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One-step synthesis of hollow periodic mesoporous organosilica spheres with radially oriented mesochannels

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A simple and effective one-step method is proposed for the fabrication of hollow periodic mesoporous organosilica spheres (HPMOSs). The obtained HPMOSs possess well-defined spherical morphology, uniform and tunable particle size, adjustable hollow void structure, and radially oriented mesochannels in their shells.

Hollow structured mesoporous silica spheres (HMSS), owing to their outstanding features of low density, large void space, mesoporous channels in shells, and large specific surface area, have gained more and more attentions and been applied in various fields, such as catalysis,[1] adsorption and separation,[2] controlled drug release,[3] diagnosis and therapy of cancers,[4] and so on.[5] However, the inert inorganic -Si-O-Si- framework of HMSS limited their applications,[6,7] but this can be broken through by integrating organic functional groups in HMSS, as this integration will provide the possibility to combine the enormous functional variations of organic chemistry with original advantages of HMSS, such as unique hollow nanostructure, high thermal stability and robust inorganic substrate.[8-10] The symbiosis of organic and inorganic components can lead to new properties different from those of their individual, isolated components,[9,11] and create a new kind of materials which has more wider applications in biomedicine and catalysis.

Periodic mesoporous organosilicas (PMOs) are the most representative organic–inorganic hybrid porous materials which are synthesized by the method through hydrolysis and condensation reactions of bissilylated organic precursors ((R′O)$_3$Si-R-Si(OR′)$_3$), a type of bridged organosilica precursors.[12] Compared with other methods, such as post-synthetic or co-condensation, the organic bridges in this method are incorporated in the silica network through two Si-C covalent bonds.[8] So this method can significantly change the intrinsic framework nature of HMSS and results in organic units

being completely and homogeneously distributed over the whole framework at the molecular level.[13] Among various PMOs, hollow PMO spheres (HPMOSs) have attracted great interests in the past few decades, due to their unique nanoscale hollow structure and spherical morphology.[14,15] Several template assisted methods have been developed for the synthesis of HPMOSs.[15] The first HPMOS with the particle size of 200–800 nm reported by Lu and co-workers was synthesized by a vesicle and a liquid crystal "dual templating" approach.[15-17] Yang and co-workers synthesized HPMOSs with the particle size less than 100 nm via the single surfactant micelles method based on F127-NaH$_2$PO$_4$-Na$_2$HPO$_4$ and F127-TMB-HCl systems.[18,19] Shi and co-workers synthesized HPMOSs with the average particle size of 450 nm though etching silica hard template with various bissilylated organic precursors.[20,21] Lu and co-workers synthesized monodisperse multi-shelled HPMOSs with the average particle size of 300-550 nm by "multi-interface transformation" approach.[22]

Although great efforts have been made in the preparation of HPMOSs, to the best of our knowledge, there is no report about synthesizing HPMOSs with particle size about 100 nm and radially oriented mesochannels in their shells. It is still a great challenge to synthesize HPMOSs by a simple one-step method. Here, we report a novel one-step method to synthesize nanometer sized HPMOSs with radially oriented mesochannels in shells. The method is based on O/W microemulsion system, but in particular, it doesn't need to add another oil as an oil phase, just utilizing organic silicon source (1,2-Bis(triethoxysilyl) ethane, BTSE) itself as an oil phase, meanwhile by using it as sphere template to form hollow void. A microemulsion is a thermodynamic equilibrium system, so it can offer advantage in giving uniform nanometer sized hollow spheres because the small microemulsion droplets are thermodynamically stable. A limited number of studies on the fabrication of hollow silica spheres (HSNs) by microemulsion method have been reported,[23-25] however, to the best of our knowledge, there is no report on preparing HPMOSs utilizing O/W microemulsion. The method used here utilizes hydrolysis and condensation reactions of BTSE to build sphere shells, meanwhile utilizes the templating effect of cetyltrimethyl ammonium bromide (CTAB) to form ordered mesoporous structure in their shells, and simultaneously utilizes continuous reaction

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consuming organic silicon source to leave inner hollow void structures. The method just has one turning step, doesn't need any post-treatment procedures to remove core template and only needs 1h to form HPMOSs at room temperature. So it is very simple, effective and easy to be scaled up. The obtained HPMOSs combine multiple advantages of well-defined nanoscale hollow structure, radially oriented mesochannels in shells, functionalized organic units, well spherical morphology and uniform particle size. Furthermore, the particle size, the hollow void size and the thickness of mesoporous shells can be controlled by modulating the synthetic composition.

