

Nano-sized silica hollow spheres: Preparation, mechanism analysis and its water retention property

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ABSTRACT

In this article, synthesis of nano-sized silica hollow spheres applying positive charged polystyrene as sacrificial templates was introduced. Firstly, nano-sized polystyrene particles were synthesized by emulsifier-free emulsion polymerization under solvothermal condition. Secondly, silica hollow nanospheres were formed through a simultaneous ‘coating–etching’ process. PVP played a key role in the evolution of nano-sized hollow spheres even if the templates were positive charged and the formation mechanism was different from that of previous studies. TEM results revealed that the morphologies of nano-sized silica hollow spheres not only strongly relied on the amount of reactant, but also the sequence of adding them. TGA illustrated that the interiors of nano-sized silica hollow spheres were not completely ‘hollow’. Brunauer–Emmett–Teller (BET) analysis showed that this material had a specific area of 399 m²/g. The water retention property of the materials was also investigated.

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1. Introduction

The synthesis of inorganic nanospheres with hollow interior has attracted more and more attention because of many extraordinary properties of this structure, such as low density, low toxicity, good chemical and thermal stability and large surface area [1–4]. These kinds of hollow nanospheres have many potential applications in chromatography, controlled delivery, catalysis, pigment, photonic crystals, artificial cells and as inorganic fillers to promote the properties of polymer matrix especially PEM for fuel cells [5–9]. Procedures for synthesis of inorganic hollow nanospheres mainly involve sol–gel process [10], self-assembly techniques [11], surface living polymerizations process [12], surfactant-assisted solvothermal decomposition [13], etc. Among these methods, template-assisted procedure is considered to be one of the efficient ways of fabricating hollow structured nanospheres.

Exploring a simple method of synthesizing nano-sized silica hollow spheres is quite significant because of their wide potential applications. Up to now, fabricating silica hollow nanospheres was basically using template-assisted procedures. For example, Armes and coworkers [14] first used shell crosslinked diblock copolymer micelles as templates to fabricate silica hollow spheres with diameters ranging from 27 to 155 nm. Nakashima and

coworkers [15] successfully prepared hollow silica nanosphere using a template of ABC triblock copolymer micelle with a core-shell-corona architecture. Teng et al. [16] reported synthesis of silica hollow nanospheres adopting nano-sized CdS particles as sacrificial templates. Ho and coworkers [17] prepared nano-sized hollow silica spheres by assembly of functional polymer nanospheres with tetraethoxysilane through hydrothermal methods, coupled with removal of the core by programmed calcination. Chen et al. [18] and Zhang et al. [19] adopted nano-sized polymer particles as templates to synthesize hollow silica nanospheres. However, those previous processes were quite time-consuming and generally the morphologies of the obtained hollow spheres were unsatisfactory.

Usually, calcination at high temperature or selective dissolution in an appropriate solvent to remove the core material is needed if applying template-assisted route [20–23], which is quite inconvenient. Recently, Wu and coworkers [24] reported a facile method of synthesizing silica hollow spheres. Firstly, micron-sized positively charged polystyrene spheres were synthesized by dispersion polymerization with a cationic monomer as functional comonomer. Then the sol–gel process was carried out in alcohol and water mixed dispersion under 50 °C with tetraethoxysilane (TEOS) as silica source and ammonia as catalyst. It was interesting to find that the PS core disappeared almost synchronously when the shell was formed. Darbandi et al. [25] also found that when applying CdSe/ZnS as sacrificial template, the formation of silica coating and the removal of core material could happen simultaneously by adjusting the concentration of ammonia.

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Herein, a facile method of synthesizing nano-sized silica hollow sphere is presented and a new formation mechanism is proposed. This method is based on PVP-participated emulsifier-free emulsion polymerization under solvothermal condition and a subsequent modified sol–gel process. In previous studies[26], the electrostatic interaction between templates and silica particles is focused. However, we find that polystyrene particles in alkali condition exhibit negative charge by Zeta potential test. As a result, electrostatic repulsion instead of electrostatic attraction should exist between templates and silica particles in the system. Thus, we believed that there was no electrostatic interaction which was thought to be responsible for the coating formation.

