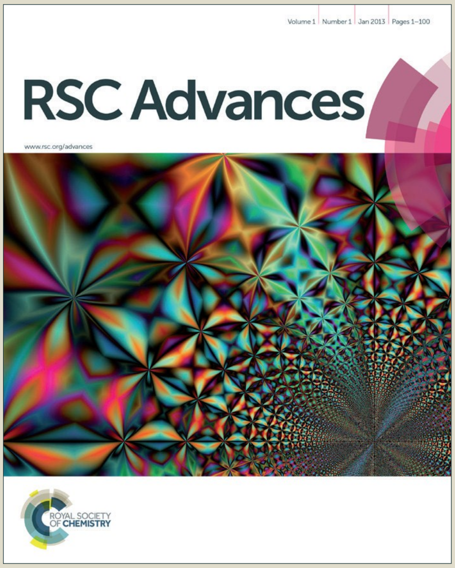
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A dual-template method was proposed to prepare dandelion-like core-shell silica microspheres with center radial pores by one step reaction.

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Dandelion-like Core-shell Silica Microspheres with Hierarchical Pores

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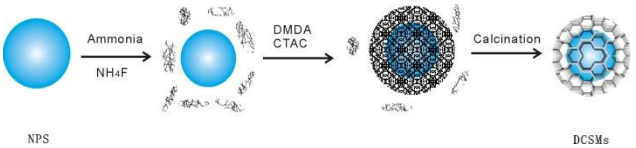
Dandelion-like core-shell silica microspheres with hierarchical pores are synthesized by condensing the dissolved silica species on the surface of homologous nonporous silica particles in microemulsion system formed by the complexes of N,N-dimethyldecylamine and hexadecyltrimethylammonium chloride. The microspheres have good monodispersity and center radial pores.

Hierarchical porous materials are highly organized structures with different scales, which are potential candidates for applications in various fields due to their excellent performance in adsorption, diffusion, reactivity and separation. [1] Compared to micropores with limited mass transfer, the hierarchical porous structure could effectively improve the diffusion of reactants inside the porous channels. For example, materials with micropores and mesopores demonstrate superior mass transfer in catalysis; [2] meso- and macroporous frameworks show high permeability and efficiency in separation. [3]

Among the hierarchical porous materials, spherical particles with center radial pores have been synthesized by template-directed methods recently, [4] with conical pore channels increased from center to the particle surface. The template-directed synthesis is a versatile method for preparation of hierarchical porous silica materials with different morphologies, such as using cetylpyridinium bromide (CPB) as a template for synthesis of fibrous silica nanospheres, [4a] and using cetyltrimethylammonium bromide (CTAB)-stabilized ethyl ether nanodroplets as dynamic templates for preparation of dendrimer-like silica nanoparticles with hierarchical pores. [5a] Those particles with center radial pores enable the access of large molecules and more reactants to the internal surface area, and thus have been successfully applied in biomedicine and catalysis. [5]

To further improve the mass transfer speed and simplify the synthesis procedure, herein, to the best of our knowledge, for the first time by one-step reaction, we prepare dandelion-like core-shell silica microspheres (DCSMs) with center radial pores via a dual-template method. As shown in Scheme 1, nonporous silica (NPS) particles are firstly prepared through a modified seeded growth method according to our previous work and characterized in Fig. S1, [6] with good monodispersity and diameter of 1.71 ± 0.08 μm. Then, they are added into the microemulsion system formed by water and dual-template, N,N-dimethyldecylamine (DMDA) and hexadecyltrimethylammonium chloride (CTAC). After the temperature is increased to 90 ℃, ammonia and ammonium fluoride are added to etch NPS particles and keep the shape spherical. The dissolved silica species would condense on the homologous NPS particles directed by DMDA-CTAC complexes for 24 h. Finally, with the templates removed by calcination, the monodisperse sub-2 μm DCSMs are obtained. Besides the facile preparation process, the monodispersity of the NPS particles could be well preserved.



Scheme 1. Preparation of DCSMs with center radial pores.