The strategy for the preparation of nanometer sized HPMOSs with radially oriented mesochannels in shells is shown in Scheme 1. Firstly, when BTSE was added into an aqueous solution, with the aid of surfactant (CTAB) and cosurfactant (ethanol), the oil (BTSE) droplets dispersed in water forming an O/W microemulsion system. After that, the BTSE molecules of the oil droplets hydrolyzed and condensed around the oil-water interface under the catalysis of ammonium, within this forming process, the oil droplets turning to the thin PMO spheroidal shells. Meanwhile, the ordered mesochannels were formed in the shells by mesoporous template effect of CTAB. Furthermore, the inward and outward interfacial reaction proceeded simultaneously. As the reaction time prolonged, the BTSE molecules on the interface were consumed continuously, and the BTSE molecules in the center of the droplet diffused continuously to the interface, at last, leaving behind hollow cores. It is worth to note that BTSE, CTAB and ethanol all probably played multiple roles in this process. First, BTSE droplet served as an oil phase to form O/W microemulsion system, as an organic silicon source to form PMO framework and as sphere template to form hollow void structure; In addition, for CTAB, it not only acted as a surfactant but also as a mesoporous template directing of the ordered mesoporous structure; What's more, ethanol in the solution was used as a cosolvent increasing the amount of BTSE dissolved in water, meanwhile, as a cosurfactant stabilizing the microemulsion.
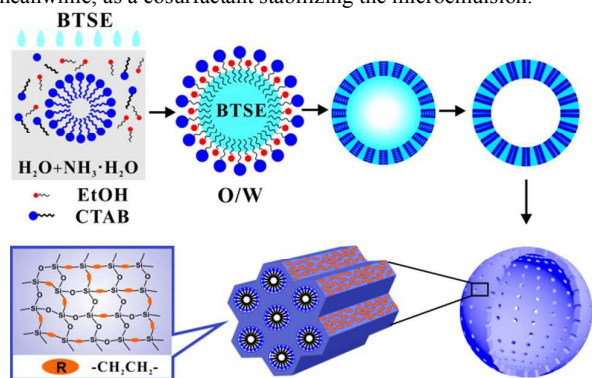
Scheme 1 Preparation strategy of nanometer sized HPMOSs with radially oriented mesochannels in shells by using a facile one-step method.

A representative SEM image of the sample HPMOS-1 indicates that the HPMOS-1 possesses a well-defined spherical morphology and it is very uniform both in size and shape (Fig. 1a). The average diameter of HPMOS-1 calculated from SEM is 100 nm. The hollow structure of the sample is confirmed by a noticeable contrast between the core and the shell (Fig. 1b and c). The average hollow void size

is 20 nm and the mean shell thickness is 40 nm. High-magnification TEM images show that HPMOSs are well-dispersed (Fig. 1b) and shells have highly ordered mesochannels which radially aligned in shells (Fig. 1c, f, S1, ESI†). The radially oriented mesochannels can offer high surface area (S_{BET}=1333 m^{2}g^{-1}) and diffusion pathways for guest molecules, and also can provide large accessible pore volume (V_{total}=1.15 cm^{3}g^{-1}) for the adsorption and encapsulation of functional groups. Especially, owing to their unique radial orientation, the mesochannels of shells are readily accessible, favoring the adsorption and release of guest molecules. The SEM and TEM results clearly indicate the coexistence of the hollow structure and radially aligned mesoporous in the one HPMOS, which confirm the proposed mechanism in the above-mentioned scheme that CTAB plays two roles at the same time. In addition, it is worth to note that the yield of the HPMO-1 is measured to be 72.1%, indicating most of BTSE molecules transformed into organosilica.
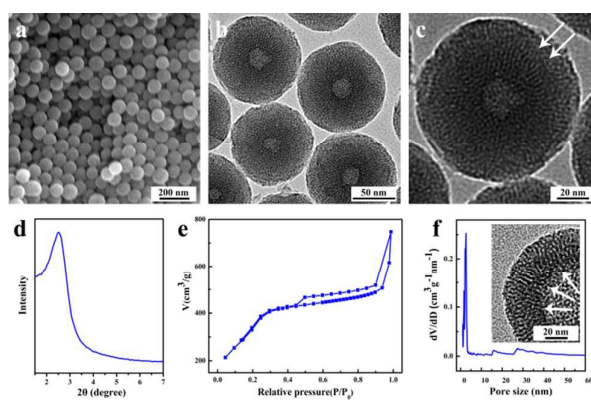

Fig. 1 Characterization of HPMOS-1, (a) SEM image; (b), (c) TEM images; (d) XRD pattern; (e) Nitrogen adsorption-desorption isotherm; (f) NLDFT pore diameter distribution curve from adsorption branch.

