Supplementary Material (ESI) for Chemical Communications
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Supporting Information

Mechanism of a Template-Free Synthesis of Monodispersed Hollow Silica Nanospheres with Tunable Size and Shell Thickness

Qiangbin Wang, Yan Liu, Hao Yan

1. Different organic solvents were used to study the hollow structures.

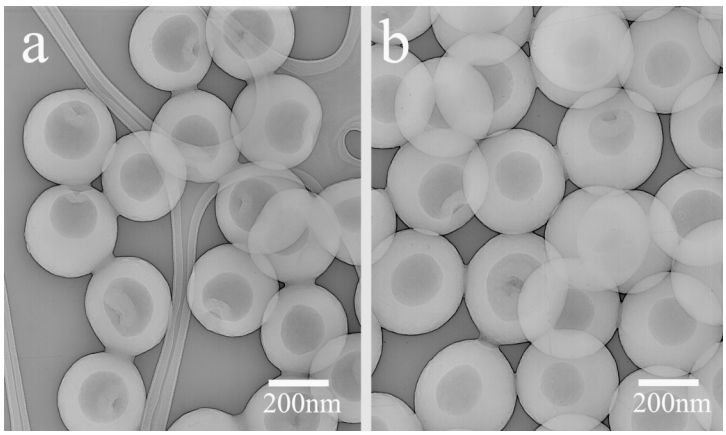

Figure S1. Effect of the different solvents on the hollow structures. a) methanol; b) ethanol. Lower polarity solvents, such as acetone, chloroform and hexanes, etc, can dissolve the hollow structure completely.

2. Different reaction conditions were investigated.

1). As the stirring speed decreases from 600 rpm to 450 rpm and 300 rpm, the particle size increases from 260 nm to 310 nm and 610 nm (Figure S2). This is because the slower stirring made larger sized emulsions which self-template the reaction leading to larger outer diameters.

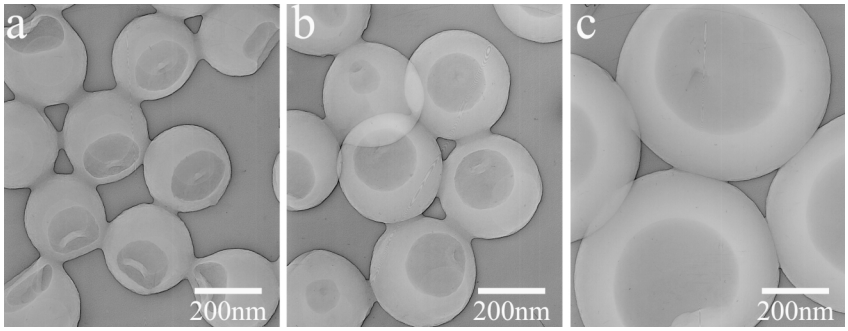

Figure S2. Effect of stirring speed on the hollow structure.

2). We varied the amount of PTMS from 750 μL, 930 μL, 1120 μL to 1310 μL and kept all other

conditions the same (hydrolysis 1 min, condensation 1 h, 43 μL HNO_3, 10 mL NH_4OH, T=60^oC). The particle size shows a small increase from 260 nm to 300 nm, and the pore size show little change (~ 140 nm).

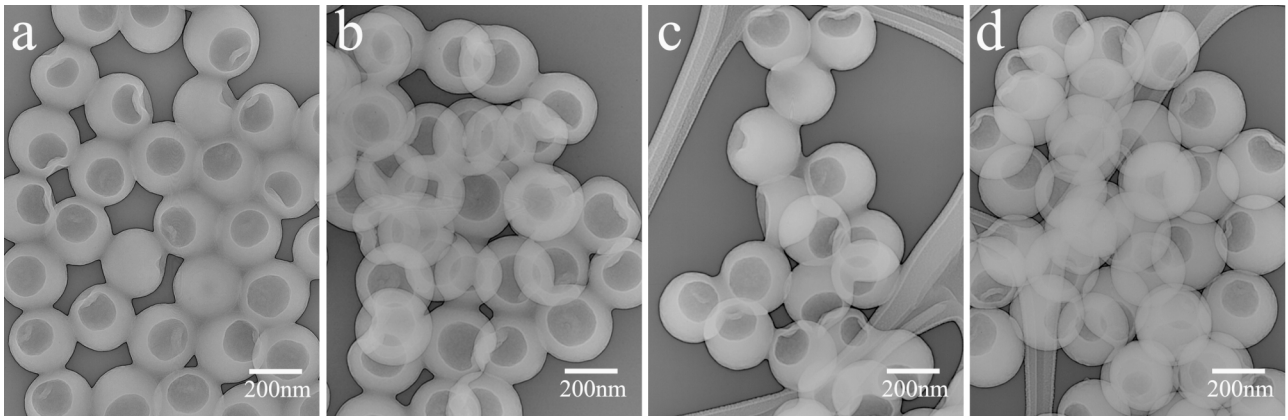

Figure S3. Effect of PTMS concentration on the SiO_2 hollow structure.

