Supporting Information

Dendrimer-like hybrid particles with tunable hierarchical pores

Xin Du,[a] Xiaoyu Li,[b] Hongwei Huang,[c] Junhui He[d] and Xueji Zhang[a]*

[a]Research Center for Bioengineering and Sensing Technology, Department of Chemistry & Biological Engineering, University of Science & Technology Beijing, Beijing 100083, P. R. China

*E-mail: duxin@ustb.edu.cn

[b]Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

[c]School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

[d]Functional Nanomaterials Laboratory, Technical Institute of Physics and Chemistry, Chinese Academy of Science, Beijing 100190, China

Table S1. Synthesis parameters and properties of HPSNs-NH_2 prepared under varied ethanol and ethyl ether volumes in our previously published paper.[1]

Ethanol (mL)	diethyl ether (mL)	APTES (mL)	Temperature (^oC)	Magnetic stirring rate (rpm)	Particle size (nm)	Fig.
4	8	0.1	20	1000	100~300	S10a
5	10	0.1	20	1000	100~400	S10b
6	12	0.1	20	1000	150~250	S10c
5	15	0.1	20	1000	180~280	S10d
7.5	20	0.1	20	1000	400~500	S10e
10	20	0.1	20	1000	300~600	S10f
15	30	0.1	20	1000	irregular	S10g

[1] X. Du, Y. Bing, J. Liang, J. Bi. S. Dai, S. Z. Qiao, Developing functionalized dendrimer-like silica nanoparticles with hierarchical pores as advanced delivery nanocarriers. ***Adv. Mater.*** 2013, *25*, 5981-5985.

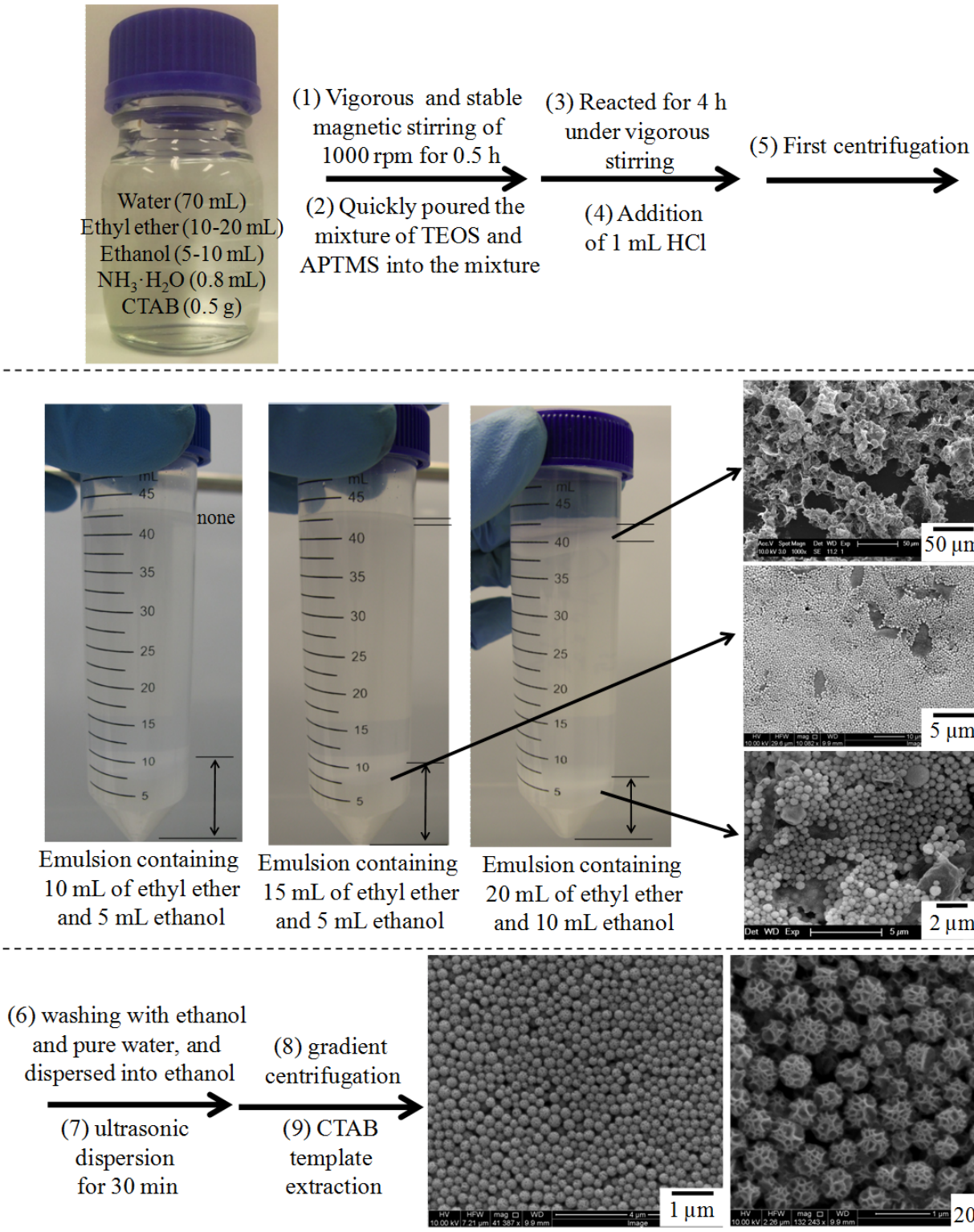

Fig. S1. The schematic illustration of experimental procedures.