The low-angle XRD pattern of HPMOS-1 shows one strong peak in the 2θ of 2.5°, further confirms the ordered mesostructured in shells (Fig 1d). Moreover, it is worth to note that the mesoporous and hollow structure is quite stable. Even after being calcined at 550 °C for 5 h or treated under 40-kHz ultrasound for 1 h, there is no apparent change in XRD patterns and no broken spheres are found in SEM images. Further evidence of the mesoporous structure of HPMOS-1 could be obtained by N$_2$ sorption analysis. Nitrogen adsorption-desorption isotherm of the HPMOS-1 shown in Fig. 1e exhibits a typical type IV isotherm with a type H4 hysteresis loop, revealing characteristic of mesoporous material with narrow pore size distribution. The detailed NLDFT pore size distribution shown in Fig. 1f indicates that there are three peaks in the pore size distribution. The first one corresponds to the mesoporous in shells with the average pore size of 2.6 nm. The narrow pore size distribution of this peak further indicates the well-defined mesoporous structure. The last two peaks are ascribed to the hollow voids of HPMOS-1 with the average pore sizes of 17 and 25 nm, respectively. This further proves the coexistence of the hollow structure and mesoporous structure in the HPMOS-1.

The compositional information of the HPMOS-1 was characterized by FT-IR spectroscopy (Fourier transform infrared

spectroscopy). The FT-IR spectrum shows absorbance peaks at 694, 766, 1107 and 1271 cm^{-1}, which can be assigned to the Si-C stretching vibrations (Fig. 2a).[18, 26, 27] In contrast, these vibration bands are not present in the FT-IR spectrum of pure HMSS (Fig. S2, ESI†), demonstrating that organic groups are incorporated into the HPMOSs framework. The absorbance peak at 1030 cm^{-1} is assigned to the TO (transverse-optical) mode of Si-O-Si asymmetric stretching vibration band. Compared with the spectrum of HMSS (Fig. S2, ESI†), this band of HPMOS-1exhibits a distinct red shift from 1074 to 1030 cm^{-1}, which indicates the higher degree of condensation of HPMOS-1.[28] The compositional information of HPMOS-1 was further characterized by ^{29}Si MAS NMR. The ^{29}Si NMR spectrum (Fig. 2b) exhibits clear signals of T sites. The signals at –56.5 and –58.7 ppm can be assigned to incompletely hydrolyzed and condensed silicon species of ^{0}T (^{0}Tn = RSi(OH)$_{3-n}$(OEt)$_{n}$, n = 0,1, 2 and 3) and ^{1}T (^{1}Tn = RSi(OH)$_{2-n}$(OEt)$_{n}$(OSi), n = 0,1 and 2), respectively. The signals at –63.0 and–65.5 ppm are correspond to silicon resonances of ^{2}T and ^{3}T units (^{n}T = RSi(OH)$_{3-n}$ (OSi)$_{n}$, n = 2 and 3), respectively.[29] The observation of these T sites in the spectrum indicates the formation of silsesquioxane framework, and further demonstrates that organic units are incorporated in the silica network by Si-C covalent bonds.
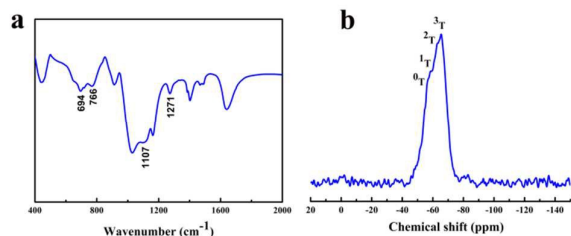

Fig. 2 (a) FTIR spectrum and (b) ^{29}Si MAS NMR spectrum of HPMOS-1.

The dynamic light scattering (DLS) measurements were further performed to confirm the size and the dispersity of the sample (Fig. S3, ESI†). The average hydrated-particulate size of HPMOS-1 is 100 nm, which is consistent with the SEM and TEM observations. And clear visible Tyndall phenomenon was observed in the aqueous solution of the HPMOS-1 (Fig. S4, ESI†), indicating that the HPMOSs are well dispersed in the aqueous solution without obvious aggregation. To further explore a possible mechanism of the formation of HPMOSs, we designed a separate experiment to analyze the size distribution of droplets of unreacted microemulsion (Fig. S3, ESI†). And we also observed the DLS particle size distributions of the reaction solution reacted at different reaction times. The results show that the average particle size of HPMOS-1 is larger than that of droplets of unreacted microemulsion, and interestingly, the hollow void size is smaller than it (Fig. 1b, c). Furthermore, the average particle size of the HPMOS-1 gradually increased with the reaction time was increased from 3 to 10 minutes, and there was no obvious change by further increasing reaction time 10 minutes later. These results indicate that the hollow spheres grow continuously around the oil/water interface, and further verify our hypothesis that the inward and outward interfacial reaction proceeded simultaneously.

