



## A dual template method for synthesizing hollow silica spheres with mesoporous shells

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### ABSTRACT

PS/silica core/shell composites were synthesized by the modified Stöber method using polystyrene spheres and cetyltrimethylammonium bromide as dual templates under room temperature. The silicate species and the templates were self-assembled to form mesoporous silica shell on the surface of the PS spheres. Hollow silica spheres with mesoporous shell were obtained by removing the polymer core and the templates through calcination. The hollow silica spheres showed high specific surface area of 1099.5 m<sup>2</sup>/g and narrow pore size distribution centered at 2.31 nm.

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### 1. Introduction

Mesoporous hollow spheres with well defined structure have been attracting interests due to their potential applications in confined nanocatalysts, adsorbents, targeted drug and gene delivery, as well as biomolecule encapsulation [1–5]. A variety of hollow materials especially for silica hollow spheres have been prepared by using polystyrene spheres (PS) as hard templates [6–8]. However, few results were reported for the synthesis of monodisperse hollow silica sphere with mesoporous shell by employing polystyrene (PS) spheres and cetyltrimethylammonium bromide (CTAB) as dual templates under mild condition.

The Stöber method used to synthesize solid monodisperse silica spheres has been developed *via* hydrolysis–condensation of TEOS in water–alcohol–ammonia solution [9]. Further modification of the method has been made by introducing cationic surfactants into the synthesis system to fabricate sub-micrometer sized solid ordered mesoporous silica spheres with high surface area [10]. Recently, more concerns for these methods have been paid because of the mild synthesis condition and the simple operation [11–14]. Therefore, it is interesting to combine the advantages of template method and the Stöber method for synthesizing the monodisperse hollow sphere with well defined pore structures.

In this paper, the Stöber method modified by using PS spheres and CTAB as dual template has been employed to synthesize monodisperse hollow silica spheres with mesoporous shells.

### 2. Experimental

The PS particles were prepared by emulsifier-free emulsion polymerization [15].

A typical procedure for synthesizing the mesoporous hollow silica spheres was carried out as follows: 0.625 g of CTAB and 2.000 g of PS spheres were dispersed in 30 mL of absolute ethanol and 25 mL of distilled water. 3 mL of ammonia (28 wt.%) was added and then stirred for 2 min. 2 mL of TEOS was added quickly in above solution and stirred for 2 h at room temperature. Finally, it was centrifuged and washed by distilled water for several times. The obtained white powders were dried at 313 K overnight and calcined at 823 K for 5 h in air to remove the templates.

Powder X-ray diffraction (XRD) patterns were recorded on a D/Max-b X-ray diffract meter at 40 kV, 40 mA. SEM images were taken with a KYKY-AMRAY-1000B electron microscope operated at 25 kV. TEM images were obtained with a JEOL JEM-2000Ex electron microscope at 120 kV. Nitrogen adsorption isotherms were measured at 77 K on a NOVA4000 volumetric adsorption analyzer. Prior to the measurements, the samples were out-gassed at 623 K for 4 h.

### 3. Results and discussion

The low angle XRD patterns of samples were shown in Fig. 1. Three Bragg diffraction peaks could be observed at  $2\theta$  low angles between 2.5 and 7.0°, which could be assigned

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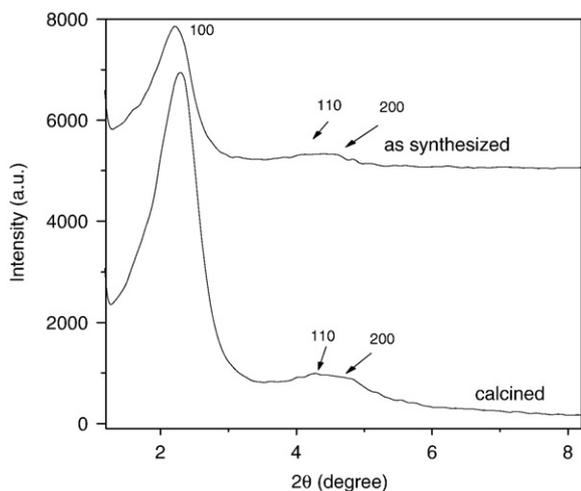


Fig. 1. The low angle XRD patterns of the as-synthesized and calcined samples.

