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Facile and Scalable Synthesis of Monodispersed Spherical Capsules with a Mesoporous Shell

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Hierarchically structured mesoporous silica, especially hollow spherical particles with mesoporous shells (HMSs), are of special interest, because they combine the characteristics of both macroporous and mesoporous structures in one single unit. The hollow cavity in these highly engineered particles can act as a storage reservoir or a microreactor, whereas the mesoporous shell provides controlled release pathways for encapsulated substances or substantial surface area for reactions. As a result, HMSs have attracted intense interest in a wide variety of applications, such as catalysis, separation, sensors, and drug delivery.[1−5]

A number of approaches have been already developed to synthesize HMSs. They can be generally divided into two categories on the basis of the templates for the formation of hollow interiors. Soft templates such as micelles, vesicles, or block copolymer aggregates,[6−13] emulsions,[14−17] and acoustic cavities or bubbles[18−20] have been used to produce HMSs. Unfortunately, strict control of reaction conditions is generally required as soft templates are sensitive to the reaction environment. The hollow particles synthesized via soft templates usually have nonuniform sizes and the morphology of mesoporous shells is difficult to control.

Compared to soft templates, hard templates such as polymer latices and metal oxides are more effective in synthesizing mesoporous particles with defined particle size and morphology.[21−26] A hollow interior forms after removal of the hard template. The structured shell can be tuned separately with the assistance of mesopore directing agents. Tan et al. reported the synthesis of HMSs in concentrated ammonium solution using polystyrene latices as templates.[21] Several different groups have synthesized HMSs with mesoporous raspberry-like shells.[22,27] Zhao et al. also prepared hollow MCM-41 microspheres from a poly(styrene-methyl mathacrylate) latex by adding silica source in batches.[24] Zhao et al. fabricated HMSs and ellipsoids of tunable size using hematite particles.[25] Recently, Blas et al. successfully prepared HMSs with radially oriented mesopores in the shell but at a relatively low yield.[26]

For most practical applications, a facile and scalable process that allows precise control of the particles is required. The following three structural/morphological characterstics are especially critical: (1) particle size and polydispersity; (2) hollow core size and shape; and (3) thickness and structure of mesoporous shell. These key parameters are directly related to the perfomance of HMSs, such as catalytic acitivity and drug delivery efficiency. Although intense efforts, as mentioned above, have been already devoted to the synthesis of hollow mesoporous particles, a facile and scalable synthesis of high-quality monodispersed HMSs has yet to be developed. The reported approaches to date fail to control

