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MESOSTRUCTURED MATERIALS

A facile dual templating route to fabricate hierarchically mesostructured materials

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Abstract Hierarchically mesostructured materials have been successfully synthesized via a facile route using amphiphilic block copolymer polystyrene-*b*-poly (acrylic acid) (PS-*b*-PAA) and cetyl trimethyl ammonium bromide (CTAB) as dual templates. It is found that the dimension of spherical micelle-like aggregates of PS-*b*-PAA could be adjusted by changing the kind of solvents. With *N*,*N*-dimethylformamide (DMF) as solvent, spherical micelle-like aggregates with an average diameter of 35 nm were obtained, and bimodal mesoporous materials (BMM) possessing large pores of $\sim$35 nm and small pores of 2.5 nm could be prepared. As the solvent was changed to *N*,*N*-dimethylformamide (DMF)/tetrahydrofuran (THF) (v/v = 1:1), the average diameter of the spherical micelle-like aggregates of PS-*b*-PAA was increased to 200 nm, and hollow mesoporous spheres (HMS) with 200-nm hollow cores and 25-nm shells were thus achieved.

Introduction

Recently, hierarchically (macro–micro [1], macro–meso [2], meso–micro [3], and meso–meso [4]) porous materials have attracted significant attention owing to their important role in the systematic study of structure–property relationship and their technological promise in applications [5]. Furthermore, well-defined multimodal mesopore systems are needed for the elucidation of fundamental aspects of sorption theory such as diffusion and hysteresis. Therefore, such materials, especially for hierarchically mesoporous materials which possess adjustable and well-defined macropores and tunable, interconnected mesopore types of different size (between 2 and 50 nm in size) in the macropore walls have been synthesized by using two or three templates [4, 6]. The macroporosity could be easily introduced by using colloidal particles and the mesopores were obtained from surfactants templating. However, such mixing templates strategy did not necessarily result in the desired bimodal mesopores, because the co-template could just lead to a mono-modal pore system. Thus, selection of suitable template materials to prepare hierarchically mesostructured materials still remains a challenge.

Amphiphilic block copolymer is a very important class of polymeric surfactants. For example, polystyrene-*b*-poly (acrylic acid) (PS-*b*-PAA) consists of hydrophilic acrylic acid, and hydrophobic styrene is a useful template for porous materials. It has been demonstrated previously that PS-*b*-PAA with very short PAA blocks in solution can form stable aggregates of various morphologies, i.e., spheres, cylinders, vesicles, and large compound micelles (LCMs) consisting of a spherical assembly of reverse micelles [7]. These micelle-like aggregates can be used as templates for the preparation of organic–inorganic hybrid microparticles [8, 9]. But to the best of our knowledge, it has not been reported that hierarchically mesostructured materials can be synthesized by using PS-*b*-PAA micelle-like aggregates/surfactant system.

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In this article, we report a facile route for synthesizing bimodal mesostructured materials with small pores of 2.5 nm and large pores of ~35 nm, respectively, or hollow mesoporous spheres with the average sphere diameter of 250 nm by using spherical aggregates of PS-*b*-PAA with different sizes and cetyl trimethyl ammonium bromide (CTAB) as co-templates. Here, PS-*b*-PAA micelle-like aggregates were used as the large mesopore template or hollow template, CTAB was used templating the small mesopore structure, and TEOS was used as the silica source.

Experimental

Synthesis of polystyrene$_{100}$-*b*-poly (acrylic acid)$_{16}$

Amphiphilic block copolymer, polystyrene$_{100}$-block-poly (acrylic acid)$_{16}$ (PS$_{100}$-*b*-PAA$_{16}$, the numbers in the subscripts indicate the number of repeat units in the blocks) was synthesized via sequential atomic transfer radical polymerization (ATRP) as previously reported [10].