As shown in **Fig. S1**, after first centrifugation, when 5 mL of ethanol and 10 mL of ethyl ether were added, no product is suspended on the upper surface of centrifuged liquid; when 5 mL of ethanol and 15 mL of ethyl ether were added, a small amount of product appears on the upper surface of centrifuged liquid; when 10 mL of ethanol and 20 mL of ethyl ether were added, the increased amount of product is present on the upper surface of centrifuged liquid. These results indicate that the increase of the added ethyl ether volume results in the formation of more suspended products, which are composed of micrometer-sized hollow spheres and broken hollow spheres. In addition, the precipitates contain porous silica particles (HPSNs-NH_2) and a small amount of impurities (micrometer-sized hollow spheres and broken hollow spheres). Then, the uniform HPNSs-NH_2 (using St3' as example) were obtained after impurities were effectively removed by gradient centrifugation based on the sizes of HPSNs-NH_2 (see Experimental Section). Finally, CTAB surfactant is extracted from particles in solution of ethanol and concentrated HCl.

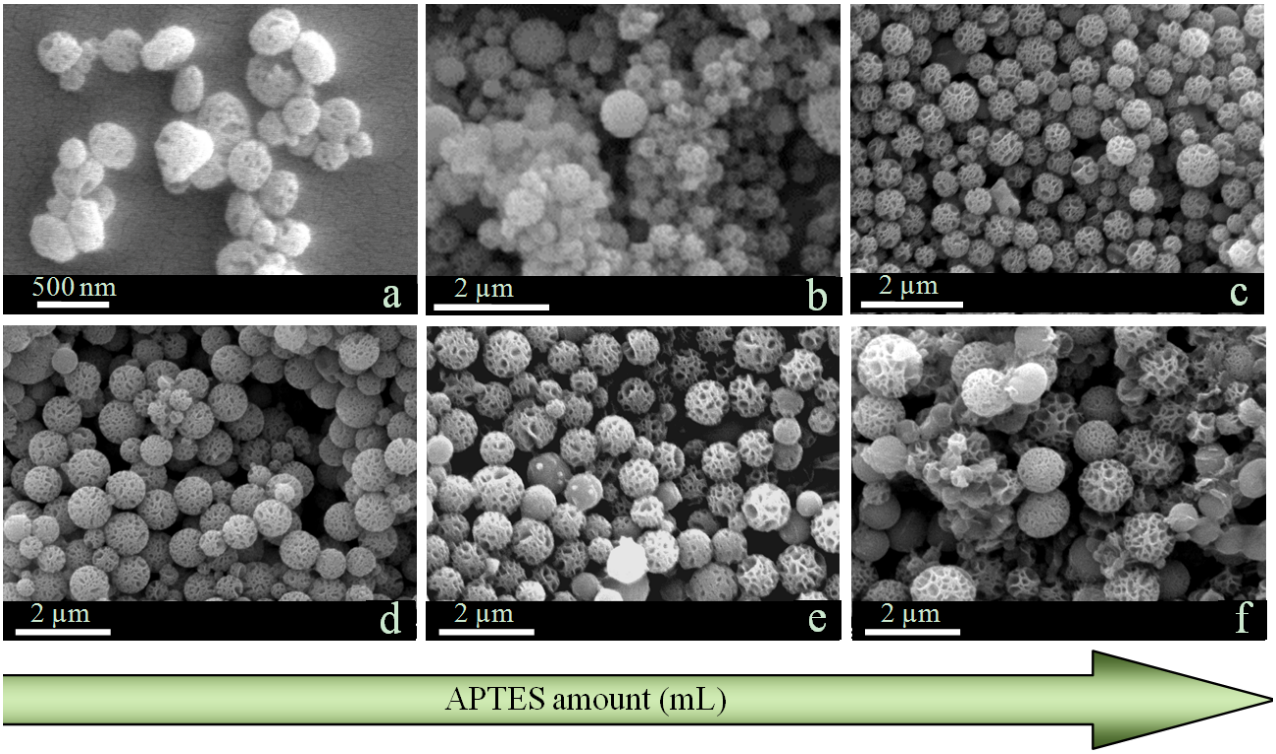

Fig. S2. SEM images of HPSNs prepared under varied APTES amount at 20 °C: 0 (Sa1) (a), 0.05 (Sa2) (b), 0.1 (Sa3) (c), 0.2 (Sa4) (d), 0.3 (Sa5) (e) and 0.4 mL (Sa6) (f).