Because of the special properties of nano-sized PS latexes, there are quite some other differences in our experiments compared with the process presented previously [27,28]. On one hand, the amount of H₂O in this system has an obvious effect on the subsequent morphology of hollow spheres, which has never been mentioned in the previous studies. On the other hand, it is found that not only the amount of reactants influence the morphology of as-synthesized spheres, the adding sequence is also quite crucial. Other factors that influence the morphology of hollow structure are discussed in detail, and the specific surface area, thermal stability and moisture retention of nano-sized hollow spheres are also studied.

2. Materials and methods

2.1. Materials

Styrene (Sinopharm Chemical Reagent Co. Ltd.) was purified by vacuum distillation to remove the inhibitor before used. 2,2'-(Azobis(isobutyramidine) dihydrochloride (AIBA) (Sigma-Aldrich), acetone, absolute ethanol, polyvinyl pyrrolidone (PVP) ([C₆H₉NO]_n, K-30), tetraethoxysilane (TEOS) and ammonia solution (25 wt%) (Sinopharm Chemical Reagent Co. Ltd.) were used as received. The deionized water was from our laboratory.

2.2. Synthesis of nano-sized polystyrene latex particles

A typical procedure of synthesizing nano-sized polystyrene (PS) particles through solvothermal process is presented as follows: firstly, 30 mL deionized water and 30 mL acetone were mixed in a reaction vessel made of polytetrafluoroethylene, 0.8 g PVP and 0.13 g AIBA were added consecutively into the mixed solvent with magnetic stirring until these materials completely dissolved. Next, 2.0 g styrene was added into the solution and kept stirring under room temperature for 10 min. Then, the vessel was shifted to an airtight container. The polymerization reaction was carried out at 85 °C under gentle stirring for 48 h. After that, the obtained PS latex was dialyzed in ethanol using a cellulose membrane in order to remove the undesirable water and acetone.

2.3. Synthesis of nano-sized silica hollow sphere

In order to determine the effects of each reagent to the morphology final product, we carried out several experiments with different amounts of ammonia solution, ethanol, H₂O and TEOS. The detailed recipes were listed in Table 1, and the pH of each recipe was tested to provide an evidence of condensation velocity, since in base-catalyzed condensation, higher pH brings faster reaction velocity. The typical procedure was described as follows: 0.5 g dialyzed polystyrene emulsion was added into 30 mL mixed solution of deionized water and ethanol with different volume ratio in a flask with constant magnetic stirring.

Table 1

Recipes of synthesizing nano-sized silica hollow spheres.

Sample no.	Ammonia (mL)	Ethanol (mL)	H ₂ O (mL)	TEOS (mL)	pH
1	0.4	27.5	2.5	0.2	12.48
2	0.5	27.5	2.5	0.2	12.50
3	0.6	27.5	2.5	0.2	12.54
4	0.7	27.5	2.5	0.2	12.56
5	0.8	27.5	2.5	0.2	12.60
6	0.5	30.0	0	0.2	12.41
7	0.5	25.0	5.0	0.2	12.60
8	0.5	27.5	2.5	0.1	12.50
9	0.5	27.5	2.5	0.3	12.50
10	0.5	27.5	2.5	0.4	12.50

Then, TEOS was added dropwise, after that, ammonia solution was added twice and the reaction was kept at 50 °C for another 3 h. Then the nano-sized silica hollow spheres were obtained.

2.4. Characterization

Transmission electron microscopy (Hitachi H-600, Hitachi Co., Japan) was used to observe the morphologies of the obtained nano-sized polystyrene particles and nano-sized silica hollow spheres. The dispersions were diluted with ethanol and ultrasonicated for 5 min and then dried onto carbon-coated copper grids before examination. The as-synthesized hollow spheres were separated from the reaction medium by centrifuging, and washed with deionized water for five times. The obtained spheres were used for other tests.

Thermogravimetric analysis data were recorded using TA Instruments Q500. Before testing, the sample was dried in vacuum oven at 100 °C for 24 h to remove as much water as possible. The test was carried out in a range of 30–700 °C at a heating rate of 10 °C/min. Moisture retention of silica hollow spheres was also tested using TGA. Before testing, the sample was immersed in deionized water for 24 h, and the water adsorbed on the outer surface of spheres was removed. The test was carried out in the range of 60–150 °C at a heating rate of 1 °C/min.

Nitrogen sorption curves, pore size distributions and surface areas were obtained using a Micromeritics Tristar 3000 surface area and porosity analyzer. Before measurement, the samples were degassed at 90 °C under vacuum for 8 h. The pore sizes were calculated from desorption isotherm curves using Brunauer–Joyner–Halenda (BJH) method.