In principle, the droplet size in the microemulsion system can be controlled by tuning the cosurfactant composition or solution conditions.[30, 31] Here, we found that the particle size, the hollow void size and the shell thickness of HPMOSs can be controlled by tuning the volume ratio of ethanol and H$_2$O (V$_{EtOH/water}$). As shown in Fig. 3, the particle size and the shell thickness decreased with the decrease of V$_{EtOH/water}$ (Fig. 3, S5, S6 and S7, ESI†). In addition, the sample synthesized with V$_{EtOH/water}$ of 0.3 (HPMOS-2) has the largest hollow void size of 36 nm. This may be because when the V$_{EtOH/water}$ was decreased, the curvature of oil droplets was changed resulting in the decrease of oil droplet size (Fig. S8, ESI†). Meanwhile, when the content of water was increased on the surface of the droplet, as the hydrolysis and condensation reaction, more BTSE molecules would be consumed which made more BTSE molecules diffusing from the center of the droplet outward to the reaction inferface, and finally lead to the increase of the hollow void size. Interestingly, if very small amount of octane was added into the reaction system (0.02 ml), it didn't break the balance of the microemulsion system, the obtained HPMOS-4 kept the uniform particle size (Fig. S5d, ESI†). And more importantly, compared with HPMOS-1, the HPMOS-4 has larger hollow void size and smaller particle size (Fig. 3d). However, if the volume of octane is greater than that of BTSE (0.2 ml), although the obtained HPMOS-5 also has well-defined spherical morphology, large hollow void size and ordered mesochannels, it doesn't have uniform particle size (Fig. S9, ESI†). This is probably due to overmuch octane will break the balance of the microemulsion system. As a result, the reaction system changed from thermodynamically stable microemulsion system to unstable emulsion system.
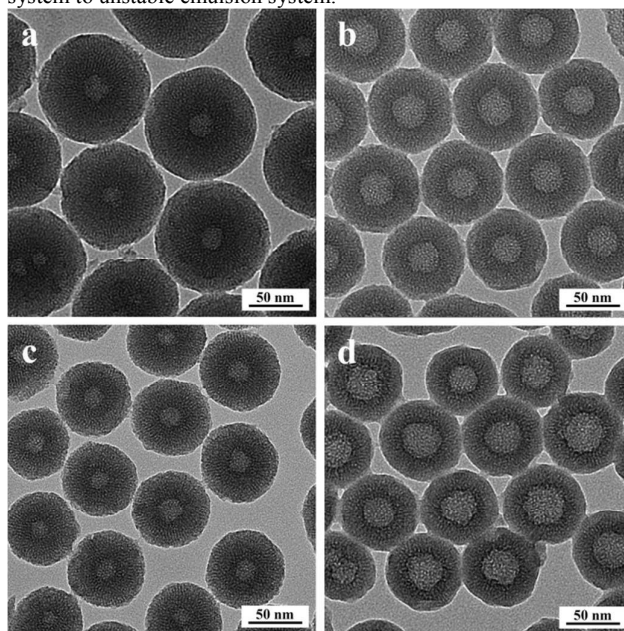

Fig. 3 TEM images of HPMOSs synthesized with various V$_{EtOH/water}$, (a) 0.4 (HPMOS-1), (b) 0.3(HPMOS-2), (c) 0.2 (HPMOS-3) and (d) HPMOS-4 synthesized with octane (0.02ml).

In summary, we have demonstrated a new strategy to synthesize HPMOSs. The method utilizes the organic silicon

source itself as a "sacrificial template". The organic silicon source just exists temporarily as an oil phase and then is totally consumed to form the sphere shell. So it is easy to obtain the stable hollow HPMOSs, easy to control the size of hollow void and particles by controlling the size of the oil droplet, and more importantly it doesn't need additional surface functionalization process or any post-treatment procedure to remove a core template. This method just has one turning step and only needs 1h at room temperature to form HPMOSs which possess well-defined spherical morphology, tunable particle size, adjustable hollow void structure, and radially oriented mesochannels in shells. It is very simple, effective and easy to be scaled-up. It is expected that this method will provide many opportunities for the synthesis of a series of HPMOSs by utilizing different organic silicon source with various function to meet different application requirements.

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