Synthesis of PS-*b*-PAA spherical aggregates

In a typical synthesis, 50 mg of PS$_{100}$-*b*-PAA$_{16}$ powder was diluted in 10 mL of organic solvent (DMF, DMF/THF (v/v = 1:1) or THF), followed by the addition of 40 mL of H_2O to induce the formation of spherical micelle-like aggregates. Then, the resulting suspension was subjected to the dialysis against pure water to remove the organic solvents, and spherical micelle-like aggregates of PS-*b*-PAA were obtained.

Preparation of bimodal mesostructured materials

In order to prepare bimodal mesostructured materials, 30 mL of ethanol and 5 mL of ammonia aqueous solution (28 wt%) were first added into the polymeric aggregates solution prepared by using DMF as solvent, and then a 3 mL ethanol solution containing 0.1 g of CTAB was slowly added.

The mixed solution was homogenized for 30 min, and then 0.3 g of TEOS was added dropwise to the solution with continuous stirring. After stirring for 24 h, the solid product was recovered by filtration and dried at 100 °C. The as-synthesized product was then calcined in air at 550 °C for 6 h to remove the copolymer and CTAB templates.

Preparation of hollow mesoporous spheres

Firstly, the pH value of the polymeric aggregates solution prepared by using DMF/THF (v/v = 1:1) as solvent was adjusted to around 10 with a diluted NaOH solution (0.1 M) and 0.1 g of 3-aminopropyltrimethoxysilane (APTMS, p*K*a = 10.6) was added dropwise to the solution with vigorous stirring. After stirring for 12 h, the obtained solution was subjected to centrifugation (6000 rpm/min, 10 min) and washed with de-ionized water and ethanol three times.

After above purification, the resulting solution was diluted with 30 mL of ethanol and 60 mL of water, 3 mL of concentrated ammonia aqueous solution (28 wt%), followed by the addition of 0.1 g of CTAB to form a uniform dispersion. After stirring for 0.5 h, 0.30 g of TEOS was slowly added to the dispersion with continuous stirring. After reaction for 24 h, the solid product was recovered by filtration and dried at 100 °C. The as-synthesized product was then calcined in air at 550 °C for 6 h to remove the templates.

Characterization

The powder XRD patterns were recorded on Rigaku D/MAX-2550 V at 40 kV and 40 mA (Cu$K\alpha$ radiation). FE-SEM image was obtained on JSM-6700F field emission scanning electron microscope at 10.0 kV. TEM was performed using a JEOL 200CX electron microscope operated at 200 kV. N_2 adsorption–desorption isotherms were obtained on Micromeritics Tristar 3000 at 77 K under a continuous adsorption condition. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}) using adsorption data in a relative pressure range from 0.05 to 0.35. By using the Barrett–Joyner–Halenda (BJH) model, the pore volumes and pore size distributions were derived from the desorption branches of isotherms, and the total pore volumes (V_t) were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.99.

Results and discussion

PS-*b*-PAA spherical aggregates

Prior to our study, Eisenberg et al. [11–13] have reported that the morphologies of PS-*b*-PAA crew-cut aggregates were mainly controlled by a force balance involving three factors, i.e., the stretching of the PS blocks in the core, the repulsive interaction among the corona chains, and the surface tension at the core–corona interface at the onset of micellization. Various morphologies such as spherical aggregates, rods, vesicles, and large compound micelles (LCMs) of PS-*b*-PAA diblock copolymer could be created by changing kinds of solvent, the addition of various ions, etc.

In this study, DMF, THF, and a mixture of DMF/THF (v/v = 1:1) were used as solvents, respectively, for the preparation of polymeric aggregates. Figure 1a, b and c show the TEM images of spherical aggregates formed in different solvent systems. As can be seen, PS_{100}-*b*-PAA_{16} yields spherical aggregates in all the three solvents. With DMF as solvent, the average size of the spherical aggregates was calculated to be 35 ± 2 nm based on statistical calculation of 300 micelles. With increasing THF content in the solvent, the average diameter of the aggregates increased progressively, 200 ± 5 nm for DMF/THF (v/v = 1:1) (Fig. 1b, e) and 100 nm–1.6 μm for THF (Fig. 1c, f), respectively. From the size distribution histograms shown in Fig. 1d–f, it can be seen that the polydispersity of the samples increases with the increasing of THF content. The increase of sizes and polydispersity of spherical aggregates may be explained that: the higher degree of swelling of the homo-PS in THF than in DMF reflects their solubility parameter values; the solubility parameter (δ) of THF is closer to that of homo-PS than that of DMF ($\delta_{\mathrm{THF}} = 20.5$; $\delta_{\mathrm{DMF}} = 24.8$; and $\delta_{\text{homo-PS}} = 16.6$–$20.2$). Interestingly, no other morphologies such as rods and vesicles were found when mixing the DMF and THF. The reason for this may be attributed to the lower PAA content of PS_{100}-*b*-PAA_{16} [14].