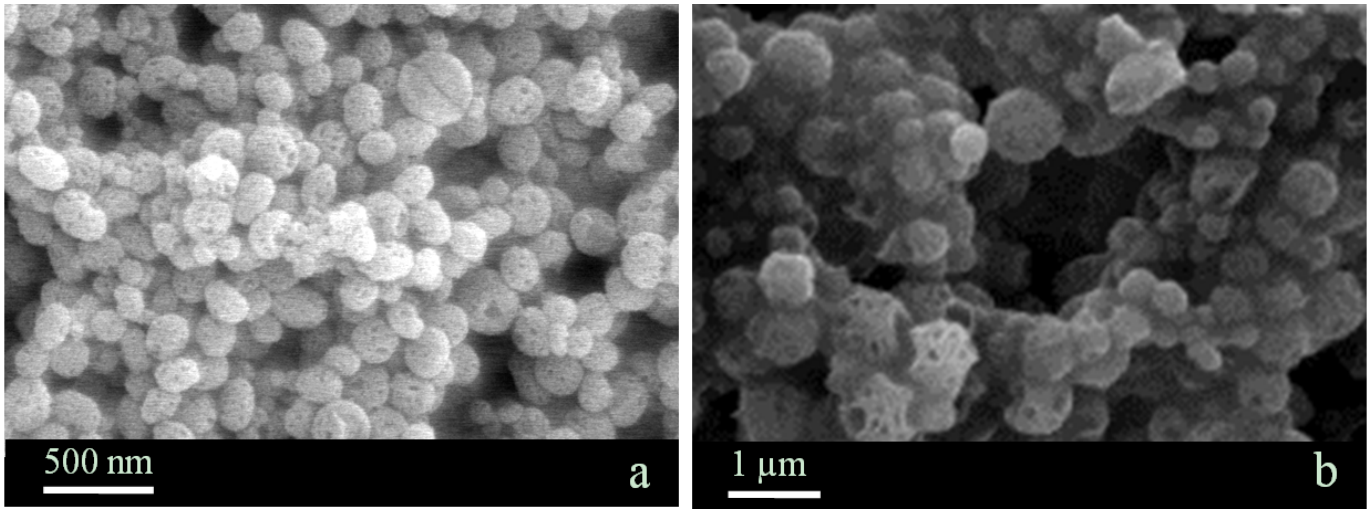

Fig. S3. SEM images of HPSNs fabricated under varied co-condensation silane at 20 ^{o}C: MPMS (S_{MPMS}) (a) and GPMS (S_{GPMS}) (b).

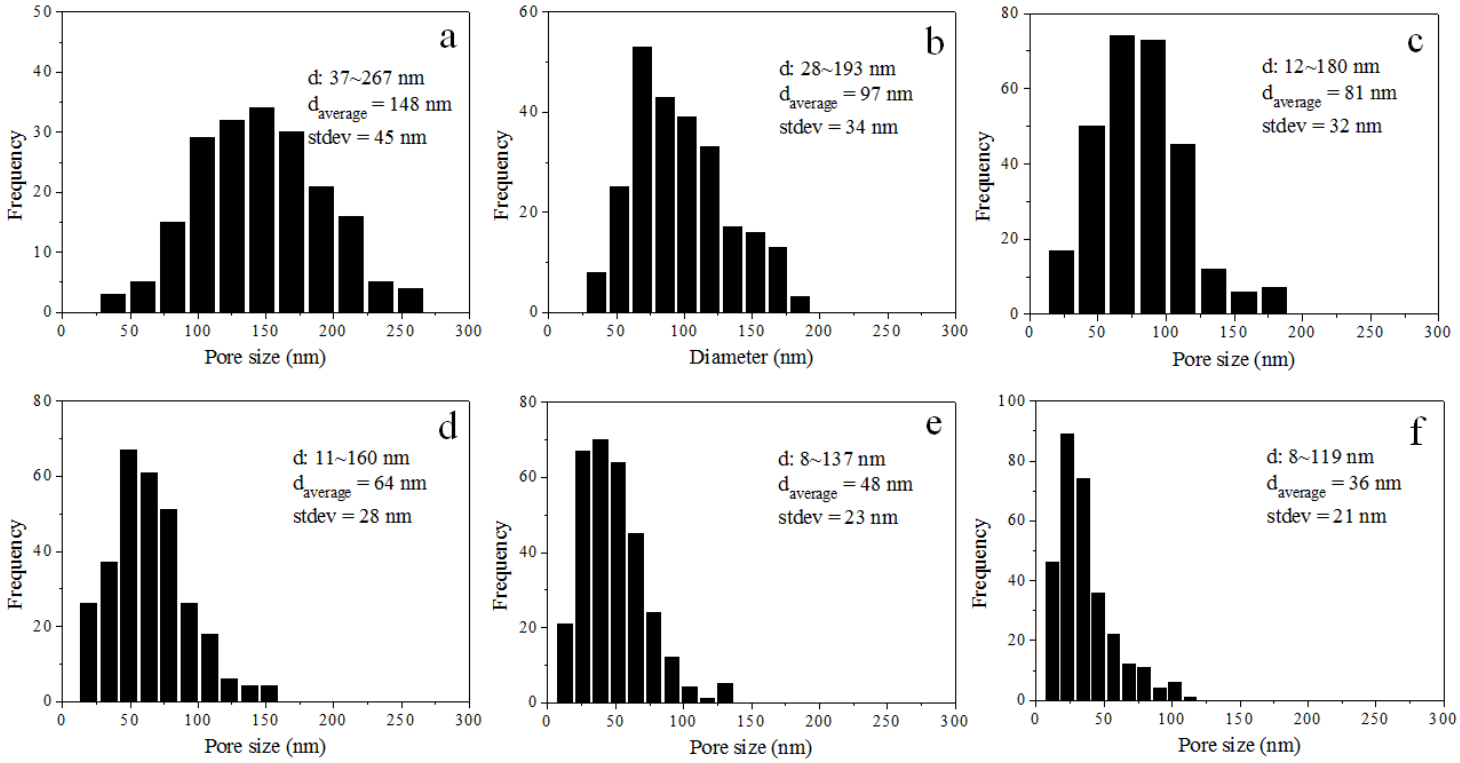

Fig. S4. Size distribution histograms (a-f) of the surface pores of HPSNs-NH_2 (St1-St6), respectively, measured from SEM images in Fig. 2.