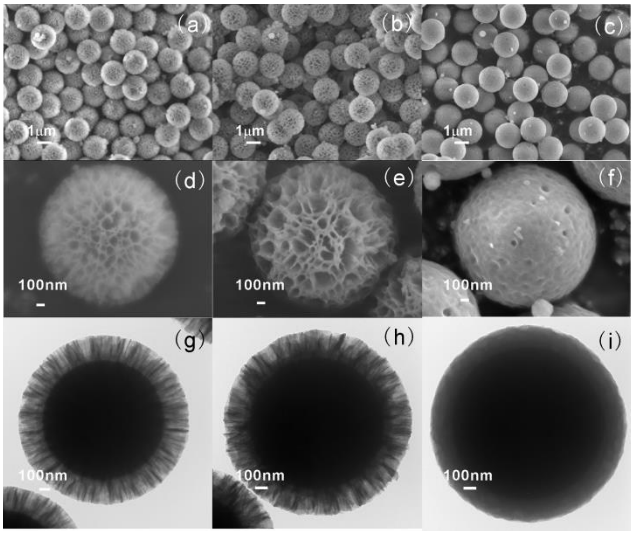


Table 1 Porosity analysis of microspheres prepared with different mass ratios of dual-template by nitrogen sorption measurements.

Samples[a]	S_{BET}[b] [m^2 g^{-1}]	S_{micro}[c] [m^2 g^{-1}]	S_{meso} [d] [m^2 g^{-1}]	V_{micro}[e] [cm^3 g^{-1}]	V_{meso}[f] [cm^3 g^{-1}]	V_{Pore}[g] [cm^3 g^{-1}]
4.5	247.5	59.8	187.7	0.02	0.36	0.38
2.3	354.9	38.4	316.5	0.01	0.35	0.36
0.8	425.4	0	425.4	0	0.38	0.38

[a] Mass ratio of DMDA and CTAC; [b] Brunauer-Emmett-Teller (BET) method; [c] *t*-plot method; [d] S_{BET}-S_{micro}; [e] *t*-plot method; [f] V_{pore}-V_{micro}; [g] Volume of N_2 adsorbed at P/P_0=0.99.

Fig. 1 FESEM (a-f) and TEM (g-i) images of particles prepared by dual-template method with mass ratios of DMDA and CTAC as 4.5 (a, d, g), 2.3 (b, e, h) and 0.8 (c, f, i).