Obviously, the size of the spherical aggregates changes progressively according to the composition of the common solvent. The above results suggest a general way to prepare aggregates with various sizes by changing the kind of solvent.

Hierarchically mesostructured materials

As described above, the self-assembly of diblock copolymer PS_{100}-*b*-PAA_{16} can form different sizes of spherical aggregates by changing the kind of solvents. By choosing the spherical aggregates with diameter of 35 ± 2 nm or 200 ± 5 nm as large mesopores' templates or hollow cores' templates, respectively, bimodal mesoporous materials (BMM) or hollow mesoporous spheres (HMS) were prepared in the presence of CTAB as small mesopores' templates.

Figure 2 illustrates the low angle X-ray diffraction (XRD) patterns of the calcined BMM and HMS. It is found that only one wide peak was presented for each sample, suggesting that they are poorly ordered, or most probably,

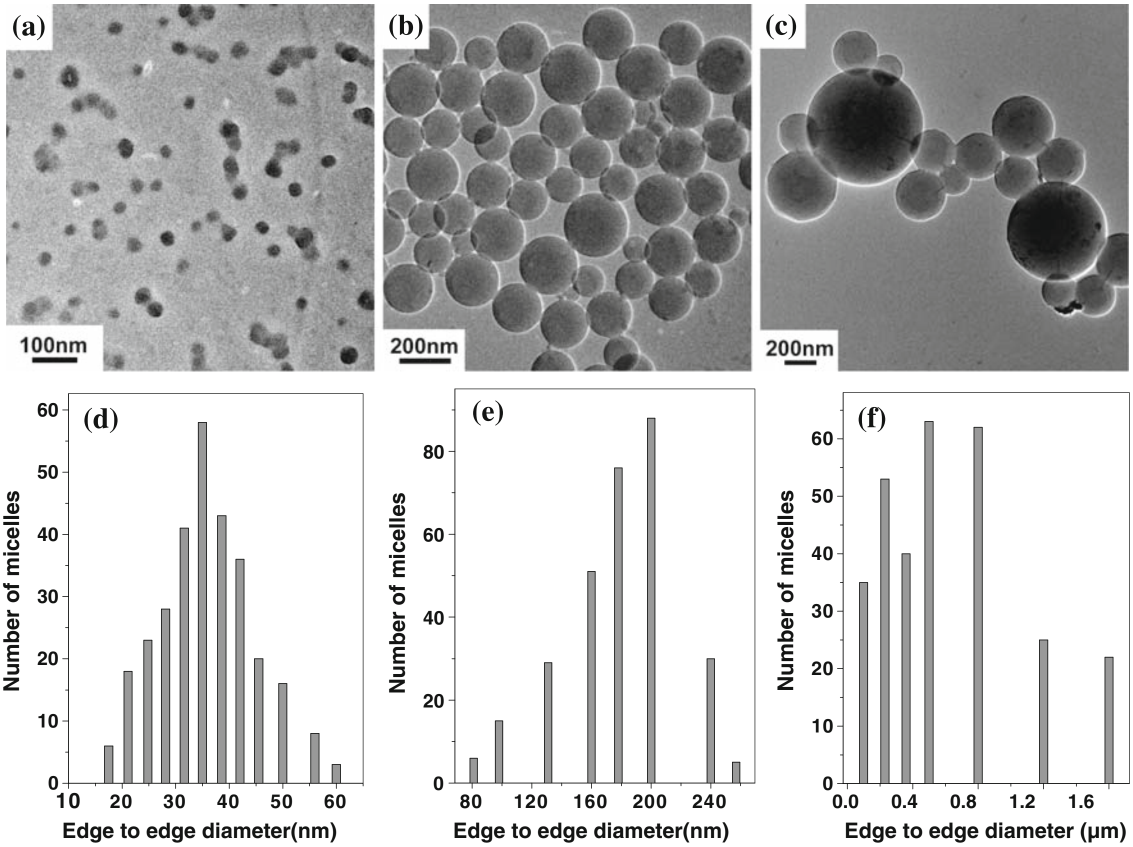


Fig. 1 TEM images (**a**, **b**, **c**) and size distribution histograms (**d**, **e**, **f**) of spherical aggregates in water made from PS_{100}-*b*-PAA_{16} diblock copolymer by using DMF, DMF/THF (v/v = 1:1), and THF as solvent, respectively

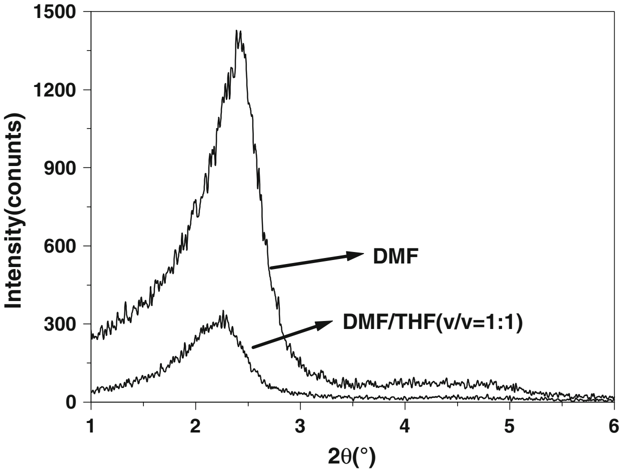
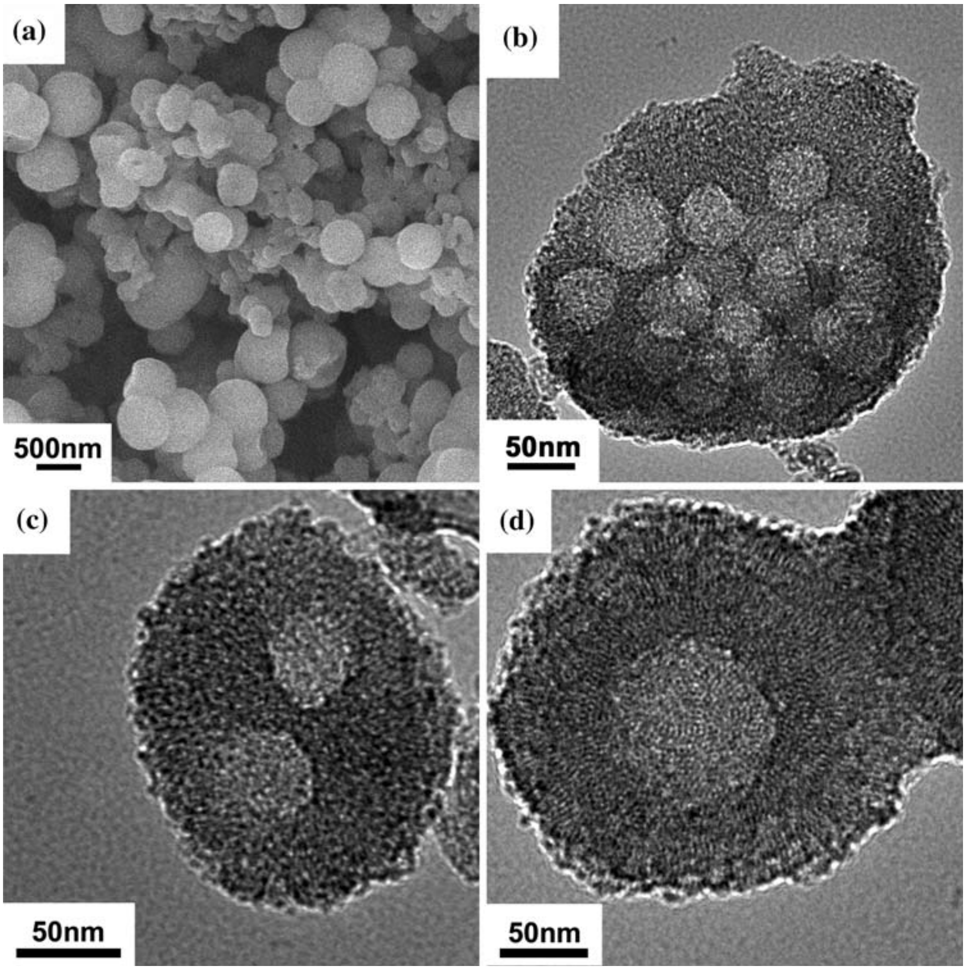