Zeta potential was measured on a Malvern Instruments Nano ZS Zetasizer, using a flow through cell with a Malvern Instruments MPT-2 Multi Purpose Titrator. Before test, 0.5 g nano-sized PS latex was diluted by 30 mL mixed solution composed of 27.5 mL ethanol and 2.5 mL deionized water. PS latex under alkaline condition was prepared by adding 0.5 mL ammonia to the dispersion above.

3. Results and discussion

3.1. Synthesis of nano-sized PS particles

Template-assisted synthesis is a quite comfortable way to obtain silica hollow sphere, but the morphology and dispersibility of the core material is crucial to the final product. Herein, nano-sized PS latex with narrow size distribution was successfully synthesized under solvothermal condition. Fig. 1 was the TEM picture of the nano-sized PS particles, the diameter of PS particles was around 30 nm and the monodispersity was good.

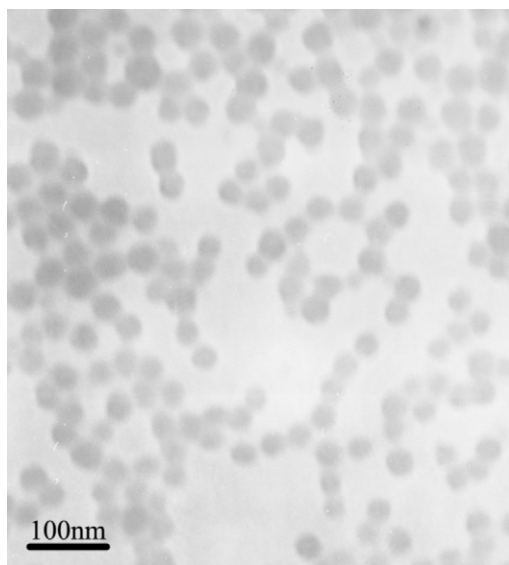
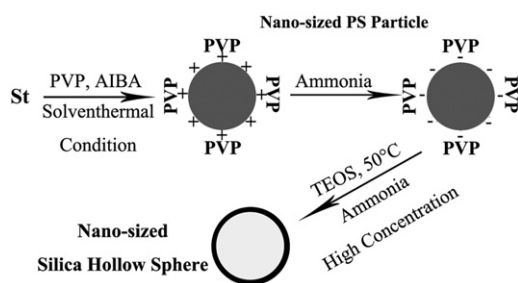


Fig. 1. TEM image of nano-sized polystyrene particle.



Scheme 1. Procedure for synthesizing nano-sized silica hollow spheres.

3.2. Formation mechanism of silica hollow spheres

The authors who employed the similar preparation approach exclusively concluded that the electrostatic attraction between templates and silica particles was the only driving force for the coating process [26]. The polystyrene particles showed a Zeta potential of +4.94 mV under neutral condition in our study. However, to our surprise, the template underwent a Zeta potential reversal to -8.91 mV after the solution changed from neutral to alkali condition which was necessary for sol-gel process. Hence the electrostatic repulsion between templates and silica particles is doubtless now. Thus we proposed the reason for porous silica shell formation, which was due to the coupling effect of PVP rather than electrostatic interaction during the coating process. PVP was attached onto the surface of polystyrene particles during the polymerization, which promoted the dispersibility of PS particles, and eventually facilitated the coating of silica shell. The mechanism was illustrated in Scheme 1.

3.3. Effect of the ammonia amount

Among all the factors that influenced the synthesis of silica hollow spheres, the amount of ammonia, H_2O and TEOS was crucial to the morphology of the obtained hollow structure. Fig. 2 displayed the morphologies of the obtained silica hollow spheres with different amount of ammonia, as we can see most hollow spheres have diameters around 40 nm, the thicknesses of shells do not have obvious variation. When the amount of ammonia was

less than 0.5 mL, as illustrated in Fig. 2(a), the PS particles were not able to be etched, and the PS/SiO₂ core-shell structure was formed. However, as ammonia was increased from 0.5 to 0.6 mL, hollow structure with smooth silica shell was obtained. By increasing the amount of ammonia to 0.7 or 0.8 mL, both silica hollow spheres and silica particles could be observed in the TEM images, as shown in Fig. 2(d) and (e). This was because, the high concentration of ammonia made the hydrolysis and condensation of TEOS so fast that some particles could not be captured by PS templates, and they would become secondary silica particles, thus two kinds of structures coexisted in TEM picture.

