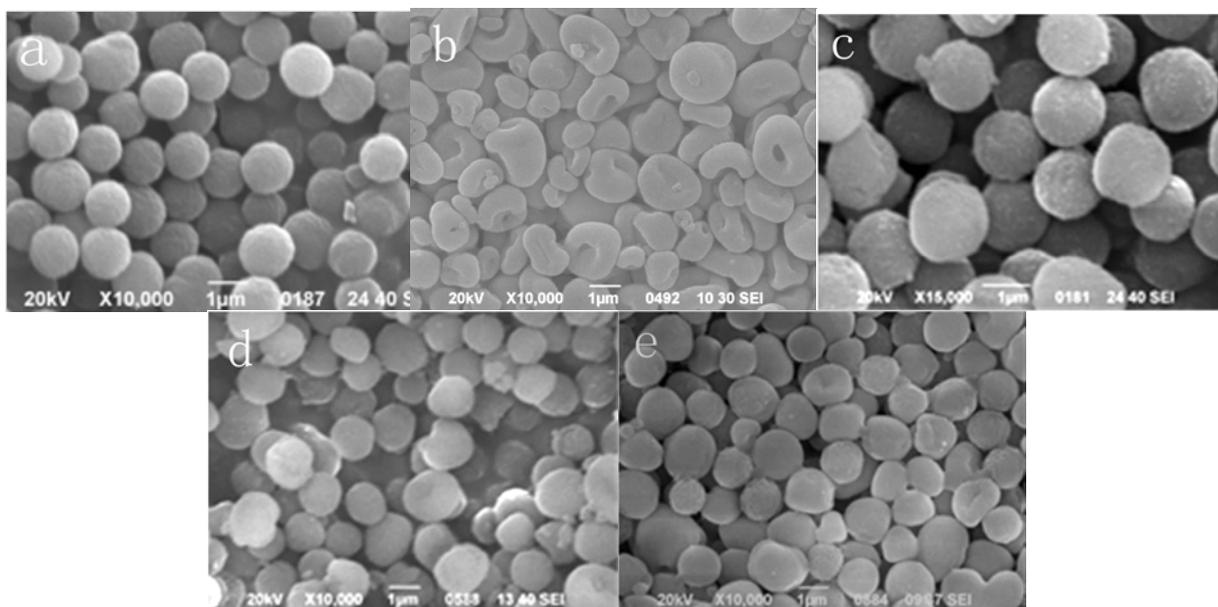


Fig. 1 SEM images: (a) MF microspheres; (b) SiO_2 colloid; MF@ SiO_2 microspheres obtained at various amounts of SiO_2 colloids: (c) 0.2 mL; (d) 0.4 mL ; (e) 0.6 mL.

The overall morphologies of different silica hollow spheres derived by calcining the core-shell intermediates of MF@ SiO_2 were examined by SEM (Fig. 2). The images from picture 2a to picture 2c were silica hollow spheres generated at various amounts of SiO_2 colloids. The mean diameter of the hollow spheres about $1.2\mu\text{m}$ increases not obviously with the addition of SiO_2 colloid increased from 0.2mL to 0.6mL, indicating that silica hollow spheres inherited the spherical shape of the MF templates, meanwhile, comparison between MF@ SiO_2 microspheres and silica hollow spheres, particle size occurred a slighter shrinkage during the calcinations treatments, which can be explained as due to the carbonization of the MF templates and the densification of the loose outer coating shell which caused the formation of a compact silica wall finally. Furthermore, it should be noted that the broken hollow spheres revealing the hollow property were obtained after the removing of the MF templates, and the destruction of the integrated hollow spheres is the most serious when the amount of SiO_2 colloid was 0.2 mL as presented in Fig. 2a, by increasing the ratio of the SiO_2 colloid in the MF / SiO_2 colloid mixture, more undestroyed hollow spheres with small openings in the shell were obtained in Fig. 2b and Fig. 2c.

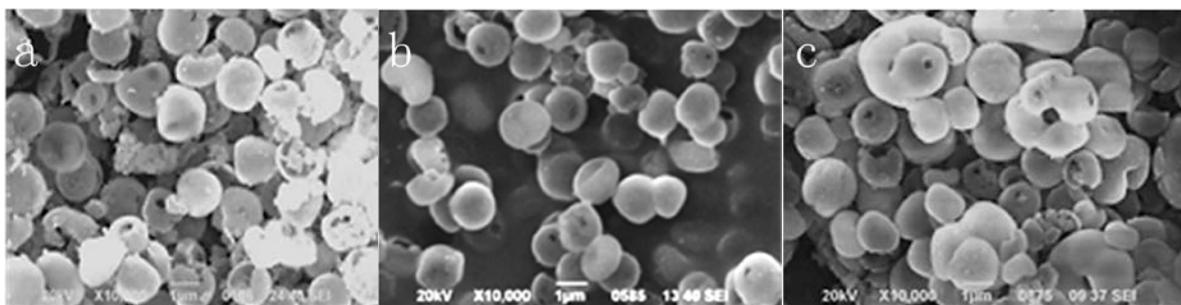


Fig. 2 SEM images of the silica hollow spheres generated at various amounts of SiO₂ colloids: (a) 0.2 mL; (b) 0.4 mL; (c) 0.6 mL.