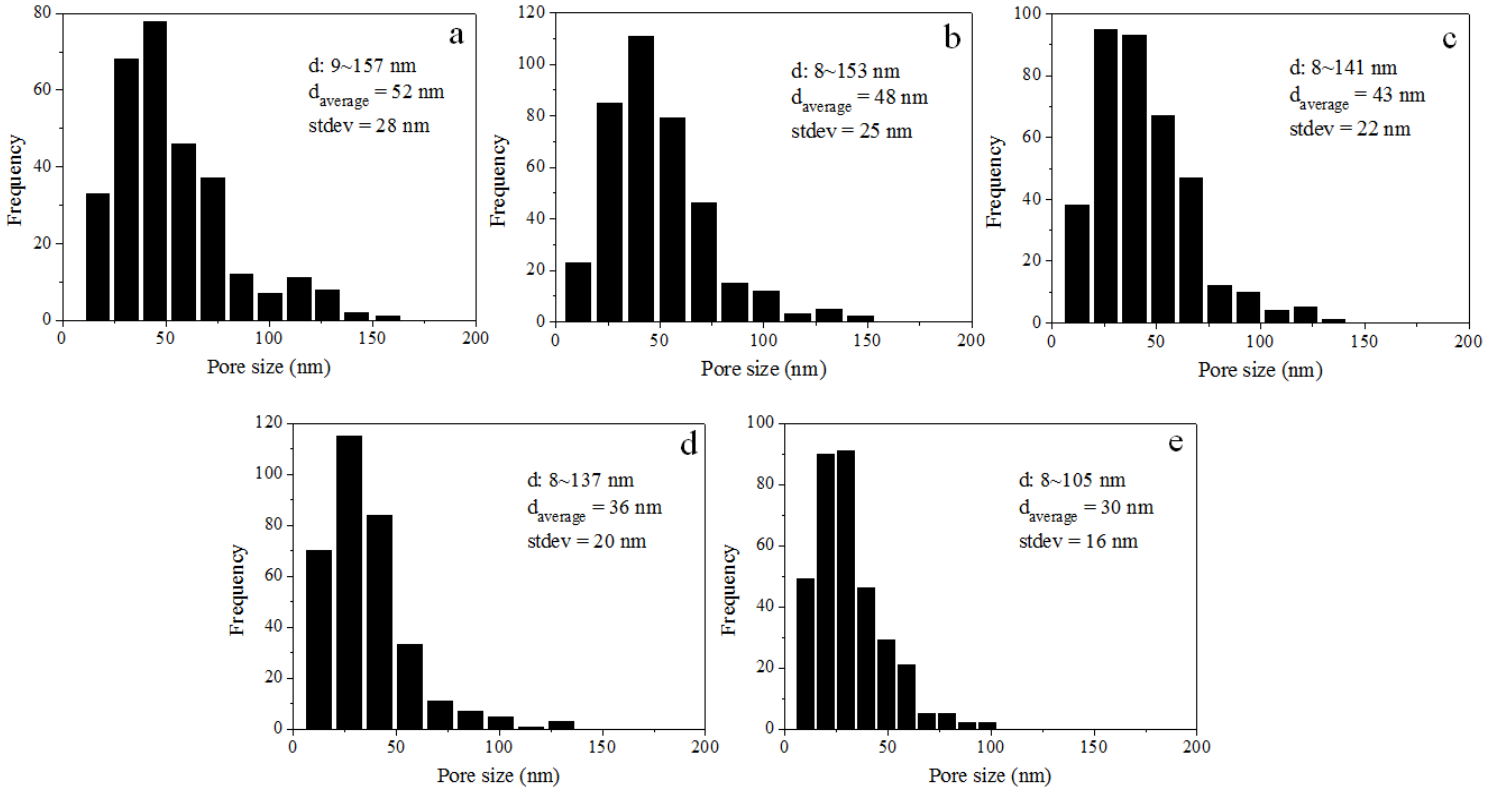

Fig. S5. Size distribution histograms (a-e) of the surface pores of HPSNs-NH_2 (St1'-St5'), respectively, measured from SEM images in Fig. 4.