3.4. Effect of the H_2O amount

The influence of the amount of H_2O in the medium on the morphologies of silica hollow spheres was also quite obvious. It was supposed that the hydrolysis and condensation of TEOS would get faster as the amount of H_2O increased. Thus the silica shell would be formed faster. In Fig. 3, it can be observed that the particle's size was around 40 nm, and the shell thicknesses of the hollow silica has not changed when the H_2O amount changes. As shown in Fig. 3(a), when only ethanol was used as dispersion medium, almost all the spheres were sticky to each other and shaped like peanuts. It was supposed that the formation of silica shell was so slow that before the spherical shell was completely formed, the surface of PS templates had been etched out and they would agglomerate with each other under this condition. Increasing the amount of H_2O to 2.5 mL, it was quite obvious that the morphologies of the obtained nanosilica hollow spheres were much better, as shown in Fig. 2(b). When the amount of H_2O was increased to 5 mL, the speed of the “dissolution” of PS particles and the formation of silica shell reached an optimal state. As displayed in Fig. 3(c), the obtained spheres had relatively good shape, and the monodispersity was also getting better.

3.5. Effect of the TEOS amount

By simply changing the amount of TEOS, the thickness of the silica shell could be adjusted, and it was quite easy to predict that the silica shell would become thicker with increasing amount of TEOS. As we can see in Fig. 4, when the amount of TEOS was increased from 0.1 to 0.3 mL, the shell thickness increased from 2 nm via 4–7 nm, and the average diameters of the as-synthesized hollow spheres were around 40 nm. However, when the amount of TEOS was increased to 0.4 mL, as illustrated in Fig. 4(d), secondary silica particles could be observed in the TEM picture, which suggested that the PS core particles were unable to capture the rapidly forming silica particles absolutely and equably at high TEOS concentration. As a result, the shell thickness decreased when 0.4 mL TEOS was added compared with hollow spheres obtained with 0.3 mL TEOS. Thus, the uniform shell thickness of the nano-sized hollow silica spheres could easily be tailored by simply altering the concentration of TEOS in a certain range.

3.6. Effects of the procedures of adding reactants

Interestingly, it was found that the morphology of the obtained silica hollow sphere depended not only on the amount of reactants but also on the procedures of adding them into the medium, which was completely different from the previous studies [24,27,28]. Some control experiments were carried out to prove this indication. Fig. 5 represented the different morphologies of nano-sized silica hollow spheres by different TEOS addition sequences. As illustrated in Fig. 5(a), 0.4 mL TEOS was added all in once, and secondary SiO₂ particles could be seen