3). We varied the reaction temperature from 40^oC to 50 ^oC, 60 ^oC, and 70 ^oC and kept all other conditions the same (hydrolysis 1 min, condensation 1h, HNO_3 43 μL, 1.12 mL PTMS, 10 mL NH_4OH). Increasing reaction temperature from 50 to 60 ^oC, the particle size was the same and the pore size decreased (Figure S4a and b), indicating more complete reactions at higher temperature. There were no particles formed at 40 ^oC, and no central pore formed at 70 ^oC (Figure S4c) due to too slow reactions at 40 ^oC (no condensation at 1h) and too fast reactions at 70 ^oC (complete condensation at 1h).

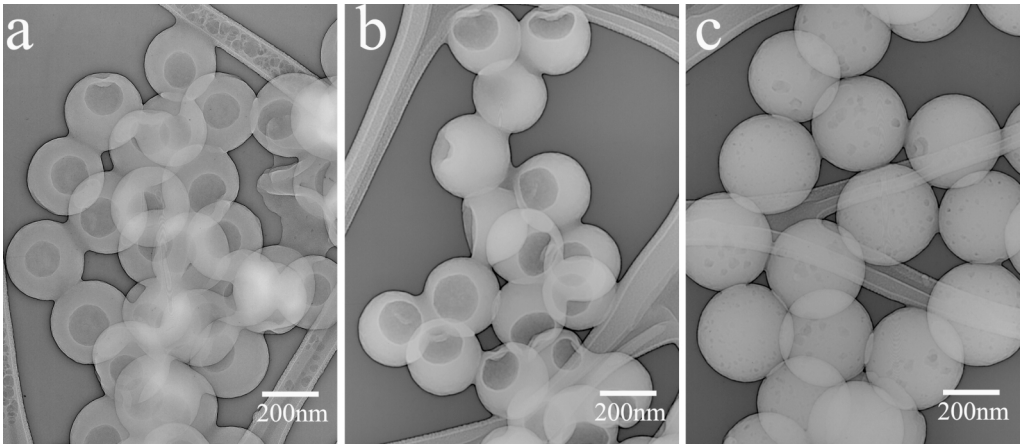

Figure S4. Effect of reaction temperature on the hollow structure.

4). We varied the amount of HNO_3 from 32.25 μL to 43 μL, 51.6 μL and 64.5 μL and kept all the other conditions the same (hydrolysis 1 min, condensation 1 h, 1.12mL PTMS, 10 mL NH_4OH, T=60^oC). Little change of the particle size (~ 280 nm) and pore size (~ 140 nm) was observed (Figure S5). This is because the hydrolysis step does not control the outer diameter nor the shell thickness.

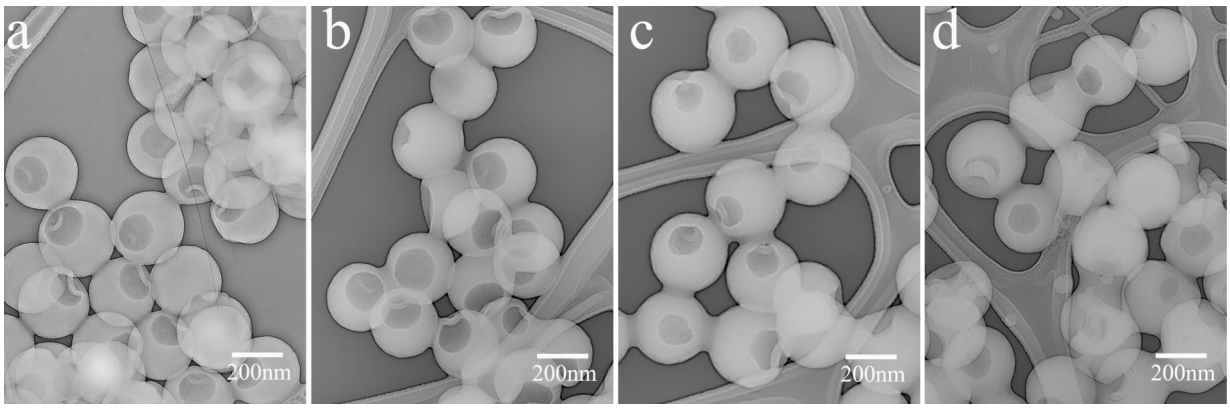

Figure S5. Effect of acid concentration in the hydrolysis step on the hollow structure.