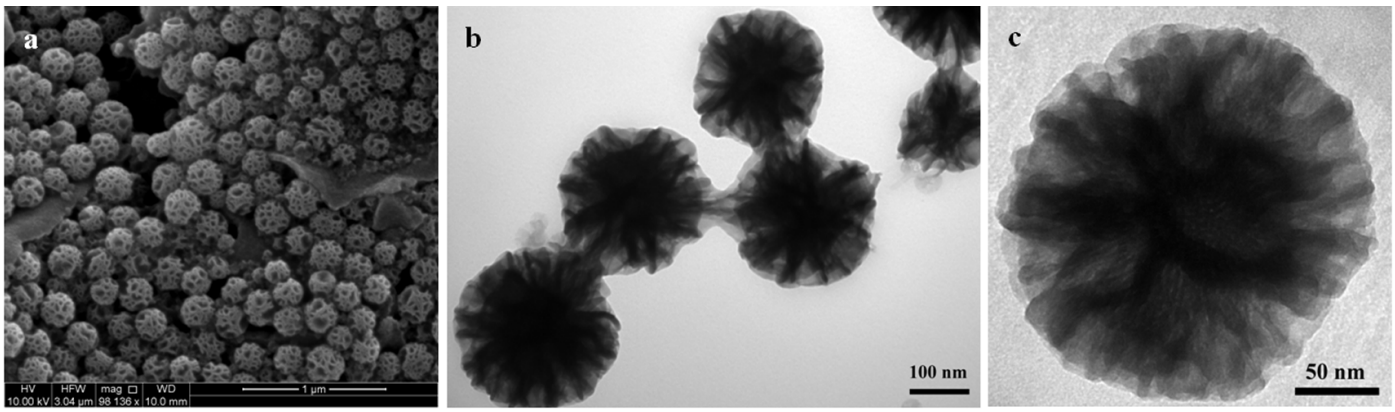

Fig. S6. SEM (a) and TEM (b,c) images of the as-prepared HPSNs-NH_2 (St3') fabricated in the emulsion system containing 5 mL of ethanol and 15 mL of ethyl ether at 20 ^{o}C. The as-prepared product solution (without ultrasonic dispersion, gradient centrifugation and solvent extraction) was directly dropped on the scanning platform and carbon-coated copper grids, which were treated first at 30 ^{o}C for 24 h and then at 60 ^{o}C for 24 h to void the shrinkage of particle structures, for SEM and TEM observations.

It can be found that the dendrimer-like structures are formed during sol-gel reaction and do not result from the post-treatment such as ultrasonic dispersion, gradient centrifugation and solvent extraction.

In previous literatures, a lot of organic solvents (such as ethanol (Langmuir 2007, 23, 1107), pentane (Langmuir 2007, 23, 7255), dioxane (Chem. Commun. 2009, 5177), trimethylbenze (Chem. Eur. J. 2006, 12, 1448), dodecanethiol (Chem. Eur. J. 2011, 17, 8165), tetraethyl orthosilicate (ACS Appl. Mater. Interfaces 2015, 7, 1040), *etc*.) have been investigated to fabricate the porous silica materials, however, all the products do not have the dendrimer-like silica nanoparticles with hierarchical pores.

Here, hexanol is used to replace ethyl ether in the identical experimental conditions. From the below TEM images, it can be seen that the formed product is irregular porous particles.

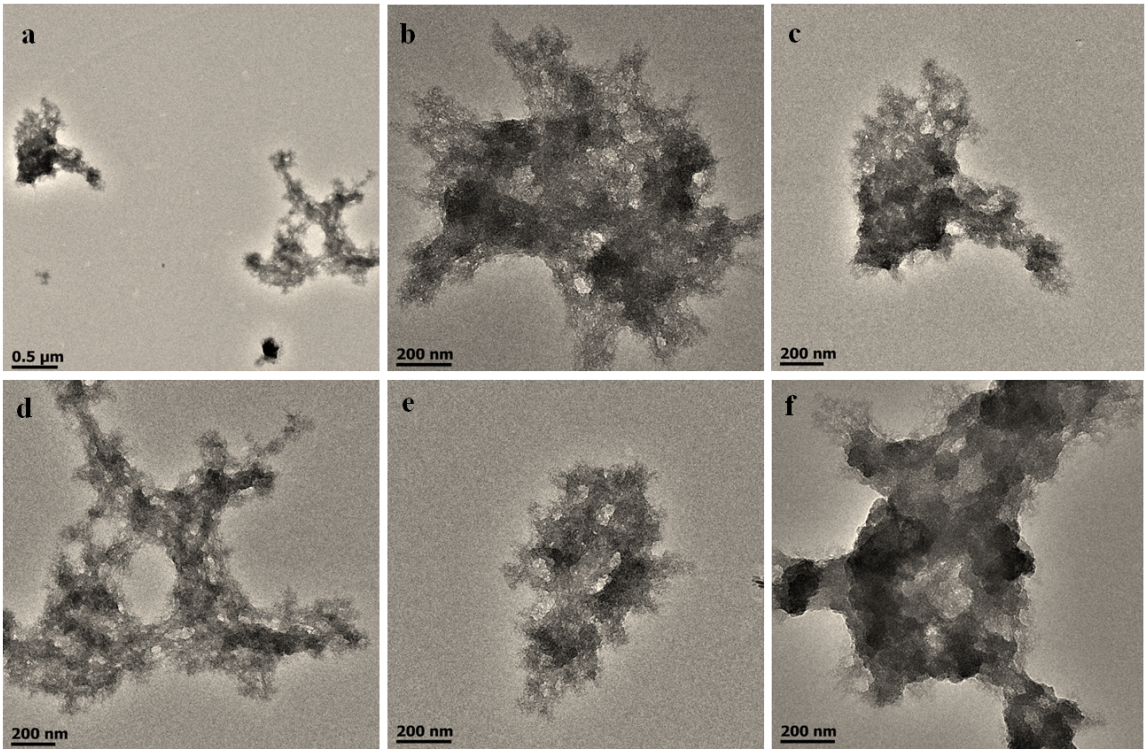

Fig. S7. TEM images of the product fabricated in the identical emulsion system with St3 except the use of hexanol to replace ethyl ether.

These results indicate that ethyl ether is special hydrophobic solvent for the synthesis dendrimer-like silica particles with hierarchical pores.

