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## Original article Fabrication of hollow silica microspheres utilizing a hydrothermal approach

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#### ARTICLE INFO

#### ABSTRACT

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Keywords: Silica Hollow materials Glucose Hydrothermal method Hollow silica microspheres (HSMSs) have been successfully fabricated *via* a facile hydrothermal route using D-glucose as the sacrificial template and sodium silicate powder as the silica precursor. The resulting silica hollow particles were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and infrared spectroscopy (IR). The surface area was determined using the BET method. SEM and TEM images exhibited micro-sized silica hollow particles with a size of  $\sim$ 1.5 µm.

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#### 1. Introduction

Inorganic hollow particles represent a distinct class of materials which are of great interest from both an academic and an industrial point of view [1,2]. Due to their unique properties, such as chemical and thermal stability, large specific surface area, low density and biocompatibility, these silica hollow particles are promising for use in diverse applications, including encapsulation of chemicals for controlled-release applications, catalysis, coatings, artificial fillers [3,4], as examples.

To date, a variety of synthetic approaches, including sol-gel process [5], emulsion/interfacial polymerization strategies [3], surface polymerization processes [6,7], and colloidal templating [8], have been reported to prepare inorganic hollow particles. The most often used technique is the sacrificial templating method which is based on the synthesis of core-shell particles with the subsequent removal of the core by thermal or chemical means. Recently, carbohydrate-derived carbonaceous spheres are used as sacrificial core, which are generated by the hydrothermal treatment of aqueous solutions of saccharides [9]. These sacrificial cores inherit surface functionalities which facilitate the precipitation of the inorganic precursors and the nanoparticles on their reactive surfaces, as was reported for the synthesis of some inorganic hollow particles, such as TiO<sub>2</sub> hollow spheres [10], WO<sub>3</sub> hollow spheres [11] and noble metal nanoparticles [12].

In the present contribution, we report a simple hydrothermal synthesis route for the fabrication of HSMSs by a sacrificial templating method using glucose-derived carbonaceous spheres as the sacrificial template and sodium silicate powder as the silica precursor. Using glucose as sacrificial templates for the fabrication of the silica hollow spheres originates from the fact that the surface of the glucose-derived carbonaceous material is rich in surface functionalities which support the adsorption of the precursors onto their surface layers without any further surface modifications. Moreover, it is inexpensive and one of the broadly available carbohydrates.

#### 2. Experimental

D-Glucose monohydrate (3170 mg, 16 mmol) was dissolved in 20 mL of distilled water. In a standard experiment, 284 mg (1 mmol) sodium silicate nonahydrates, as precursor for silica, was dissolved in 10 mL of distilled water. The two solutions were mixed immediately before the experiment and placed in 100 mL Teflon-lined stainless steel autoclave, which was heated in an oven to 180 °C for 24 h. The products were filtered off; washed three times, first with distilled water and then ethanol, and finally dried in a vacuum oven at 60 °C for 5 h. After synthesis, the silica–carbon composites were calcined in air at 550 °C (heating rate of 5 °C/min) for 5 h to remove the carbon core, leading to hollow silica particles.

D(+)-Glucose monohydrate ( $C_6H_{12}O_6\cdot H_2O$ ) and sodium silicate nonahydrates powder ( $Na_2SiO_3\cdot 9H_2O$ ) were obtained from Merck (Darmstadt, Germany). All mentioned chemicals were analytical

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grade and employed without further purification. Distilled water (conductivity  $\sim$ 1.7 µs/cm) was used.

The products were characterized by infrared spectroscopy using IFS 88 from Bruker. The silica particles were examined by Xray powder diffraction (X'Pert MPD, Pananalytical, Cu-K $\alpha$  radiation). The surface area and the pore size were studied by nitrogensorption measurements which were performed on a Micromeritics ASAP 2020 gas sorptometer. Samples were degassed in vacuum at 0.003 mm Hg for at least 3 h at 350 °C. The measurements were then carried out at 77 K over a wide range of relative pressures  $(P/P^{\circ})$  from 0.01 to 0.995. Specific surface areas were calculated by the Brunauer-Emmet-Teller (BET) method, with pore sizes estimated from pore size distribution curves from the adsorption branches of the isotherm. The particle size and morphology was visualized using a JEOL JSM-7500F field emission scanning electron microscope at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) was conducted on a IEOL model JEM-3010 electron microscope operated at 300 kV.

#### 3. Results and discussion

Uniform hollow silica microspheres (HSMSs) with a shell of silica nanoparticles and shell thickness of *ca.* 150 nm, as seen in Fig. 1(a1–a3), have been readily obtained by a hydrothermal one-pot synthesis approach involved in the production of core–shell composites. This was followed by thermal treatment – in air – leading to selective etching of the core and the production of HSMSs.