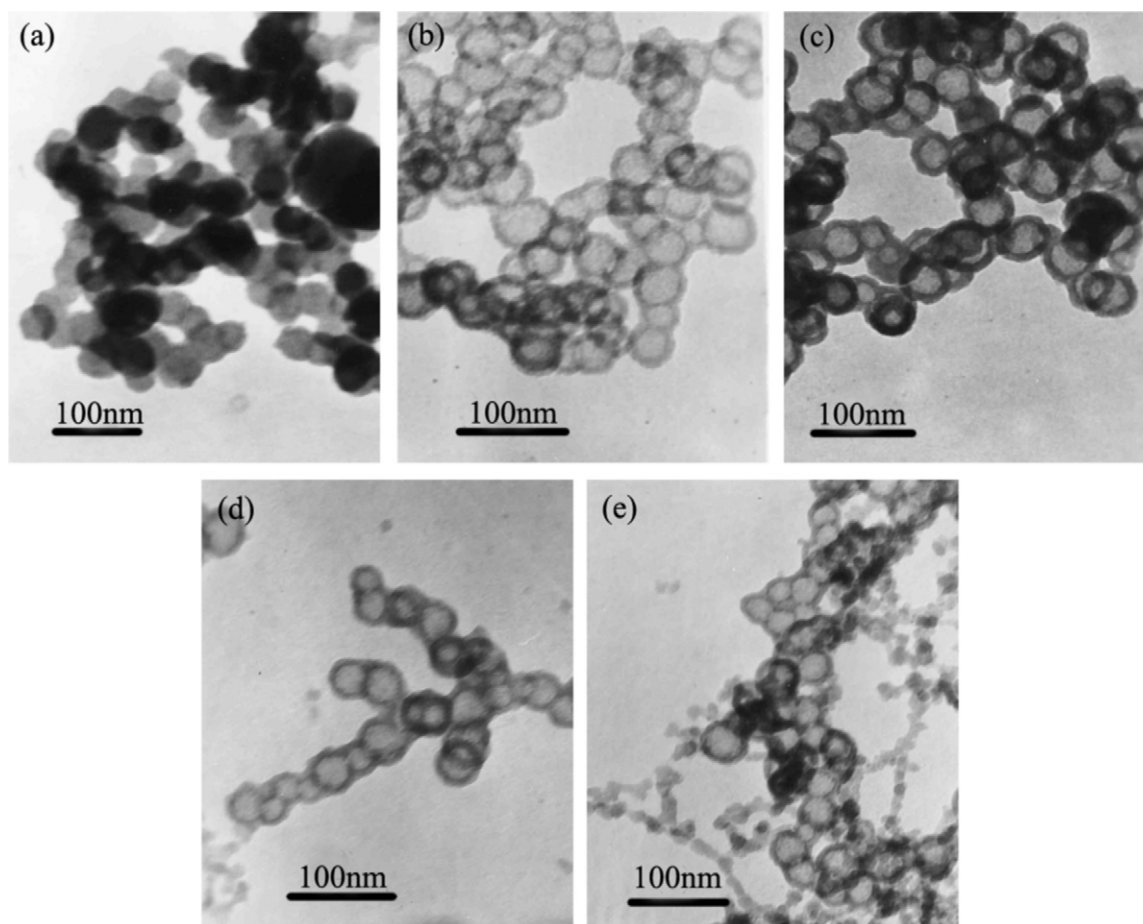


Fig. 2. TEM images of silica hollow spheres: (a) sample no. 1, (b) sample no. 2, (c) sample no. 3, (d) sample no. 4 and (e) sample no. 5.

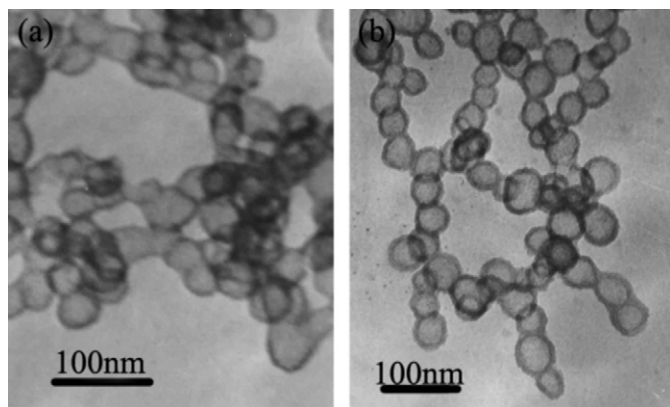


Fig. 3. TEM images of silica hollow spheres: (a) sample no. 6 and (b) sample no. 7.

clearly in the picture. However, when TEOS was added twice, as shown in Fig. 5(b), no silica particles could be observed. The reason was that the concentration of TEOS was not so high and the formation of silica particles was slow enough to be captured by templates absolutely when TEOS was added in two steps, and obviously, the thickness of silica shell also increased under this condition.

Except for the way of adding TEOS, procedure of adding ammonia also had a great impact on the morphologies of the obtained silica hollow spheres. Fig. 6 showed the different morphologies of silica hollow nanospheres by two ways of

adding ammonia into the reaction system. It could be seen that only hollow structure was formed when ammonia was added twice. However, if 0.5 mL ammonia was added into the system all in once, secondary silica particles appeared in the TEM image. This was because that the hydrolysis and condensation of TEOS was too fast when the concentration of ammonia was very high. Therefore, from the discussion above, we reached a conclusion that the speed of dissolution of templates and the formation of amorphous silica shell should be adjusted to an appropriate ratio in order to obtain nano-sized silica hollow sphere with satisfactory morphology.

3.7. TG analysis

Thermogravimetry Analysis (TGA) was used to investigate the thermal stability of the obtained silica hollow nanospheres. As shown in Fig. 7, the slight weight loss occurred from 60 to 100 °C was believed to be the evaporation of H₂O adsorbed on the surface of hollow spheres. In the temperature range from 350 to 450 °C, about 35% weight was lost, and it was caused by the decomposition of templates. Considering the amount of PS latex and TEOS used in the experiment, PS spheres weighted over 90% of the hybrid particles if core/shell structure was obtained. Thus, we concluded that the templates could only be partly removed after the simultaneous 'dissolution' of PS by ammonia, and the interior of nano-sized silica hollow sphere was not absolutely 'hollow'.