Fig. 2 The low angle XRD patterns of the calcined bimodal mesostructured materials and hollow mesoporous spheres, respectively

that ordered domains are quite small. The intensity difference between the samples is probably due to the quantity of ordered domains that are probed, which is related to being in the Bragg conditions.

FE-SEM and TEM images of the calcined BMM are shown in Fig. 3. In Fig. 3a, it is clearly observed that BMM is mainly in spherical-shaped particles with the diameter ranging from 200 to 600 nm. Interestingly, different quantities of voids were found in BMM after the removal of copolymer and CTAB, as shown in Fig. 3b–d. In the relative large particles (~300 nm, Fig. 3b), tens of voids with the diameter of 35 nm were observed. In the smaller particles (150–200 nm), only one or two voids were found. Besides, mesopores with diameter of 2.5 nm are present in all the particles. These demonstrate that bimodal mesoporous materials have been fabricated by using PS_{100}-*b*-PAA_{16} and CTAB as dual templates. To the best of our knowledge, there is no report that pores as large as 35 nm could be created by CTAB. It is thus believed that bimodal mesopores were resulted from the dual templates, PS_{100}-*b*-PAA_{16} and CTAB. In addition, the mesopore channels in Fig. 3d are found to perpendicular to the particles surface, which is favorable for the access of guest molecules. As for the broad distribution of particle sizes, it is probably dependent of the dispersion of polymer aggregates in the solution. It is well known that the copolymer micellar

Fig. 3 FE-SEM (**a**) and TEM images (**b**, **c**, **d**) of the calcined bimodal mesostructured materials



aggregates are not stable with silica precursor diffusing into the corona, leading to the formation of second-order or higher-order aggregates in which two or more particles are bound to each other. In the present study, the ionic PAA blocks of PS-*b*-PAA were easy to agglomerate in the presence of cationic surfactant (CTAB) by electrostatic interaction, resulting in conglomerations of two or more spherical aggregates and formation of different quantities voids after removal of the polymer template.

The N_2 adsorption–desorption isotherms and corresponding pore diameter distribution curve of the calcined bimodal mesostructured materials were shown in Fig. 4. A narrow pore size distribution with a mean value of 2.5 nm and a broad pore distribution located at $\sim$35 nm were present, which further confirmed the bimodal mesostructure of BMM. Form the N_2 adsorption–desorption isotherms (inset of Fig. 4), it can be seen that two obvious capillary condensation steps ($0.2 < P/P_0 < 0.4, 0.80 < P/P_0 < 0.95$) in the isotherms, associated with the small pores of 2.5 nm and large pores of 35 nm, respectively. The specific surface area and pore volume were calculated to be 889 m^2/g and 0.99 cm^3/g, respectively.

