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Synthesis of porous silica structures with hollow interiors by templating nanosized calcium carbonate

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Abstract

Shape-controlled porous silica structures with hollow interiors were synthesized by using $CaCO_3$ nanoparticles with the corresponding morphologies and sizes as the inorganic templates. Through the hydrolysis of sodium silicate, a continuous coating of SiO_2 was deposited over the surface of $CaCO_3$ cores to form core–shell structures. Hollow silica structures were finally obtained after calcining process and dissolving $CaCO_3$ in HCl dilute solution. The as-prepared hollow products were characterized with TEM, SEM, EDS, BET, and FT-IR.

Keywords: Nanosized calcium carbonate; Shape control; Hollow silica; Core–shell structure

In recent years, there has been great interest concerning the synthesis of hollow materials with specific structures and different compositions [1–4]. Among them, hollow spherical materials with various diameters attract the most attentions since they can serve as small containers for applications in catalysis, controlled release for drugs, dyes and perfumes, development of artificial cells, and protection of biologically active agents such as proteins and enzymes [5,6]. Furthermore, hollow spheres also exhibit some advantages over their solid counterparts due to lower densities, higher surface area, and more unique optical and chemical properties.

Several methods have been reported for the synthesis of hollow spherical materials, such as nozzle reactor approaches, emulsion/phase extraction techniques, and self-assembly processes including layer-by-layer (LBL) approaches [7,8]. Of these methods, self-assembly processes, also called core–shell techniques, are probably the most effective approaches to the formation of inorganic hollow spherical particles. In such processes, the assembly of the shell materials onto the core template is carried out to obtain composite materials with the core–shell structure, followed by removal of the templates via calcination in air or exposure to appropriate solvents to generate hollow structures with inner diameters determined by the size of the templates. The sacrificial templates that have been used are mainly organic templates, including polystyrene latex spheres [9], resin spheres [10], liquid droplets [11], and vesicles [12], etc., while the utilization of some inorganic templates, such as silica and CS_2, to produce hollow spheres has also been reported [13,14]. However, many of these templates are organic or inorganic spheres with sizes of several hundred nanometers, by which it is difficult to produce nanosized hollow spheres and obtain controllable hollow morphologies.

In this communication, we present a simple and novel pathway to fabricate shape-controlled hollow silica particles via core–shell structure of $CaCO_3/SiO_2$ by a sol–gel route. Scheme 1 shows the overall procedure used to synthesize the spherical hollow silica. Nanosized $CaCO_3$ particles with cubic and needle-like morphologies, which were synthesized by a high gravity reactive precipitation method [15], were employed as novel inorganic structure

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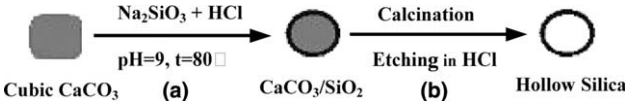

Scheme 1. The procedure for preparation of spherical hollow silica. (a) Hydrolysis and condensation of sodium silicate occurred, then SiO_2 coated $CaCO_3$ cores to form core–shell structures. (b) After calcinations, $CaCO_3$ was removed by dissolving it in HCl dilute solution.

directing templates to produce the hollow particles, instead of the normally used organic templates.

In a typical process, 500 ml of nanosized calcium carbonate aqueous suspension (8 wt%) was heated and kept at 80 °C under vigorous stirring. 180 ml of sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) solution (2 wt% SiO_2) was then added dropwise into the suspension to form core–shell composites with the molar ratio of $SiO_2/CaCO_3 = 1/10$, while the system was maintained at pH 9.0 by simultaneously adding HCl dilute solution. After the adding process was completed, the slurry was further stirred at the same condition as above for 2 h and subsequently filtered, rinsed with deionized water, dried at 100 °C, and followed by calcination in air at 700 °C for 5 h to yield a core–shell composite with $CaCO_3$ as the core and SiO_2 as the shell. The as-prepared composite was afterwards put into HCl dilute solution maintaining $pH < 1$ for 12 h to remove the $CaCO_3$ templates completely. Finally, the resulting gel was filtered, rinsed with deionized water and ethanol in sequence, and dried in the oven at 90 °C to obtain hollow silica powder.

