Supporting information

Direct fabrication of complex 3D hierarchical nanostructures by reactive ion etching of hollow sphere colloidal crystals

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Experimental section

1. Materials

All chemicals were used as purchased without further purification. Tetraethoxysilane (TEOS, 98%), ammonia (28%, in water), styrene (99.5%), ethanol (100%), and 2,2′-azobis(2-methylpropionamidine) dihydrochloride

(AIBA) were obtained from Sigma-Aldrich. Microslides (75 mm×25 mm×1 mm) were cut into small pieces as substrates for the deposition of colloidal crystals.

2. Synthesis of PS@SiO_2 core-shell particles

PS@SiO_2 core-shell particles were synthesized based on the procedure described by Liu et al.[1] The size and the shell thickness can be controlled by adjusting the ratio of PS cores and the concentration of TEOS precursor. The PS cores（~214±11 nm）were synthesized by emulsifier-free emulsion polymerization. Uniform silica shells were directly coated on the surface of PS particles via the Stöber method.[2] The obtained PS spheres were subsequently dispersed in 50 ml ethanol with a concentration of 0.6 wt%. Then, 1.5 mL TEOS and 4 mL ammonia were added to the diluted PS suspension and stirred for 4 h at 50℃. The PS@SiO_2 colloids were purified by repeated centrifugation and redispersion in ethanol (5 cycles).

3. Fabrication of complex 3D hierarchical nanostructures from hollow SiO_2 sphere colloidal crystals (HSCCs) via reactive ion etching

First, PS@SiO_2 spheres CCs were prepared via convective self-assembly at 35℃ from an ethanol suspension with volume fraction of 0.10% for three days. Subsequently, the obtained PS@SiO_2 CCs were sintered at 550℃for 6 h with a heating rate of 2℃/min to remove the PS cores to produce HSCCs. Afterwards, the obtained HSCCs was put into a reactive ion etcher chamber (Oxford Plasmalab 100) at a pressure of ~20 mTorr. SF_6 gas with a flow of 25 SCCM was used to generate reactive ions. A forward power and ICP power of 5W and 150W was applied, respectively.

Characterization

Colloids and colloidal crystals were imaged by a scanning electron microscope (SEM, Philips XL 30 ESEM FEG). The hollow SiO_2 particles were characterized by a transmission electron microscope (TEM, JEOL 1011). The reflectance

spectra of the samples were obtained using an ocean optics spectrometer USB 4000 connected to a fiber optic reflectance probe.

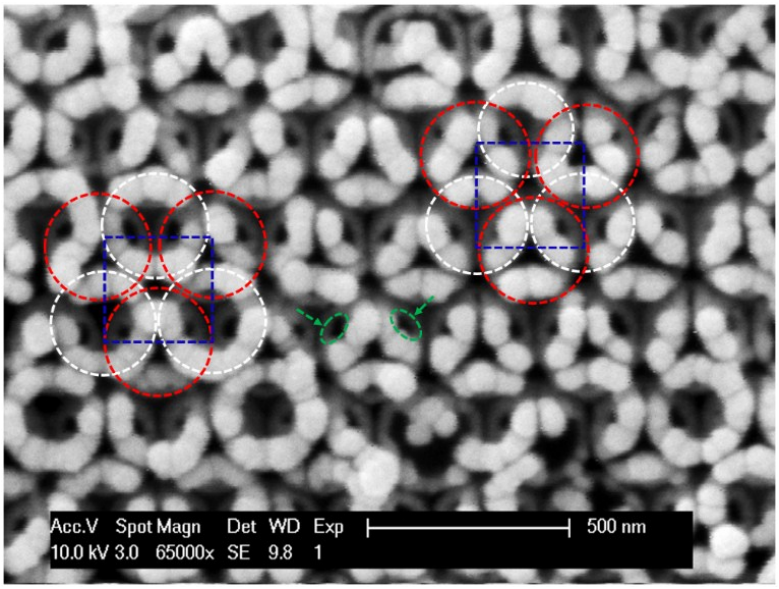

Figure S1. High magnification SEM image with slightly tilted angle (~10°) obtained after etching of ~ 7min, where each hollow sphere in the first layer was transformed into splitting nanorings, as indicated by white circles; meanwhile a more complex morphology was also introduced into the second layer of hollow spheres as indicated by red circles. The holes formed on the hollow spheres of the second layer indicated by green arrows result from the mask effect of the upper layer hollow spheres themselves because their top and bottom surface were opened, allowing the reactive species through the hollow spheres to reach the top surface of the hollow spheres of the second layer.