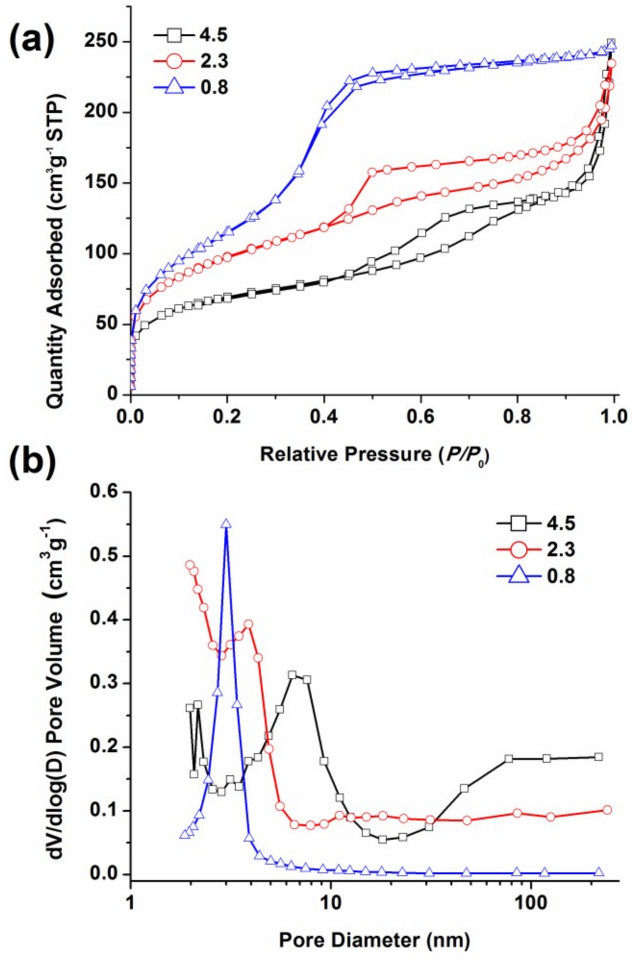


Fig. 2 Porosity analysis of microspheres prepared by dual-template with mass ratios of DMDA and CTAC as 4.5, 2.3 and 0.8. (a) Nitrogen adsorption-desorption isotherms, (b) BJH pore size distributions calculated from the adsorption branch (in order to show all samples clearly, the ordinate value × 0.2 for sample denoted as 0.8).

The morphology of prepared DCSMs by our method was investigated by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The DCSMs are highly spherical with radially pore channels, dandelion-like surface and core-shell structure (Fig. 1a, d, g). By comparison, the original NPS particles demonstrate smooth surface and no core-shell structure (Fig. S1). As shown in Fig. 1, DCSMs with large center radial pores on the surface could be prepared with the mass ratios of DMDA and CTAC as 4.5 and 2.3, but such structure disappears with the decrease of mass ratio as 0.8. When the mass ratios decrease from 4.5, 2.3 to 0.8, the particle diameters change slightly from 1.79±0.07 μm, 1.88±0.05 μm to 1.86±0.05 μm, respectively, and the ratios of core to particle diameter vary from 0.74±0.02, 0.70±0.02, to 0.74±0.02, respectively. So the mass ratios of DMDA and CTAC have little effect on the shell thickness, core diameter and pore volume (Table 1). It is worth noting that the diameters increase from the original NPS particles to DCSMs due to the formation of porous structure.

The porosity of prepared particles was further studied by nitrogen sorption measurement. As shown in Fig. 2, the isotherms of DCSMs with the mass ratio of DMDA and CTAC as 4.5 exhibit type II-IV with the hysteresis loop in the range of P/P_0 = 0.45-0.85, which indicates the existence of large nanopore, and it is further convinced as 7 nm by Barrett-Joyner-Halenda (BJH) pore size distribution curves. Here the adsorption branch isotherm is preferred for calculating pore size distribution because it is hardly affected by any tensile strength effect phenomenon and reveals the real pore size. [7] In addition, the diameter of nanopore decreases with the mass ratio of DMDA and CTAC as 2.3. As shown in Table 1 and Fig. 2, in both cases, the prepared DCSMs are of combined structure of micropore and large nanopore. However, for microspheres prepared with the mass of 0.8, only mesopore (3 nm) exists.

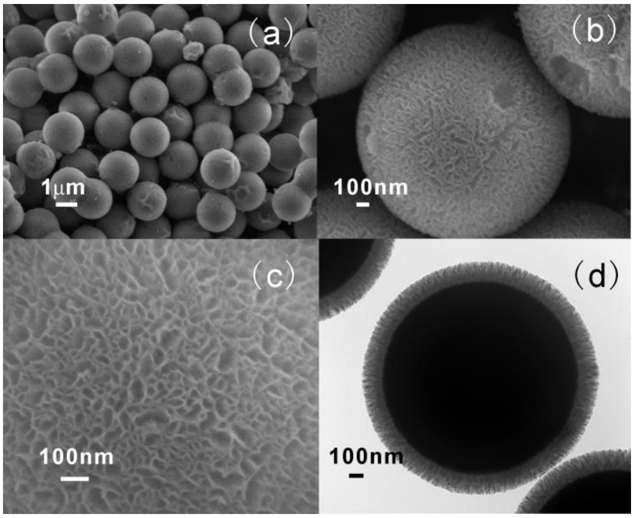


Fig. 3 Images of particles prepared by dual-template of DMHA and CTAC. (a, b, c) FESEM. (d) TEM.