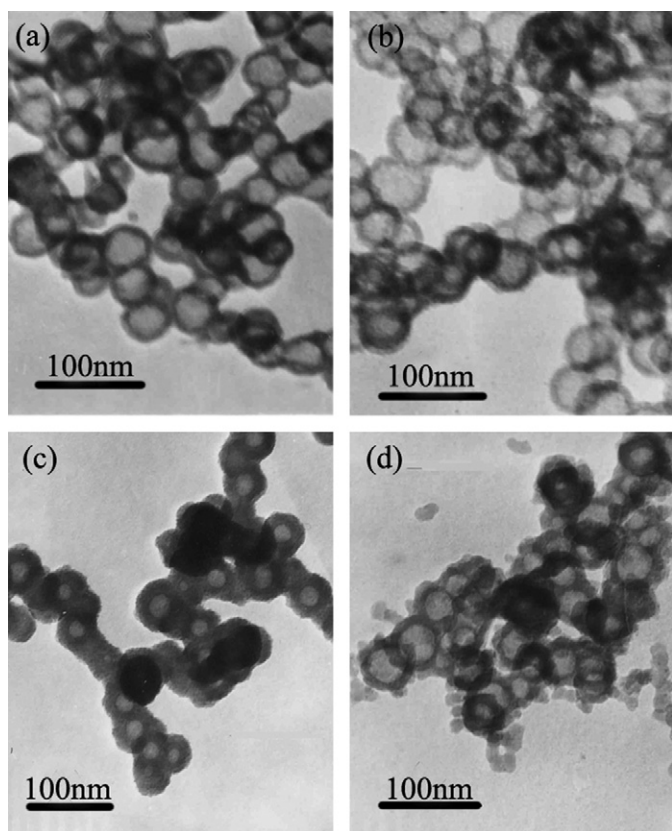


Fig. 4. TEM images of silica hollow spheres: (a) sample no. 8, (b) sample no. 2, (c) sample no. 9 and (d) sample no. 10.

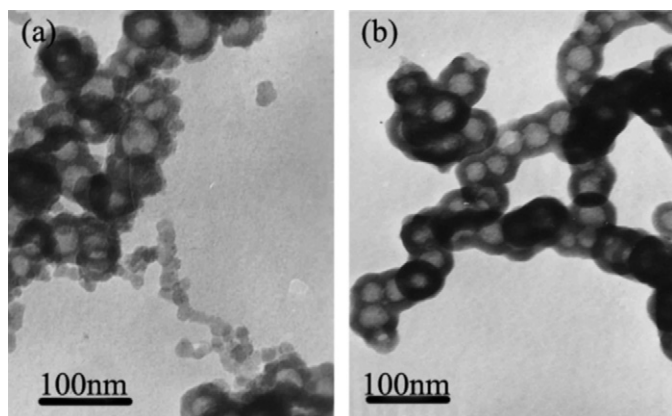


Fig. 5. TEM images of silica hollow spheres obtained with different sequences of adding TEOS: (a) added all in once and (b) added at twice. The usage of TEOS was 0.4 mL. The amount of H₂O and ammonia was 2.5 and 0.5 mL, respectively.

3.8. Porosity and pore size

Nitrogen sorption isotherms were applied to investigate the porosity and specific surface area of the as-synthesized hollow spheres. To identify this structure, a control sample was prepared by calcinating the obtained silica hollow spheres in atmosphere under 700 °C for 1 h to compare with the original sample in BET analysis. Fig. 8 gave two sorption isotherms of both original nano-sized silica hollow spheres and the control sample. Under relative low pressure ($P/P^0 < 0.6$), the slope of the curves was very small, which indicated the existence of micropores while composing the shell of silica hollow spheres. When the relative pressure was increased to more than 0.6, the slope of the curves increased