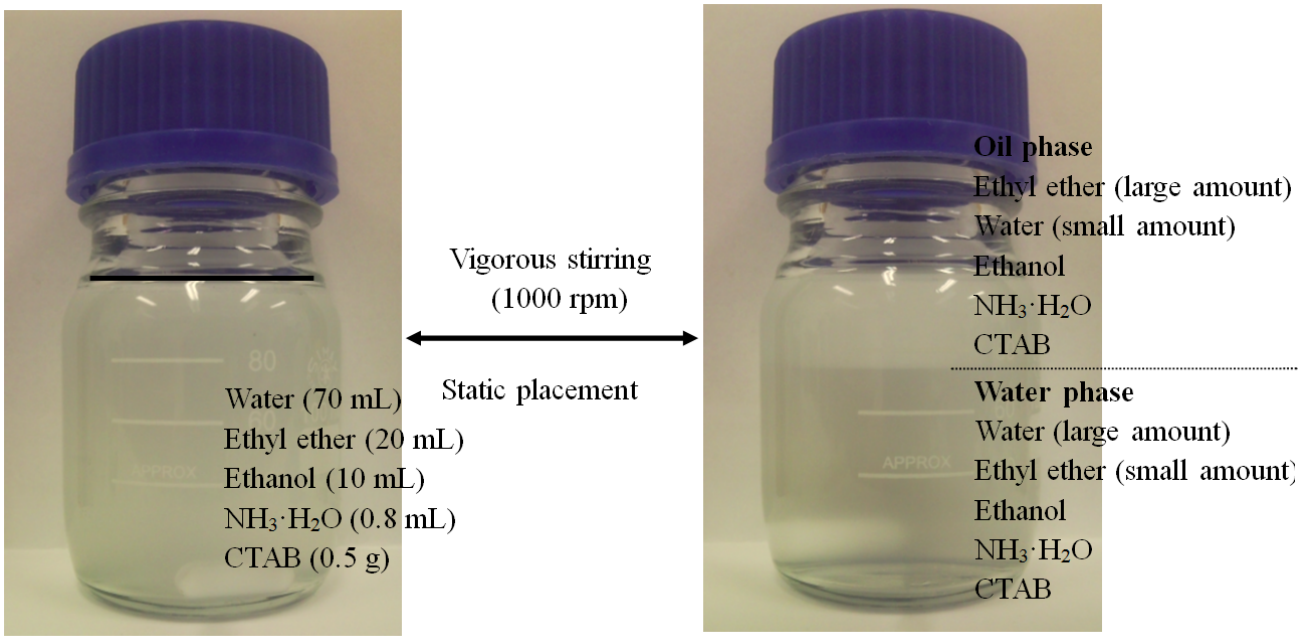

Fig. S8. Digital images of CTAB-stabilized ethyl ether emulsion systems after vigorous stirring (1000 rpm) for 30 min (left) and after static placement for 10 min (right). After vigorous stirring for 30 min, the apparent observation of emulsion is uniform, however, after static placement for 10 min, the stratification of oil phase and water phase is found, indicating that the formed emulsion system is very unstable (not microemulsion, which is clear, thermodynamically stable, isotropic liquid mixtures of oil, water and surfactant).