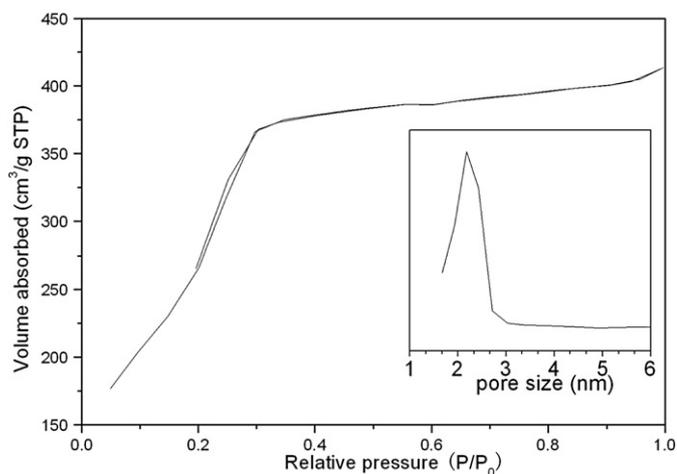


Fig. 2.  $N_2$  adsorption/desorption isotherms for the calcined silica spheres inset: pore size distribution curves calculated from the adsorption branch of  $N_2$  isotherms.

to the (100), (110) and (200) reflections of a hexagonal symmetry structure, respectively. An increase of the diffraction intensity of the calcined samples was observed compared to the as synthesized samples. A slight left-shift of the (100) diffraction peak could be seen upon high temperature calcination.

Typical nitrogen adsorption/desorption isotherm at 77 K and pore size distribution curve for the calcined hollow silica spheres are exhibited in Fig. 2. The nitrogen sorption isotherm for the calcined silica could be classified as type IV isotherms characteristic of mesoporous materials according to the IUPAC nomenclature. The well-defined step between 0.2 and 0.3 of  $P/P_0$  indicates a highly narrow mesoporous structure. The

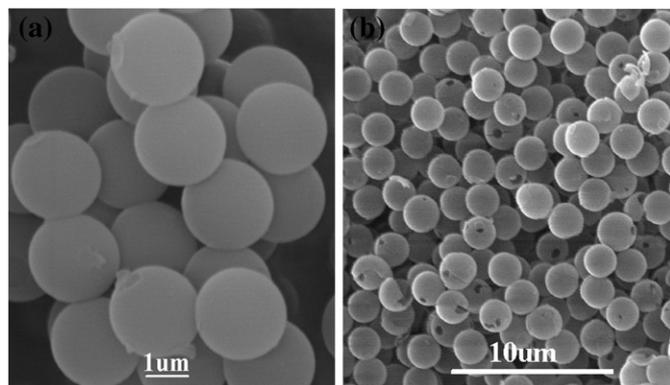


Fig. 3. SEM images of PS core-silica shell composite (a), and hollow core-silica shell spheres (b).

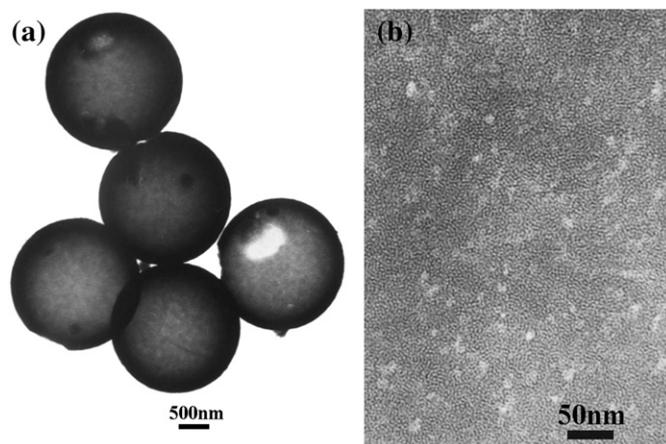


Fig. 4. TEM images of calcined hollow core-silica shell spheres (a) and the detail on the shell of the hollow spheres (b).

corresponding pore size distribution data in the inset of Fig. 2 calculated from the adsorption branch of nitrogen adsorption isotherm by the BJH method show narrow pore size distributions centered at 2.31 nm. The specific surface area of the hollow silica spheres was  $1099.5 \text{ m}^2/\text{g}$  with corresponding total pore volumes of  $0.636 \text{ mL/g}$ .

Fig. 3 showed the SEM images of as-synthesized and calcined samples. Well dispersed spheres could be observed for the as-synthesized sample in Fig. 3. The spherical morphology with a smooth surface could be obtained for the calcined sample even though the material was calcined at 823 K for 5 h. Moreover, some obvious small holes on the surface of calcined samples (Fig. 3b) could be found whereas they are not seen on the surface of the as-synthesized samples, indicating the removal of PS spheres under high temperatures lead to the formation of hollow structure. Fig. 4 exhibited the TEM images of calcined samples. Small holes also could be observed in Fig. 4a. Furthermore, it is deserved to point out that worm-like mesopores could be seen on the surface of calcined samples in Fig. 4, suggesting that shell material with well defined mesoporous structure has been formed.

#### 4. Conclusion

Hollow silica spheres with mesoporous shells were successfully synthesized by a modified Stöber method using CTAB and PS spheres as dual templates. The characteristics of these materials such as high specific surface areas, narrow pore size distribution and large pore volumes are expected to find potential application in catalysis, adsorption and encapsulation, and relevant studies are in progress.

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