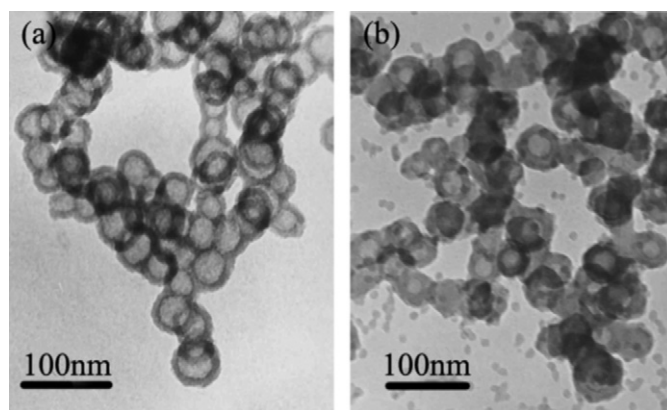


Fig. 6. TEM images of silica hollow spheres obtained with two ways of adding ammonia into the reaction system: (a) added 0.1 mL first, then 0.4 mL 2 h later and (b) added 0.5 mL all in once. The amount of H₂O and TEOS was 5 and 0.2 mL, respectively.

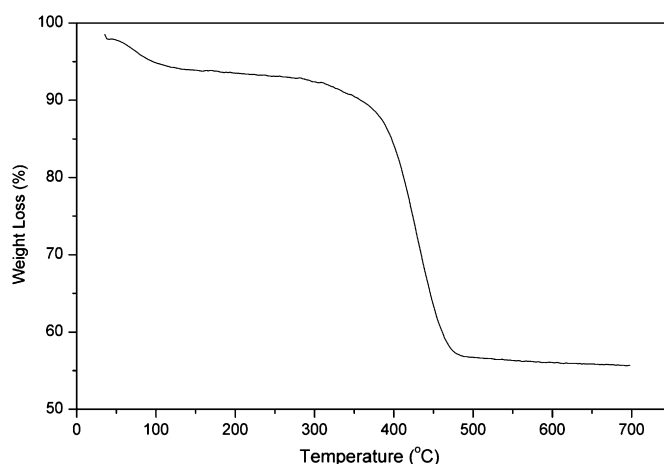


Fig. 7. TGA curve of as-synthesized nano-sized silica hollow sphere.

sharply. Also, hysteresis loops can be observed in the curves of all the samples, which was the evidence of the existence of mesoporous structure. The pore size distributions of the obtained hollow silica spheres were measured by the nitrogen sorption method and calculated by BJH method from the desorption curves. It can be seen that the pore size of the two samples was mainly in range of 2–25 nm, but it also showed that the distribution seemed much narrower than micro-sized hollow spheres synthesized with similar method [29], and the majority of pores were around 10 nm in size.

The surface areas and pore volumes of the nano-sized hollow silica spheres were listed in Table 2. After calcination, both properties of the control sample increased greatly, which also indicated that there was residual template that blocked the channels of micropores inside the hollow spheres. The large surface area showed that this kind of material had many potential applications in many fields.

3.9. Water retention of silica hollow spheres

Maniwa et al. [30] found that heat-treated SWNTs with an average diameter of 1.36 nm can adsorb water molecules onto the interior wall of the tube, where the adsorbed water exhibits liquid–solid phase transition at 235 K. This means water retention capability of nano-materials can be improved from its nano-sized effect.