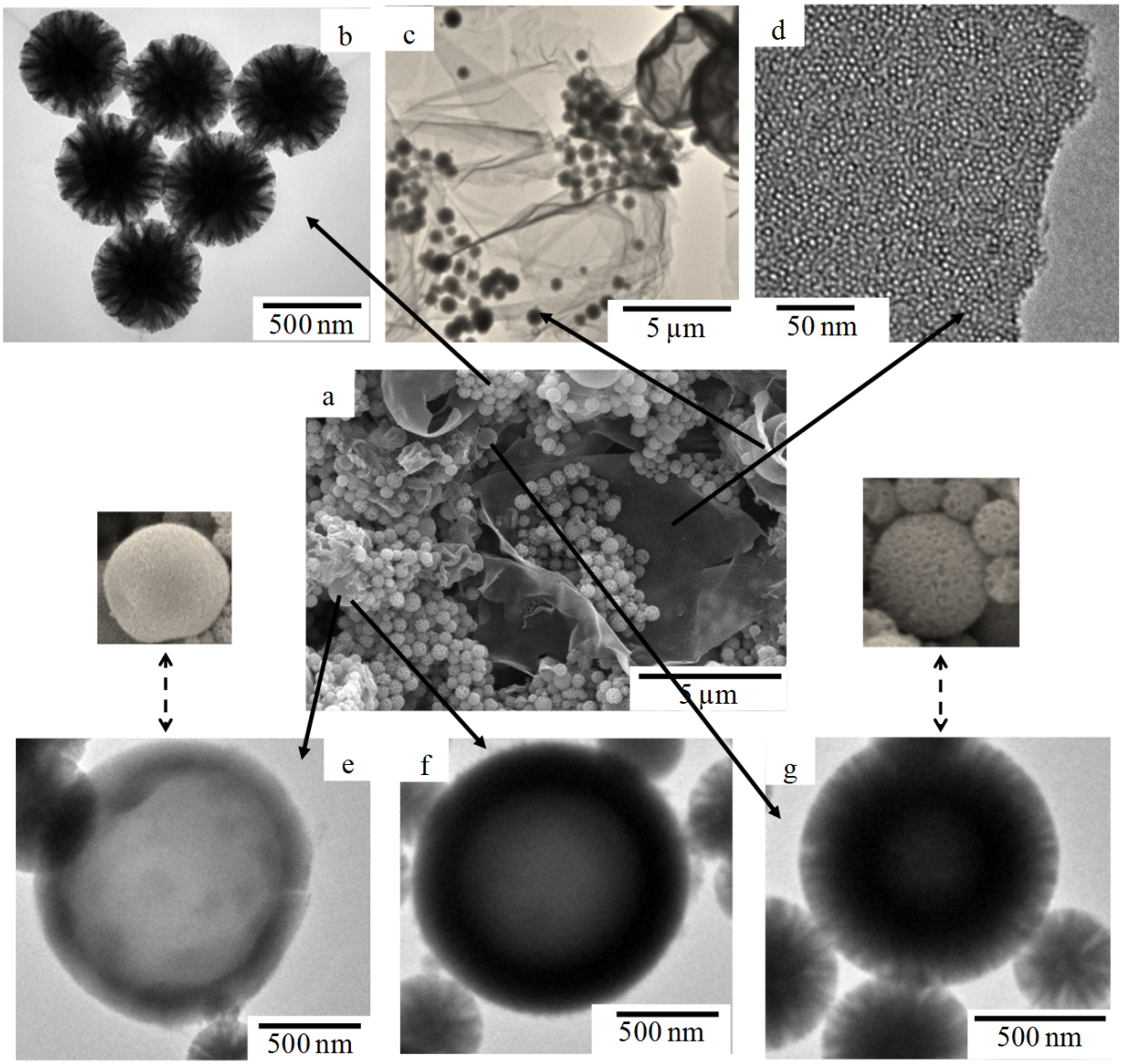

Fig. S9. SEM (a) and TEM (b-g) images of the Sa3 product synthesized in the emulsion containing 20 mL of ethyl ether and 10 mL of ethanol (before gradient centrifugation). The product contains silica nanoparticles with hierarchical pores (HPSNs-NH2) (b), large hollow spheres with mesoporous shell (size: 1-10 µm) (c,d), small hollow spheres (size: 1-2 µm) with varied shell thickness (e,f), and hollow spheres with hierarchical pores (g).