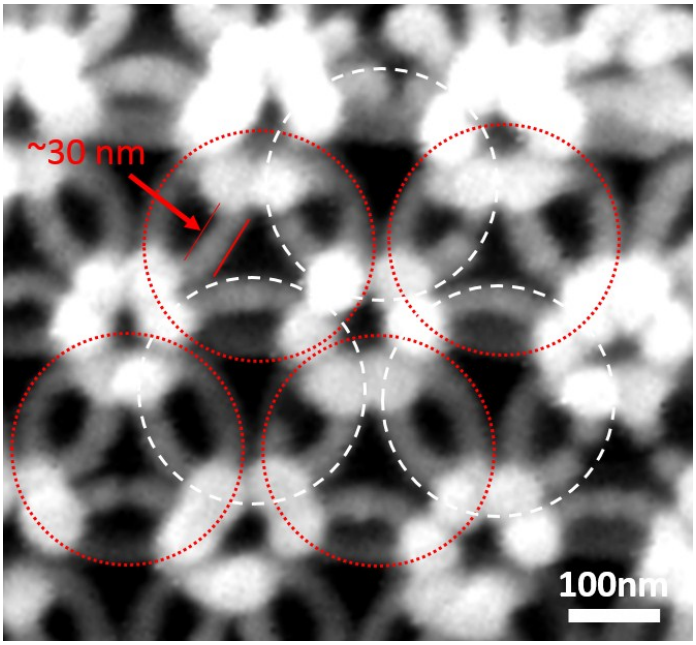

Figure S2. Magnified SEM image of the HSCCs was obtained after etching of 8 min, where each hollow spheres in the first and the second layer was transformed into six nanodots and hollow nanocage, respectively, as indicated by the white and red circles. The feature size of the hollow nanocage is as small as ~30 nm, as indicated by the red arrow.

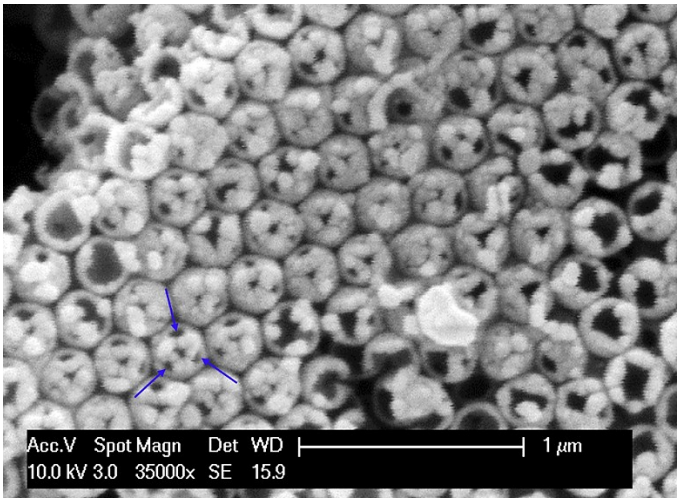

Figure 3. SEM image of the morphology of the second layer of HSCCs obtained after 5 min etching, in which the upper layer was removed by using adhesive tape. Blue arrows indicate the holes on the hollow spheres of the second layer resulting from the mask effect of the upper layer hollow spheres themselves, that had top and bottom surface opened.

1. Z.-F. Liu, T. Ding, G. Zhang, K. Song, K. Clays and C.-H. Tung, *Langmuir*, 2008, **24**, 10519.
2. W. Stober, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62.