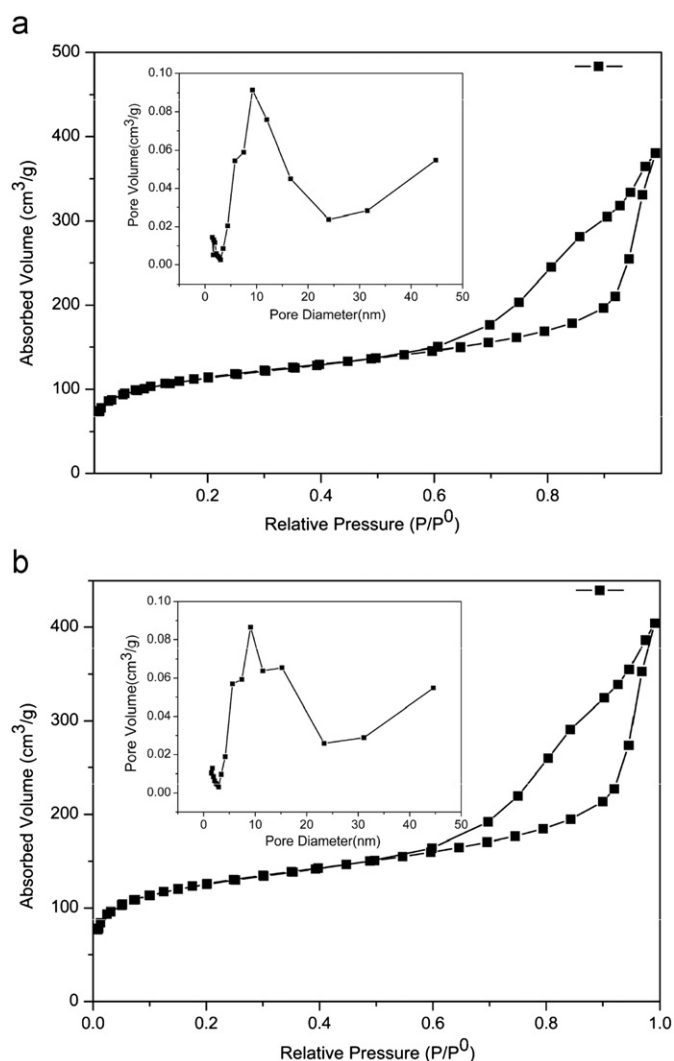


Fig. 8. Nitrogen sorption isotherms of (a) the original hollow sphere and (b) the control sample. The insets show the pore size distribution of the corresponding sample from desorption branch.

Table 2

Surface areas and micropore volumes of the original nano-sized hollow silica spheres and the control sample after calcination.

Sample	Brunauer–Emmett–Teller area (m ² /g)	Micropore volume (cm ³ /g)
Original hollow sphere	399.23	0.05
Control sample	439.22	0.07

We explored the water retention properties of the obtained nano-sized silica hollow spheres, Fig. 9 showed the TGA curve for the sample which experienced 24 h immersion in deionized water. We observed that an abrupt weight loss occurred from ca. 50 to 70 °C, then a relatively flat weight loss between 70 and 80 °C followed by a platform after 80 °C. The first part of weight loss should be from free water, so it evaporated so fast, while the second weight loss was conjectured as the water existing in the interior of nano-sized hollow spheres and/or adsorbed on the spheres through certain physical conjunction such as capillary effect. After 80 °C, all the water was evaporated completely. The nano-sized silica hollow spheres exhibited clearly inferior water retention capability in comparison to carbon nano-tubes.

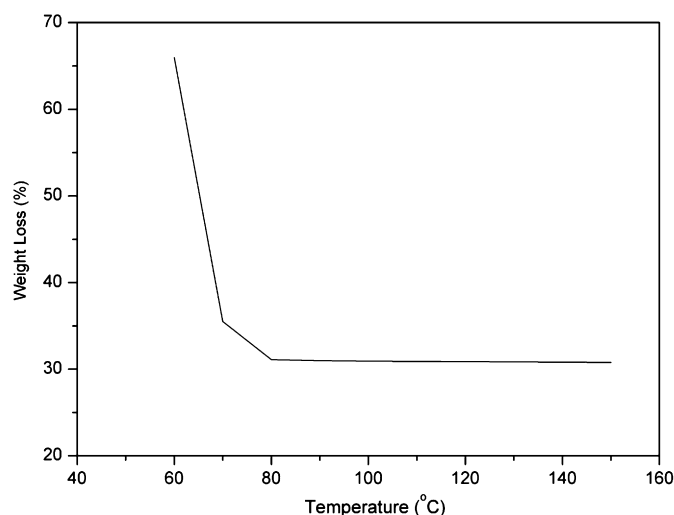


Fig. 9. TGA curve of silica hollow spheres after immersed in deionized water.

The plausible explanation for this behavior was the relatively large pore size compared with the size of sphere itself, water vapor was able to access inside and exit outside the spheres quite easily, which eventually resulted in inferior water retention of hollow nano-sized spheres.

4. Summary

In this study, the research focusing on the fabrication of nano-sized silica hollow spheres through a simultaneous ‘coating-etching’ procedure was presented. From the above discussion we can draw a conclusion that, the driving force of the coating process was the coupling effect of PVP rather than the electrostatic attraction as mentioned in previous studies. It was also found that not only the amount of H₂O, ammonia and TEOS, but also the procedure of adding them influenced the morphologies of the obtained silica hollow spheres. The key to success was adjusting the speed of hydrolysis and condensation of TEOS and ‘dissolution’ of PS templates to an appropriate ratio. For the special structure and particle size, the hollow spheres have a promising application in various fields, such as drug delivery and catalyst supporter. The material’s water retention property was not so good as we conceived. On the basis of this study, different kinds of nano-sized hollow spheres with inorganic shell could be prepared by this convenient method.

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