Although pseudomorphic transformation (PT) and templated dissolution and redeposition (TDR) methods can be used to prepare mesostructured silicas while maintaining the existing morphology, [8] the 1,3,5-trimethylbenzene in PT and tridecane in TDR are used separately as the auxiliary templates to increase pore size. Here we use DMDA and CTAC as dual-template. As shown in Fig. 1 and Table 1, DMDA has great effects on the formation of hierarchical pores. To illustrate the importance of DMDA, we further replaced it with *N*,*N*-dimethylhexadecylamine (DMHA, with additional 6 methylene units versus DMDA) and investigated the effects of dual-template composed of DMHA and CTAC (mass ratio of DMHA and CTAC as

4.6) on particle morphology and porosity. As shown in Fig. 3, for the particle prepared by DMHA, the particle diameter is 1.92±0.06 μm, with ratio of core to particle diameter as 0.82. The pores are primarily shallow tunnels and confined to the outer region of particle, with very little porosity beyond 50 nm on the outer surface. Type IV isotherms are shown in further nitrogen adsorption measurement (Fig. 4), which indicates capillary condensation in large nanopore. The BET surface area is 172.4 $m^2 g^{-1}$, and pore volume is 0.30 $cm^3 g^{-1}$. According to t-plot method, there is no micropore in this material. The large nanopore is possibly due to the hydrophobic interaction between DMHA and CTAC, similar to DMDA and CTAC. However, the DMHA and CTAC interaction only gives rise to large nanopore and no dandelion-like structure, which are caused by the solubility and hydrophobicity of DMHA. Therefore, we conclude that the unique structure of DCSMs is mainly contributed by the unique interaction between DMDA and CTAC.

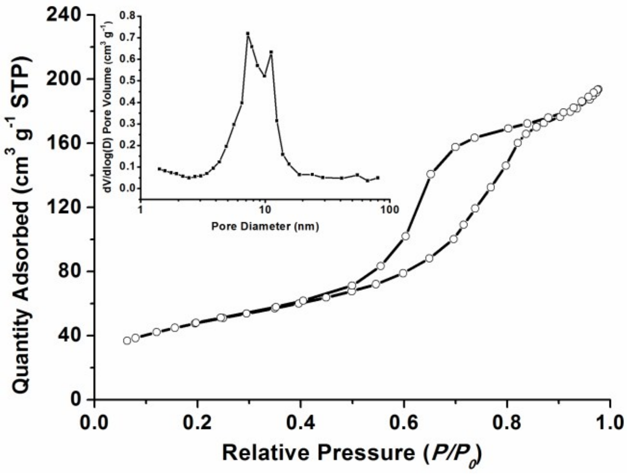


Fig. 4 Porosity analysis of particles prepared by dual-template of DMHA and CTAC. Nitrogen adsorption-desorption isotherms and BJH pore size distribution calculated from the adsorption branch (inset).

Based on the above-mentioned results, we postulate that DCSMs could be prepared by the cooperative assembly effects among silica species, DMDA and CTAC, among which DMDA and CTAC act as the structure-directing agents. CTAC is often used to construct highly ordered mesophase, resulting in silica materials with pore size of 3 nm. [9] DMDA can be used as pore expander agent because of its swelling nature. [10] Therefore, DMDA may self-assemble into the hydrophobic cavity of the micelles of CTAC, to enlarge the size of the original micelles by hydrophobic interaction between carbon chains. Such deduction can be confirmed by the increase of pore diameter from 4 to 7 nm with more DMDA added (Fig. 2). Meanwhile, the arrangement of mesophase formed by CTA^+ in water could be disturbed by the addition of DMDA and lead to phase redistribution. [11] By comparing DMDA and DMHA (Fig. 3), it is assured that DMDA is crucial for preparation of DCSMs. In order to further confirm the unique interaction between DMDA and CTAC essentially for the preparation of DCSMs, we replace CTAC with cetylpyridinium chloride (CPC). As shown in Fig. S2, all particles display the fragmentary core-shell structure. Apparently, the interaction between DMDA and CPC is unstable. Although CTAC and CPC are cationic surfactants with the same methylene units, they have different substituents on nitrogen atom. In contrast to the dual-template of DMHA-CTAC and DMDA-CPC, DMDA and CTAC coordinate well and give rise to dandelion-like structure with intact shell. In addition, the surface area of micropore increases with the increment of DMDA (Table 1), which can be attributed to DMDA alone as template to form micropores. After the removal of the DMDA and CTAC by calcinations, DCSMs are formed.