Fig. 1(b) shows the uniform core-shell composite, microspheres particles, of *ca*.  $3-4 \mu m$  in diameter before calcination. The SEM image of HSMSs shown in Fig. 1(a) reveals that the spheres after calcination remained intact and preserved the three dimensional, spherical shaped particle, even after etching of the core.

In addition, in Fig. 1(a2), the observed broken shell provides an indication of their hollow nature. The TEM image of the same product displayed in Fig. 1(a3) shows a variation in contrast between the inner void and the outer shell which provide further indications of the fabrication of the hollow structure of the silica spheres with wall thickness of *ca.* 150 nm. One can observe from Fig. 1 that the size of the HSMSs is reduced about *ca.* 40%–50% from the original size of the core–shell composite.

Fig. 2 represents a schematic illustration (cross-sectional view) of the formation of the HSMSs. The mechanism of the formation of the resulting HSMSs can be understood from the fact that glucosederived carbonaceous spheres which are formed during the hydrothermal reaction have reactive surface layers with *O*-functionalities [13,14]. These reactive surface functionalities facilitate the coating of their surfaces with thin layers of the desired materials forming core–shell composite spheres without any need for surface modifications. Subsequently, the selective removal of the carbonaceous templates by the calcination process leads to the production of HSMSs replicas of composite spheres but of lesser size. This is likely because during the calcination process the incorporated ions in the surface layer of the carbonaceous core are densified and cross-linked to form the hollow oxide replicas of the carbonaceous spheres templates with reduced size.



**Fig. 1.** (a1) SEM micrograph of the porous HSMSs after calcination at 550 °C for 5 h, (a2) SEM micrograph of HSMSs with broken shell, the arrow refers to a broken shell, (a3) TEM micrograph of porous hollow silica microsphere, (b) SEM micrograph of the core-shell composite before calcination.

The powder X-ray diffraction patterns of the resulting HSMSs after calcination and its corresponding composite sample before calcination (see Figs. S1 and S2 in the Supporting information) reveal the amorphous nature of the silica sample before and after calcinations [15].

There are remarkable differences between the two IR spectra of HSMSs and its related composite as can be noticed in Fig. 3. The reduced intensity of the broad peak between  $3000 \text{ cm}^{-1}$  and  $4000 \text{ cm}^{-1}$  which is characteristic to the OH group that exists in water, and in addition, the absence of the peaks around 2932 cm<sup>-1</sup> and  $1704 \text{ cm}^{-1}$  in the spectrum of the hollow spheres ascribed to C–H stretching and the carbonyl group, respectively [9], indicate the removal of most water molecules and the carbonaceous core after firing at 550 °C for 5 h to produce HSMSs. The absorption bands observed around 1634 cm<sup>-1</sup> in the two figures are assigned to the stretching and deformation vibration of adsorbed water molecules [16]. Peaks around 468 cm<sup>-1</sup>, 805 cm<sup>-1</sup> and 1102 cm<sup>-1</sup>



Fig. 2. Schematic illustration (cross-sectional view) of the formation of the HSMSs.



Fig. 3. IR spectra of the core-shell composites and the HSMSs obtained by calcination of the composite at 550  $^\circ C$  for 5 h.



Fig. 4. Nitrogen sorption isotherm of the porous HSMSs. The inset shows the pore size distribution.

in the HSMSs spectrum correspond to the rocking, bending and the asymmetric vibration bands of the Si–O–Si bond, respectively [17].

Nitrogen sorption isotherms were acquired to study the porosity and specific surface area of the as-synthesized hollow spheres. Fig. 4 represents the sorption isotherm of hollow spheres. The inset shows the pore size distribution of the corresponding sample. It is a typical type IV isotherm characteristic of mesoporous materials according to the International Union of Pure and Applied Chemistry (IUPAC) [18]. Hysteresis loops can be observed in the curve, which is evidence of the existence of a mesoporous structure. The pore size distributions of the resulting silica hollow spheres were measured by the nitrogen sorption method and calculated by Barrett–Joyner–Halenda (BJH) method from the desorption curves [19]. It can be seen that the pore sizes are mainly in range of 5–30 nm. The surface area of the HSMSs is equal to  $264 \text{ m}^2/\text{g}$ .

The high surface area is attributed to the combination of the surface areas of the outer surface, the pore channels and the inner surface, which altogether form the surface area of the particles. This large surface area showed that these kinds of materials can applied as inorganic vehicles or containers in many potential applications, such as the slow release applications.

#### 4. Conclusion

In conclusion, glucose has been successfully applied as a sacrificial template for the fabrication of hollow SiO<sub>2</sub> microspheres. Therefore, mesoporous hollow silica microspheres can be readily fabricated *via* hydrothermal hydrolysis by employing glucose as the sacrificial template and sodium silicate powder as the silica precursor. The large specific surface area of the resulting HSMSs, as support by BET measurements, indicates that this class of materials is promising for diverse applications as inorganic containers. Further work to investigate and develop a method for fabrication of hollow silica nanoparticles is in progress.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2014.01.043.

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