5). We varied the amount of NH_4OH from 7 ml, 9 ml to 12 ml and kept all the other conditions the same (hydrolysis 1 min, condensation 1 h, 43 μL HNO_3, 930 μL PTMS, T=60^{o}C). The particle size show little variation, with average diameter ~ 340 nm. But the pore size decreased from 180 nm, 165 nm, to 150 nm with increasing NH_4OH concentration (Figure S6), indicating more condensation reaction is completed with higher base concentration.

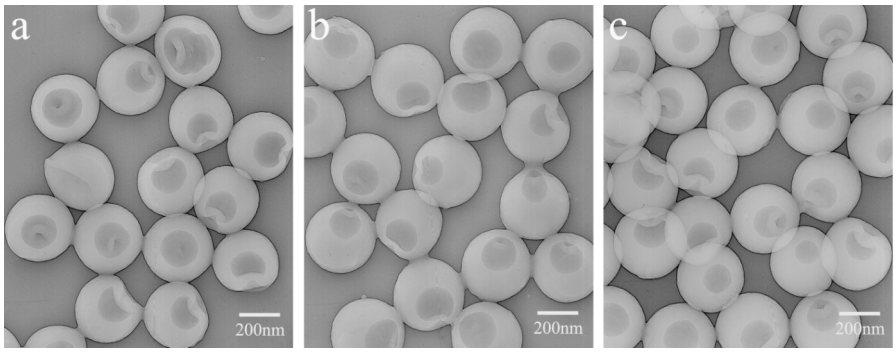

Figure S6. Effect of the base concentration in the condensation step on the hollow structure.

3. Different drying procedures were used to study the morphology of the hollow structures.

It is noted that the hollow structures with thinner shells could be deformed by the drying process showing an inward dent on the surface (apple shaped，Fig. 1a-c in the main text). This is because that during the air-drying process, the evaporation of the solvent entrapped in the shell caused a negative pressure within the hole. The material of the shell (polymer of PTMS) is soft and compressible, which yields to the negative pressure to form the dent. Thicker shells are more resistant to the pressure change, showing fewer dents or no dent (Fig. 1d-f in the main text). Changing the drying method, from air-drying to drying accelerated by IR lamp caused more denting (Fig. S7b). While using freeze-drying, i.e. freezing the sample in liquid nitrogen then subliming the frozen sample under vacuum can avoid the change in the surface tension of a liquid/solid interface, thus result more perfect spherical morphology (Fig. S7c).

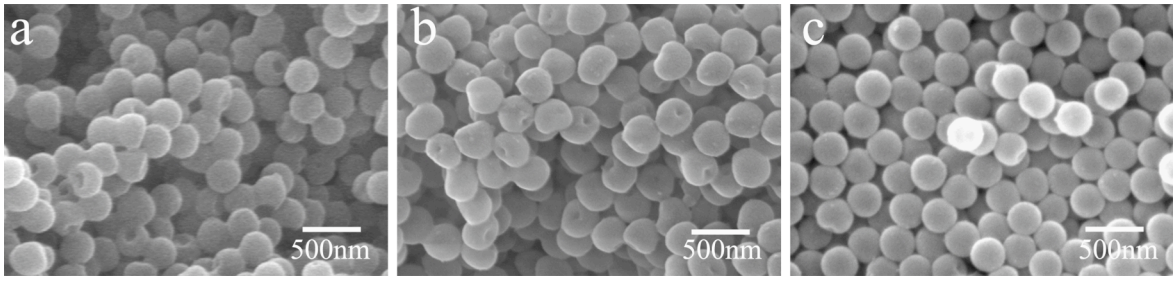

Figure S7. SEM images of the hollow structures that prepared and washed with ethanol. The samples were dried by different methods and showed different surface morphology. a) air-drying, b) IR-lamp accelerated drying, and c) freeze-drying.

4. Characterization method.

The shell thickness of the hollow structure is measured by subtracting the diameter of the hollow cavity from the diameter of the whole particle, and divided by 2 to get the shell thickness. Over 100 particles from several TEM images are measured to get the particle average size, and the standard deviation is calculated from the above measurement.