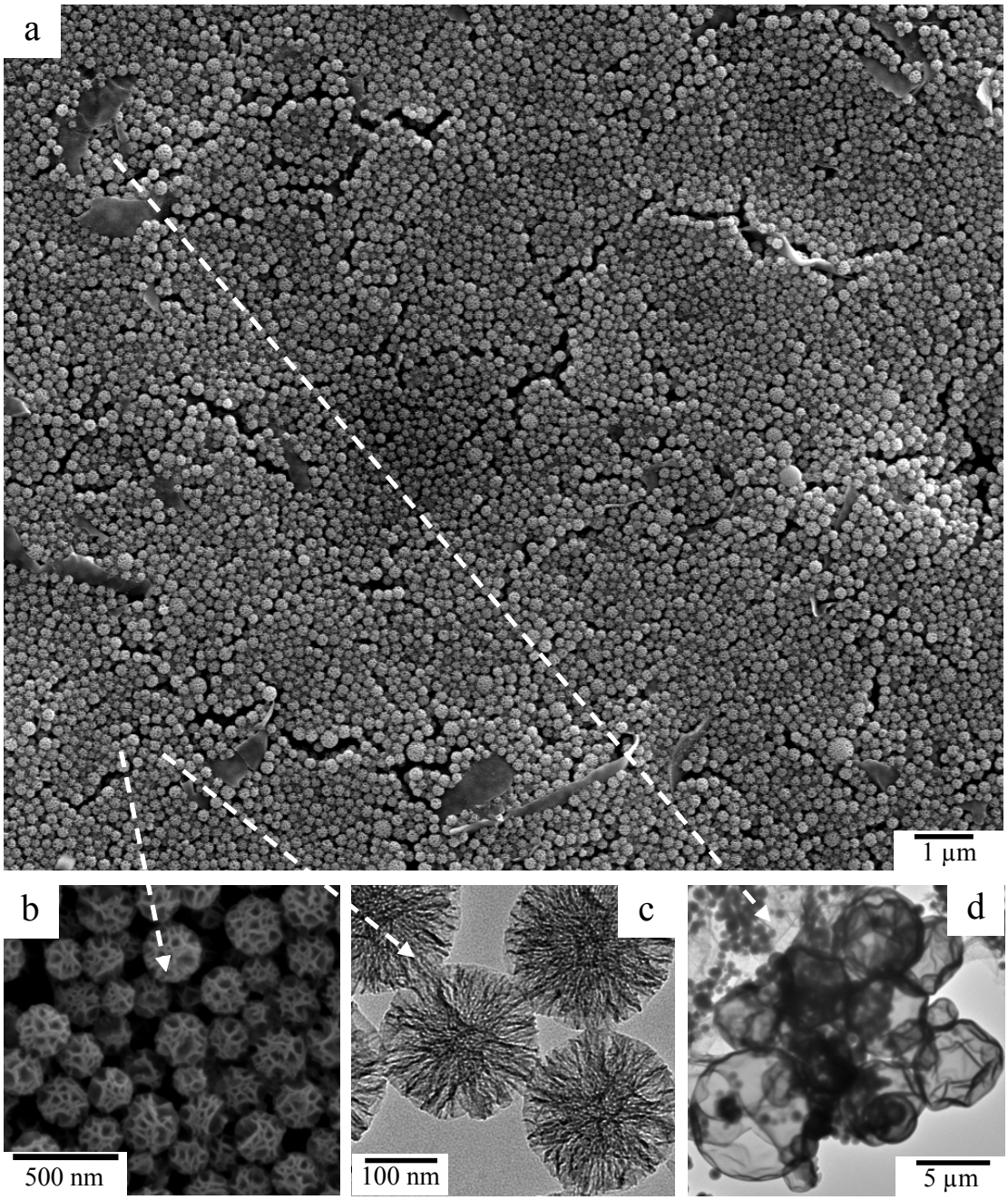

Fig. S10. SEM (a,b) and TEM (c,d) images of the St2' product synthesized in the emulsion containing 15 mL of ethyl ether and 5 mL of ethanol (before gradient centrifugation). The product contains silica nanoparticles with hierarchical pores (HPSNs-NH2) (b,c) and hollow spheres with varied particle sizes (size: 1-8 μm) (c,d).

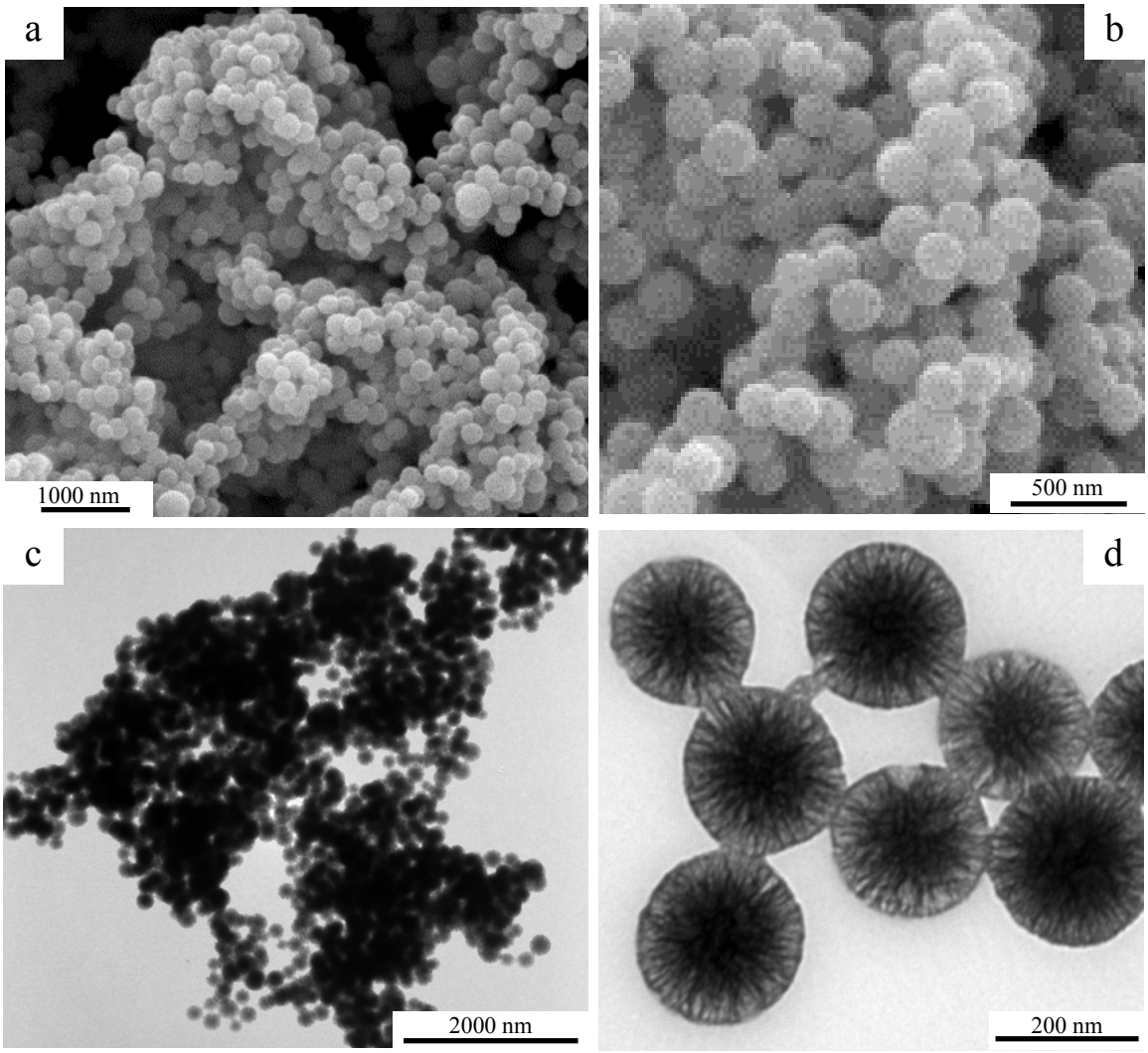

Fig. S11. SEM (a,b) and TEM (c,d) images of the product synthesized in the emulsion containing 10 mL of ethyl ether and 5 mL of ethanol (before gradient centrifugation). The product only contains silica nanoparticles with hierarchical pores (HPSNs-NH_2). And the pore sizes on particle surface become too small to observe (b), although the center-radial wrinkle structures still can be seen in the particles from TEM images (d).