Fig. 1 shows the transmission electron microscope (TEM) (HITACHI-800) images of the as-synthesized hollow silica structures. Fig. 1(a) consists of spherical hollow silica nanoparticles with a diameter of 70–100 nm and wall thickness of approximately 10 nm, which was fabricated via a $CaCO_3$ template with cubic morphology, while Fig. 1(b) shows tubular hollow silica synthesized through a needle-like $CaCO_3$ template. The strong contrast between the dark edge and pale center is

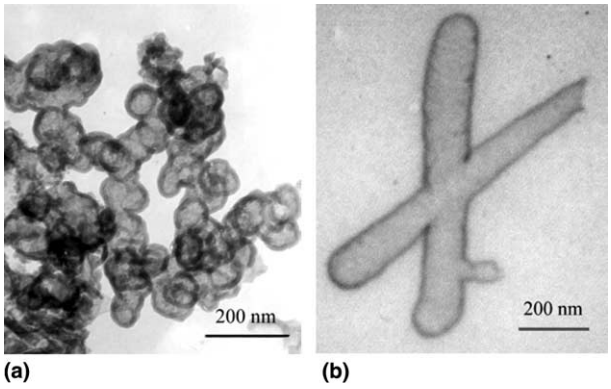

Fig. 1. TEM images of hollow silica particles: (a) spherical particles by cubic $CaCO_3$ templating; (b) tubular particles by needle-like $CaCO_3$ templating.

evidence for their hollow nature [16]. Some twin spheres are also observed in Fig. 1(a). This is because the coalescence of $CaCO_3$ nanoparticles may result in condensation and coating of SiO_2 on the surface of aggregate $CaCO_3$ nanoparticles. Typical field emission scanning electron microscope (FE-SEM) (JEOL-6301F) images of spherical and tubular hollow silica are shown in Fig. 2. Some broken spheres are observed in Fig. 2(a), providing further proof of their hollow nature. Fig. 2(b) also shows hollow tubes with openings consistent with the TEM image in Fig. 1(b), indicating a tubular hollow structure of silica.

Energy dispersive spectroscopy (EDS) (LINKISIS-300) indicates the presence of Si and O and the absence of Ca, confirming the complete removal of the $CaCO_3$ templates. The XRD results are those expected for non-crystalline materials. By IR spectroscopy (NEXUS-470) (Fig. 3), there are three characteristic peaks (at 1081.15, 798.51 and 456.65 cm^{-1}), respectively, belonging to three fundamental vibration bands for the silica structure in the wavenumber range of 450–1200 cm^{-1} [17–19].

The typical nitrogen adsorption isotherm at 77 K for hollow silica spheres and its pore size distribution

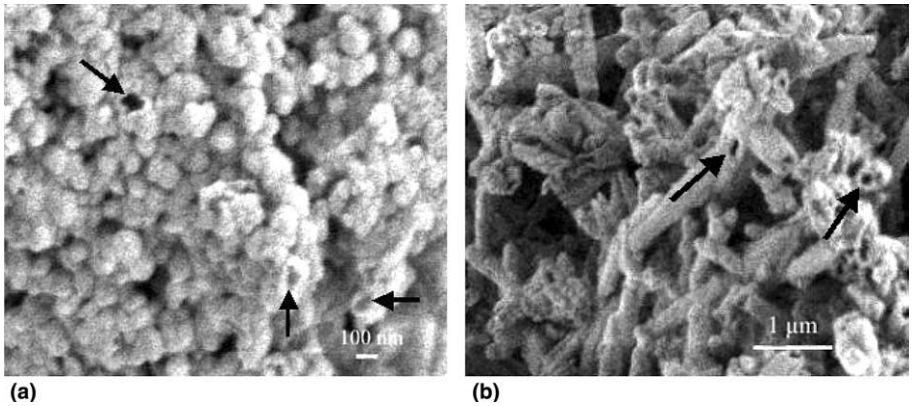

Fig. 2. SEM images of hollow silica particles: (a) spherical particles; (b) tubular particles.