Figure 5 shows the TEM images of the calcined HMS. It is clearly observed that HMS presents a hollow particle structure with mesopores in the shell. The average diameter of the spheres and the thickness of the shells are about 250 and 25 nm, respectively. Besides, disordered mesopores are exhibited on the shell, as shown in Fig. 5b. The N_2 adsorption–desorption isotherms for the calcined HMS are shown in Fig. 6. The type IV isotherms with a well-defined step between 0.2 and 0.3 of P/P_0 indicate that HMS possesses mesoporous structure. Also, a narrow pore size distribution centered at 2.6 nm was shown in the inset of Fig. 6. The specific surface area of 563 m^2/g and pore volume of 0.5 cm^3/g was obtained for HMS using the BET and BJH methods, respectively. These demonstrate that

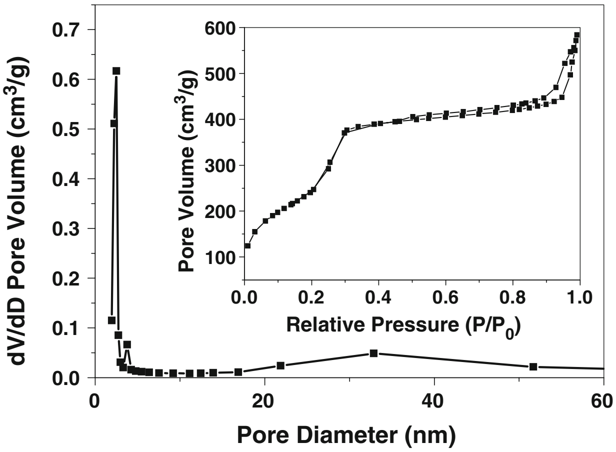


Fig. 4 The pore diameter distribution of the calcined bimodal mesostructured materials (inset for N_2 adsorption–desorption isotherms)

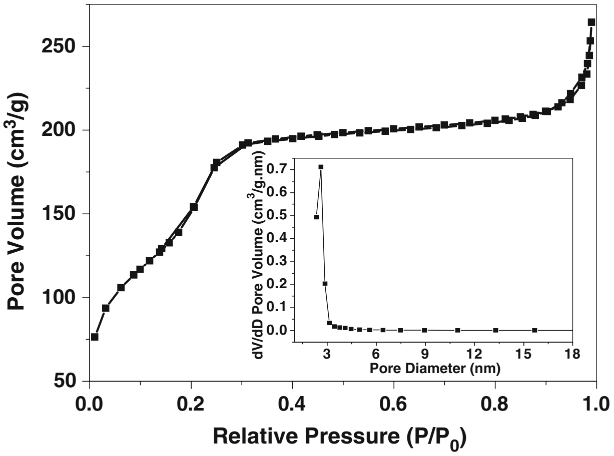
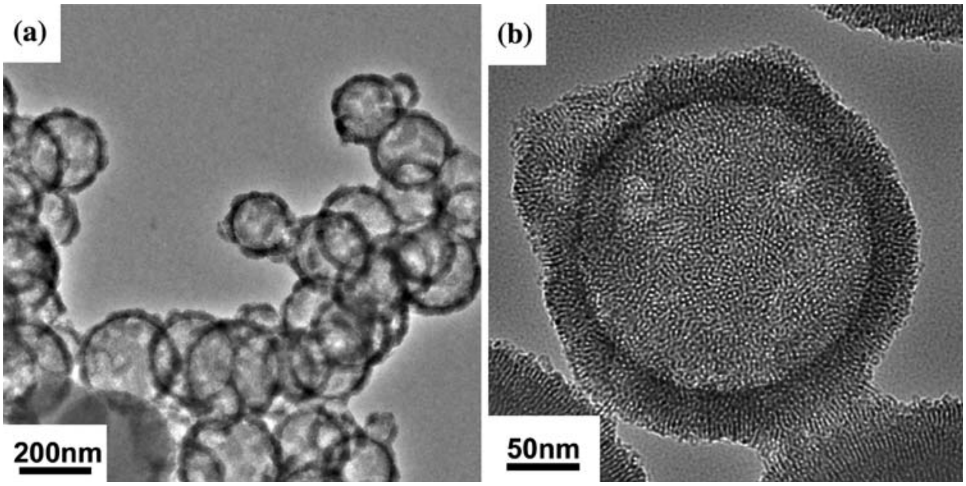