In summary, we proposed an approach to prepare DCSMs by using DMDA and CTAC as dual-template and NPS particles as silica source, which represented new structure in the family of hierarchical porous silica materials. The DCSMs have spherical and core-shell structure with radially pore channels and hierarchical pores, which might be potential candidates for applications in separation, bioanalysis, catalysis and biomedicine.

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Notes and references

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† Electronic Supplementary Information (ESI) available: materials, instrumentation, particle preparation. See DOI: 10.1039/c000000x/

1 (a) B. Su, C. Sanchez and X. Yang in *Hierarchically structured porous materials: from nanoscience to catalysis, separation, optics, energy, and life science*, ed. B. Su, C. Sanchez and X. Yang, Wiley-VCH, Weinheim, 1st edn., 2012, ch. 1, pp. 3-26. (b) J. Liu, S. Z. Qiao, S. B. Hartono and G. Q. Lu, *Angew. Chem. Int. Ed.*, 2010, **49**, 4981. (c) H. Liu, K. Wang, Y. Shi, X. Gao, H. Liu, B. Wang and C. Xu, *RSC Adv.*, 2014, **4**, 29694.

2 (a) V. N. Shetti, J. Kim, R. Srivastava, M. Choi and R. Ryoo, *J. Catal.*, 2008, **254**, 296. (b) L. Gueudré, M. Milina, S. Mitchell and J. Pérez-Ramírez, *Adv. Funct. Mater.*, 2014, **24**, 209. (c) T. C. Keller, S. Isabettini, D. Verboekend, E. G. Rodrigues and J. Pérez-Ramírez, *Chem. Sci.*, 2014, **5**, 677.

3 (a) G. Guiochon, *J. Chromatogr. A*, 2007, **1168**, 101. (b) H. Lin, J. Ou, Z. Zhang, J. Dong and H. Zou, *Chem. Commun.*, 2013, **49**, 231.

4 (a) V. Polshettiwar, D. Cha, X. Zhang and J. M. Basset, *Angew. Chem. Int. Ed.*, 2010, **49**, 9652. (b) D. Moon and J. Lee, *Langmuir*, 2012, **28**, 12341.

5 (a) X. Du, B. Shi, J. Liang, J. Bi, S. Dai and S. Z. Qiao, *Adv. Mater.*, 2013, **25**, 5981. (b) Y. Choi, Y. S. Yun, H. Park, D. S. Park, D. Yun and J. Yi, *Chem. Commun.*, 2014, **50**, 7652. (c) A. Fihri, M. Bouhrara, U. Patil, D. Cha, Y. Saih and V. Polshettiwar, *ACS Catal.*, 2012, **2**, 1425. (d) H. Yang, S. Li, X. Zhang, X. Wang and J. Ma, *J. Mater. Chem. A*, 2014, **2**, 12060.

6 Y. Min, B. Jiang, C. Wu, S. Xia, X. Zhang, Z. Liang, L. Zhang and Y. Zhang, *J. Chromatogr. A*, 2014, **1356**, 148.

7 J. C. Groen and J. Pérez-Ramírez, *Appl. Catal., A*, 2004, **268**, 121.

8 (a) A. Galarneau, J. Iapichella, K. Bonhomme, F. D. Renzo, P. Kooyman, O. Terasaki and F. Fajula, *Adv. Funct. Mater.*, 2006, **16**, 1657. (b) H. Dong and J. Brennan, *J. Mater. Chem.*, 2012, **22**, 13197.

9 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.

10 A. Sayari, *Angew. Chem. Int. Ed.*, 2000, **39**, 2920.

11 A. Firouzi, D. Kumar, L.M. Bull, T. Besier, P. Sieger, Q. Huo, S. A. Walker, J. A. Zasadzinski, C. Glinka, J. Nicol, D. Margolese, G. D. Stucky and B. F. Chmelka, *Science*, 1995, **267**, 1138.