The hollow structure is further investigated by the TEM image as shown in Fig. 3, the intensive contrast between the black margin and the bright center of the particles confirms the direct evidence to their hollow nature. Furthermore, we can see the integrity of the hollow spherical shell gradually get better by the increase of the ratio of SiO₂ colloids, which is also in good agreement with the SEM observation (Fig. 2).

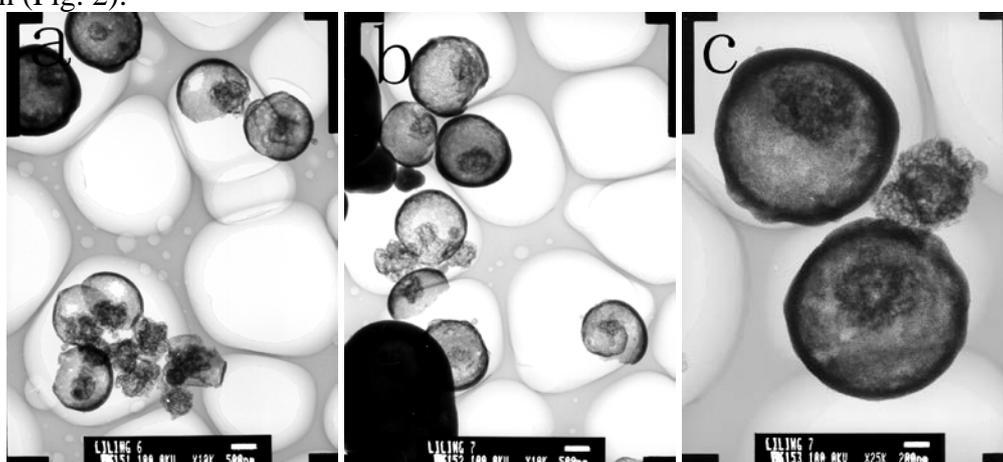


Fig. 3 TEM images of the silica hollow spheres generated at various amounts of SiO₂ colloids: (a) 0.2 mL; (b) 0.4 mL; (c) 0.6 mL.

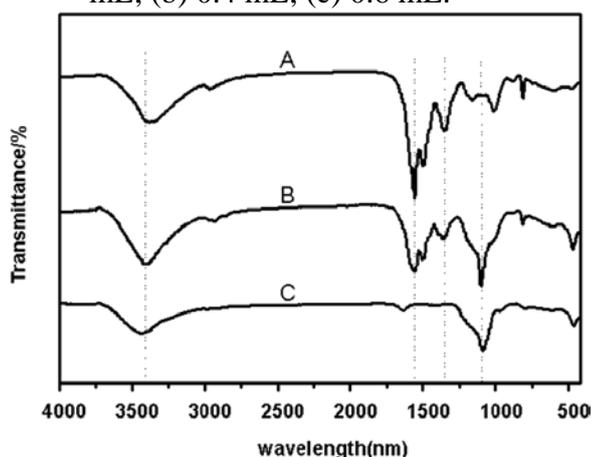


Fig. 4 FT-IR spectra of the samples: (A) MF microspheres; (B) MF@SiO₂ microspheres; (C) silica hollow spheres.

For further confirmation that the silica hollow spheres contains no remained MF microspheres inside the core, FTIR characterization was performed. The FTIR spectra of the pristine MF spheres, MF@SiO₂ core-shell composites and silica hollow spheres were presented in Fig. 4. Curves A and B show the characteristic absorption bands of MF at about 3377, 1557 (1492, 1352), 1166, 1006 and 813 cm⁻¹ originating from the vibrations of hydroxyl/amino (–OH/–NH₂), amino (–NH₂), amine (C–N), ether (C–O–C), and C–N–C groups, respectively. The broad peak of Si–O–Si asymmetric

bond stretching vibration at $\sim 1100\text{cm}^{-1}$, the bands of the Si-OH stretching vibration at 953cm^{-1} and the bending vibration of the -OH group of the silanols moieties at 3450cm^{-1} were demonstrated in curves B and C, which provides evidences to the formation of SiO_2 coated MF composite spheres. Moreover, the disappearance of the characteristic absorption bands of MF microspheres in curves C indicates that the formation of the SiO_2 hollow spheres and the complete removal of the MF cores after the calcinations^[5].

Summary

Core-shell structures of silica-coated MF microspheres using melamine formaldehyde (MF) microspheres as hard templates and silica colloid as shell precursors were prepared via in a spray drying induced in-situ coating process. Silica hollow spheres were obtained after the removal of the MF cores by calcining in air. The formation of the silica hollow spheres was confirmed by the SEM, TEM and FTIR measurements. The difference between the morphologies and structures of the hollow SiO_2 spheres derived from different amounts of SiO_2 colloids were discussed.

Acknowledgements

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