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(1) Tanev, P. T.; Chibwe, M.; Pinnavaia, T. J. *Nature* **1994**, *368*(6469), 321–323.
(2) Slowing, I. I.; Trewyn, B. G.; Giri, S.; Lin, V. S. Y. *Adv. Funct. Mater.* **2007**, *17*(8), 1225–1236.
(3) Zhu, Y. F.; Shi, J. L.; Shen, W. H.; Dong, X. P.; Feng, J. W.; Ruan, M. L.; Li, Y. S. *Angew. Chem., Int. Ed.* **2005**, *44*(32), 5083–5087.
(4) Chai, G. S.; Yoon, S. B.; Kim, J. H.; Yu, J. S. *Chem. Commun.* **2004**, *23*, 2766–2767.
(5) Scott, B. J.; Wirnsberger, G.; Stucky, G. D. *Chem. Mater.* **2001**, *13*(10), 3140–3150.
(6) Tan, B.; Vyas, S. M.; Lehmer, H. J.; Knutson, B. L.; Rankin, S. E. *Adv. Funct. Mater.* **2007**, *17*(14), 2500–2508.
(7) Kim, S. S.; Zhang, W. Z.; Pinnavaia, T. J. *Science* **1998**, *282*(5392), 1302–1305.
(8) Hentze, H. P.; Raghavan, S. R.; McKelvey, C. A.; Kaler, E. W. *Langmuir* **2003**, *19*(4), 1069–1074.
(9) Yeh, Y. Q.; Chen, B. C.; Lin, H. P.; Tang, C. Y. *Langmuir* **2006**, *22*(1), 6–9.
(10) Fowler, C. E.; Khushalani, D.; Mann, S. *Chem. Commun.* **2001**, No. 19, 2028–2029.
(11) Shiomi, T.; Tsunoda, T.; Kawai, A.; Mizukami, F.; Sakaguchi, K. *Chem. Commun.* **2007**, No. 42, 4404–4406.
(12) Feng, Z. G.; Li, Y. S.; Niu, D. C.; Li, L.; Zhao, W. R.; Chen, H. R.; Gao, J. H.; Ruan, M. L.; Shi, J. L. *Chem. Commun.* **2008**, No. 23, 2629–2631.
(13) Yu, M. H.; Wang, H. N.; Zhou, X. F.; Yuan, P.; Yu, C. Z. *J. Am. Chem. Soc.* **2007**, *129*(47), 14576–14577.
(14) Li, W. J.; Sha, X. X.; Dong, W. J.; Wang, Z. C. *Chem. Commun.* **2002**, No. 20, 2434–2435.
(15) Wang, J. W.; Xia, Y. D.; Wang, W. X.; Poliakoff, M.; Mokaya, R. *J. Mater. Chem.* **2006**, *16*(18), 1751–1756.
(16) Li, Y. S.; Shi, J. L.; Hua, Z. L.; Chen, H. R.; Ruan, M. L.; Yan, D. S. *Nano Lett.* **2003**, *3*(5), 609–612.
(17) Wang, J. G.; Xiao, Q.; Zhou, H. J.; Sun, P. C.; Yuan, Z. Y.; Li, B. H.; Ding, D. T.; Shi, A. C.; Chen, T. H. *Adv. Mater.* **2006**, *18*(24), 3284–3288.
(18) Rana, R. K.; Mastai, Y.; Gedanken, A. *Adv. Mater.* **2002**, *14*(19), 1414–1418.
(19) Ogawa, M.; Yamamoto, N. *Langmuir* **1999**, *15*(6), 2227–2229.
(20) Wang, J. G.; Li, F.; Zhou, H. J.; Sun, P. C.; Ding, D. T.; Chen, T. H. *Chem. Mater.* **2009**, *21*(4), 612–620.
(21) Tan, B.; Rankin, S. E. *Langmuir* **2005**, *21*(18), 8180–8187.
(22) Wu, X. F.; Tian, Y. J.; Cui, Y. B.; Wei, L. Q.; Wang, Q.; Chen, Y. F. *J. Phys. Chem. C* **2007**, *111*(27), 9704–9708.
(23) Yang, J.; Lee, J.; Kang, J.; Lee, K.; Suh, J. S.; Yoon, H. G.; Huh, Y. M.; Haam, S. *Langmuir* **2008**, *24*(7), 3417–3421.
(24) Zhao, Y. S.; Wang, H.; Liu, Y. M.; Ye, J. L.; Shen, S. G. *Mater. Lett.* **2008**, *62*(27), 4254–4256.
(25) Zhao, W. R.; Lang, M. D.; Li, Y. S.; Li, L.; Shi, J. L. *J. Mater. Chem.* **2009**, *19*(18), 2778–2783.
(26) Blas, H.; Save, M.; Pasetto, P.; Boissiere, C.; Sanchez, C.; Charleux, B. *Langmuir* **2008**, *24*(22), 13132–13137.
(27) Yang, M.; Wang, G.; Yang, Z. Z. *Mater. Chem. Phys.* **2008**, *111*(1), 5–8.

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well at least one of the sturcture/moprhology parameters outlined above or are difficult to scale up in a robust process. For example, aggregation or fusion of hollow particles has often been observed and this may deteriorate HMS' advantages over conventional bulk mesoporous materials. Additionally nonuniform particles with a rough shell and/or a broad size distribution are usually obtained, suggesting a poorly controlled process. Moreover, in addition to HMSs, solid mesoporous nanoparticles are frequently formed, either mixed or fused onto the shells, which makes isolation of pure HMS particles extremely difficult. Finally synthetic approaches based on micellar templates may be applicable only to a limited particle size range.[6−9] We report here a facile and scalable process to synthesize monodispersed HMS capsules. The newly synthesized HMSs possess smooth, uniform and ordered mesoporous silica shells. Both the particle size and the mesoporous shell thickness can be fine-tuned by adjusting the amount of latex templates and silica source. These specially designed particles have well-controlled sizes ranging from 100 nm to micrometers, covering the different size requirements in numerous applications including catalysis, separations, sensors, and drug delivery.