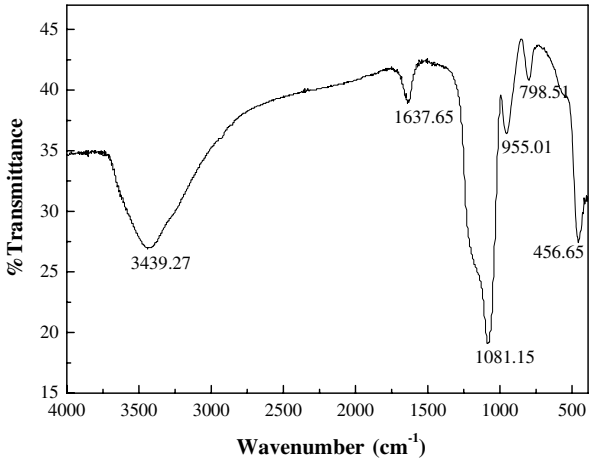

Fig. 3. IR spectroscopy for hollow spherical silica.

determined by a Micromeritics ASAP 2010 Analyzer are shown in Fig. 4. The resulting isotherm can be classified as a type II isotherm according to the International Union of Pure and Applied Chemistry (IUPAC) nomenclature [20]. The corresponding size distribution data calculated from the nitrogen adsorption isotherm by the Barrett–Joyner–Halenda (BJH) method reveals that the pores on the shell are mainly microporous with very narrow pore size distribution centered at 0.9–1.0 nm. The BET specific surface area of the hollow silica sphere is found to be as high as 725.2 m^2/g. In the same way, the BET surface area of hollow silica tube is measured to be 516.5 m^2/g.

Importantly, the inner diameter and the morphology of the hollow silica materials prepared in this work may be controlled by adopting appropriate nanosized $CaCO_3$ particles, whose size and morphology can be tailored precisely by a high gravity reactive precipitation method [15]. Further experiments to adjust the shell thickness of hollow silica by controlling the amount of deposited SiO_2 or the concentration of sodium silicate solution are underway.

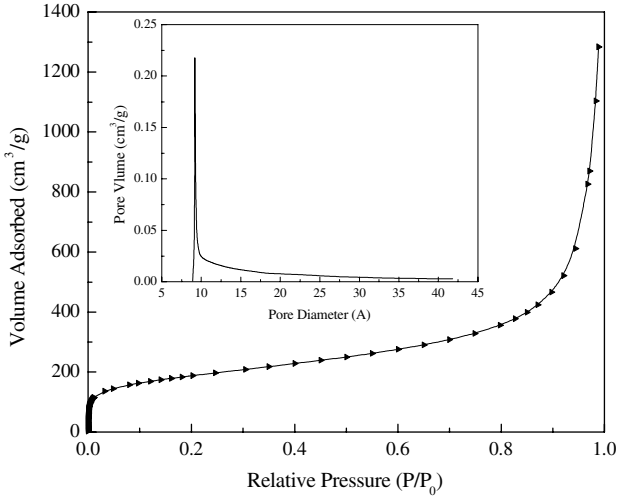

Fig. 4. N_2 adsorption isotherm for hollow silica spheres and the corresponding pore size distribution (inset).

In summary, hollow silica materials with spherical and tubular morphologies were successfully synthesized using nanosized $CaCO_3$ particles with the corresponding shapes and sizes as inorganic templates in our approach. This novel method may also be feasible to fabricate hollow materials of other compositions. Since sodium silicate and calcium carbonate can be produced with a low cost, the preparation of hollow silica by this method might benefit its commercialization. In addition, due to its large specific area, porosity, hollow structure, and compatibilities with other materials, the as-synthesized hollow silica may find wide applications in many fields.

Acknowledgements

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