Fig. 6 N_2 adsorption–desorption isotherms of the calcined HMS and inset for the pore diameter distribution

Fig. 5 TEM image (**a**) and HRTEM (**b**) of the calcined hollow mesoporous spheres



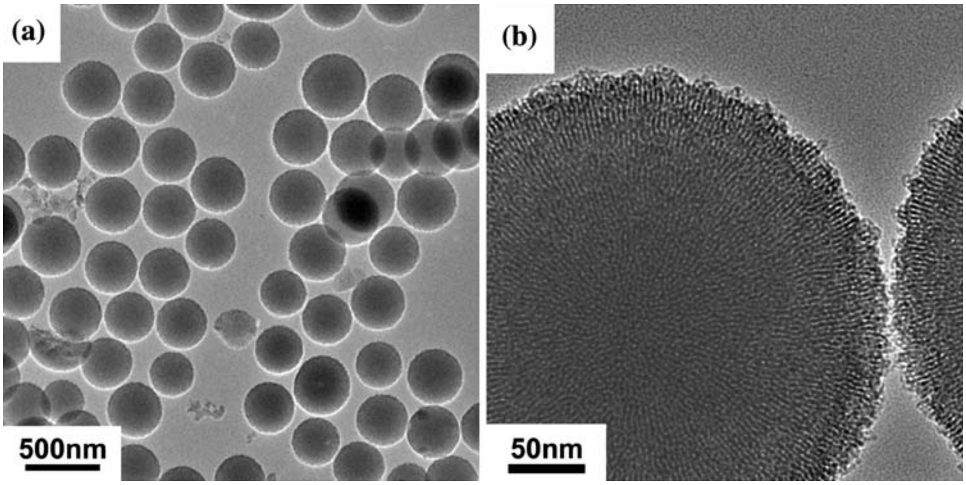


Fig. 7 TEM (**a**) and HR-TEM (**b**) images of solid mesoporous spheres prepared without adding APTMS

morphologies of the hierarchically mesostructured materials could be controlled from bimodal mesoporous materials with ordered mesostructure to hollow spheres with disordered mesopores in the shell by altering the composition of the solvent.

It is found that 3-aminopropyltrimethoxysilane (APTMS) plays a key role on the formation of hollow structure of HMS. APTMS is a common silane coupling agent (APTMS, p$Ka = 10.6$) with quaternized amino-group. During the process of reaction, APTMS molecules can serve as the stabilizing agent for micelle-like aggregates in the aqueous phase. Its positively charged ammonium parts preferred to interact electrostatically with the negatively charged head groups (PAA^-) of the anionic block copolymer [15], which would strengthen the aggregates structure due to the introduction of silicon species. Consequently, the APTMS-coated aggregates can serve as the effective hollow template for the formation of the hollow spheres. In the following process, assembly between CTAB and TEOS around the aggregates would directly result in the formation of hollow mesoporous spheres. In order to further confirm the inference, the synthesis was repeated without using APTMS. As expected, only solid mesoporous silica spheres were prepared, as shown in Fig. 7.

Conclusion

In summary, bimodal mesoporous materials and hollow mesoporous spheres have been successfully synthesized in a facile route using different sizes of PS-*b*-PAA micelle-like aggregates and CTAB as co-templates. The size of PS-*b*-PAA micelle-like aggregates could be easily adjusted by changing the kinds of solvent. With smaller sized PS-*b*-PAA micelle-like aggregates (35 nm), bimodal mesoporous materials possessing large pores of ~35 nm and small pores of 2.5 nm were prepared. As the size of PS-*b*-PAA micelle-like aggregates was changed to 200 nm, hollow mesoporous spheres with 200-nm hollow cores and 25-nm shells were obtained. Such kinds of materials have a well-fined pore structure, large BET surface area and could be good candidates for application in sorption, catalysis, etc.

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