Several HMSs with different sizes, denoted as HMS-x, where x represents the outside diameter of the mesoporous particles were syntesized. In contrast to previous reports such as Tan et al. in which a concentrated aqueous ammonium hydroxide solution was used,[21] HMSs here were synthesized in weakly basic ethanol/water solution using a relatively concentrated latex template. The weak basicity and appropriate ratio of ethanol to water allow precise control of the rate of hydrolysis tetraethyl orthosilicate (TEOS), which together with the high latex concentration reduces the possibility of forming solid mesoporous particles as well as fusing them together. For HMS-400, 25 g of polystyrene latex (~9 wt %) with a size around 400 nm was added dropwise to a solution containing 9.6 g of water, 0.80 g of hexadecyltrimethylammonium bromide (CTAB), 11.0 g of ethanol and 2.0 mL of ammonium hydroxide under vigorous stirring at room temperature. The mixture was first sonicated for 10 min and then magnetically stirred for 30 min before adding dropwise 1.5 g of TEOS. The molar ratio of TEOS/CTAB/ethanol/H_2O/NH_3 was 1:0.30:32:88:4.4, and the TEOS/polystyrene weight ratio was 0.66. The mixture was kept at room temperature for 48 h before the mesoporous silica coated latex was collected by centrifugation and washed with copious amounts of ethanol. The templates were removed by calcining in air at 600 °C for 8 h at a heating rate of 3 °C/min. HMS-140 and HMS-1500 were prepared in a similar manner using appropriate size polystyrene latex templates. HMSs with various shell thickness can be prepared simply by adjusting the amount (0.75 g or 3.0 g) of TEOS (see Figure S1 in the Supporting Information). More experimental details are provided in the Supporting Information.

Figure 1 shows TEM images of the different HMSs synthesized. The low-magnification TEM image indicates excellent particle uniformity. The electron contrast between

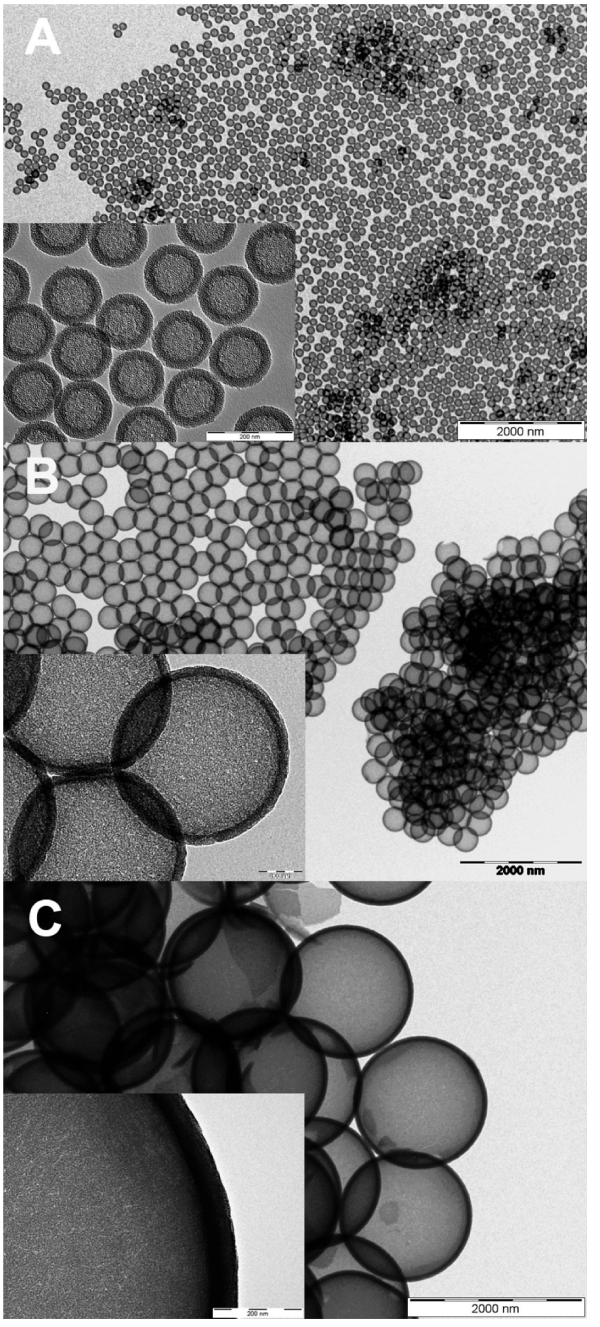

Figure 1. Representative TEM images of monodispersed hollow spherical particles. (A) HMS-140; inset scale bar, 200 nm; (B) HMS-400; inset scale bar, 100 nm; (C) HMS-1500; inset scale bar, 200 nm.

the cores and the shells in the high-resolution insets confirms the formation of hollow particles. N_2 adsorption−desorption isotherm measurements at 77 K (Figure 2, Table 1) show a multifaceted behavior consistent with the highly engineered nature of the particles. The BET surface area, pore size, and pore volume of the mesoporous shells range between 970 and 1440 m^2/g, 3.0 and 3.6 nm, and 0.19 and 1.37 cm^3/g, respectively. As the overall size of the capsules increases, the surface area increases, the pore volume decreases, and the pore size remains similar. All systems show a type IV isotherm. As the overall size of the HMS particles increases the hysteresis becomes less pronounced. HMS-140 shows a notable H1 type

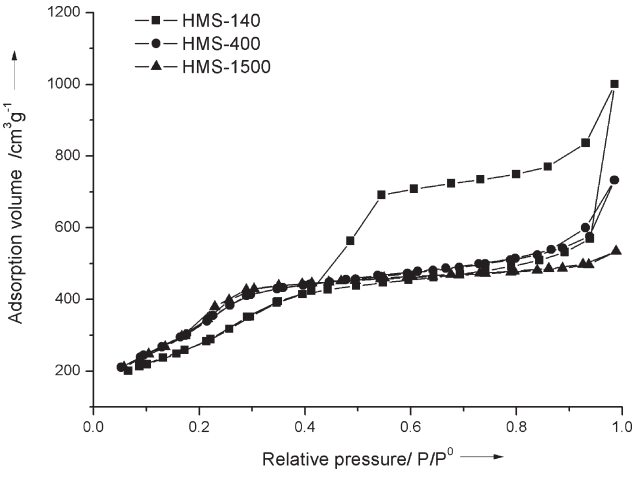

Figure 2. Adsorption desorption isotherms for different HMS capsules.

Table 1. Characteristics of Mesoporous Shell of HMS

sample	BET surface area (m^2/g) [a]	pore size (nm) [a]	pore volume (cm^3/g) [a]
HMS-140	0.97×10^3	3.61	1.37
HMS-400	1.30×10^3	3.08	0.48
HMS-1500	1.44×10^3	3.10	0.19

[a] Measured by N_2 adsorption at 77 K with the BJH method.

hysteresis loop starting from p/p_0 at 0.4 due to the presence of the mesoporous shell, whereas HMS-400 displays a small H4 type hysteresis loop at higher p/p_0 around 0.85. No significant hysteresis is found for HMS-1500. The XRD patterns of the different HMSs are shown in Figure S2 in the Supporting Information. HMS-140 and HMS-1500 capsules have similar diffraction peaks located around $2\theta = 2.15$, corresponding to a pore spacing of 4.09 nm. HMS-400 has a slightly larger diffraction peak at $2\theta = 2.55$, corresponding to a lower spacing of 3.45 nm. Based on the pore size (Table 1) and pore spacing, both HMS-140 and HMS-400 have a similar pore wall thickness ~0.4−0.5 nm, whereas HMS-1500 has a much thicker pore wall thickness close to 1 nm.

The HMS-140 and HMS-400 capsules are fairly robust during normal handling. As can be seen in Figure 1, the capsules remain mostly intact even after the sonication step required for TEM specimen preparation. The mechanical robustness as well as their hierarcical mesoporous sturcture makes HMSs promising candidates as supports for various applications. Because of our interest in developing CO_2 sorbents, HMS-400 was impregnated with tetraethylenepentamine and the CO_2 capture capacity was evaluated. The amine-impregnated HMS-400 show extraordinary capture capacity up to 6.6 mmol of CO_2/g of sorbent at 75 °C and 1 atm CO_2 (see Figure S3 in the Supporting Information). The amine loading in HMS-400 sorbent is as high as 83 wt % based on the total weight of the sorbent, which is much higher than that of sorbents using conventional mesoporous supports (~ 50 wt %).[28,29] The amine efficiency for CO_2 capture of HMS-400 is as high as 353 mg CO_2/g of amine, which is about 50% higher than sorbents prepared by impregnating amines in bulk MCM-41 supports.[28] Clearly, the structured HMSs help to enhance both the amine capacity and efficiency of the sorbent.

In summary, monodispersed HMSs with tunable particle size and shell thickness were successfully synthesized using relatively concentrated polystyrene latex templates and a silica precursor in a weakly basic ethanol/water mixture. The particle size of the capsules can vary from 100 nm to micrometers. These highly engineered monodispersed capsules synthesized by a facile and scalable process may find applications in drug delivery, catalysis, separationm or as biological and chemical microreactors.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(28) Xu, X. C.; Song, C. S.; Andresen, J. M.; Miller, B. G.; Scaroni, A. W. *Energy Fuels* **2002**, *16*(6), 1463–1469.
(29) Son, W. J.; Choi, J. S.; Ahn, W. S. *Microporous Mesoporous Mater.* **2008**, *113*(1−3), 31–40.