Synthesis and formation mechanism of 1D hollow SiO₂ nanomaterials using *insitu* formed 1D NaCl crystal templates

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Experimental Section

Materials: TEOS, ammonia, glycerinum, isopropanol, isobutanol, sodium chloride and ethanol were of analytical grade and used as received and supplied by Aldrich. The water used was deionized.

*Synthesis of SiO*₂ *hollow nanobelts*: The synthesis of SiO₂ hollow nanobelts were achieved by using the NaCl nanobelts as the templates in basic solution at room temperature. Typiclly, a certain amount of NaCl/glycerinum (1.7M) solution (0.1ml) was added into the isopropanol (20ml), and agitated for 5min. To this suspension, TEOS (0.21ml), NH₃·H₂O (0.14ml) and H₂O (0.14ml) were added step by step, which was reacted at 25°C for 2h and the NaCl@SiO₂ composites were formed. And then, TEOS (0.24ml), NH₃·H₂O (0.1ml), and H₂O (0.45ml) were added step by step and reacted at room temprature for another 4h. Then the products were collected by centrifugation, washed with deionized water several times, dried at 200°C under air atmosphere overnight.

*Synthesis of SiO*₂ *hollow nanotubes*: For the synthesis of NaCl@SiO₂ nanotubes with size of about 150nm, a certain amount of NaCl/glycerinum (0.1ml) was added into the isobutanol (20ml). To this suspension, TEOS (0.30ml), NH₃·H₂O (0.2ml) and H₂O (0.2ml) were added step by step, which was reacted at 25°C for 2h. And then, TEOS (0.4ml), NH₃·H₂O (0.1ml), and H₂O (0.45ml) were added step by step and reacted at room temprature for another 4h. Then the products were collected by centrifugation, washed with deionized water several times, dried at 200°C under air atmosphere overnight.

Characterization: The microscopic morphology was obtained using a field-emission

scanning electron microscope (FE-SEM, HITACHI S-3400, Japan) at an acceleration voltage of 15kv. The microstructure and composition of the samples were further analyzed using a transmission electron microscope (TEM, JEOL 2010) with an energy –dispersive spectrometer (EDS) attachment. The powder X-ray diffraction (XRD) patterns were recorded using a Rigaku UItima IV diffractometer with Cu Ka X-ray radiation (r=1.5405 A), using a voltage and current of 40 kV and 40mA, respectively, with a scanning rate of 5° min⁻¹. N₂ adsorption/desorption measurements were performed using Micromeritics ASAP 2010. The pore size distribution was calculated from the adsorption branch of the sorption isotherms using the Brunauer-Joyner-Halenda (BJH) method.

Figure S1. Nitrogen adsorption-desorption isotherms and pore size distributions of mesoporous SiO_2 hollow nanobelts (a) and SiO_2 hollow nanotubes (b). The inset shows the pore size distribution calculated from the desorption branch.



Figure S2. Typical SEM image of the RD-NaCl@SiO₂ composites with size of about 2um (a), NaCl@SiO₂ nanobelts (before filtration) prepared at different adding amount of water of 0.05ml (b), 0.25ml (c), 0.45ml (d), 0.65ml (e), while the adding amount of the TEOS and ammonia was fixed at 0.15ml and 0.1ml. When the adding amount of water was 0.05ml, NaCl crystals in NaCl@SiO₂ composites were partly dissolved and released (f), the red arrows shown the NaCl@SiO₂ yolk-shell composites. The inset in image e shows a TEM image of the SiO₂ hollow particles.



Figure S3. SEM (a), TEM (b) images of NaCl@SiO₂ nanobelts and SiO₂ hollow nanobelts (c), the

inset show the SEM image of the SiO_2 hollow nanobelts.



Figure S4. Typical SEM images of NaCl@SiO2 nanobelts prepared at different adding amount of

TEOS of 0.21ml (a), 0.24ml (b), 0.27ml (c), while the adding amount of the water and ammonia,



was fixed at 0.45ml and 0.1ml.

Figure S5. SEM image of ultrafine NaCl@SiO₂ nanowires that had just outflowed of the SiO₂ mesoporous shells.



Figure S6. Typical SEM image of the rhombic dodecahedron NaCl cubic crytals (a) with size of about 150nm and TEM image of the NaCl@SiO₂ cubic compsites (b). SEM image (c) of SiO₂ hollow cubic materials and NaCl@SiO₂ nanowires. TEM image (d) shows the SiO₂ hollow cubic after centrifugation. The pure NaCl@SiO₂ nanowires (e) were collected after centrifugation, and the inset in figure e shows the TEM image of the NaCl@SiO₂ nanowires. After washing with water several times, SiO₂ hollow nanotubes (e) are obtained, the insert confirms the hollow structure of the SiO₂ hollow nanobelts.







Table S1

Table S1. The influence of coating ratio of TEOS: NH₃H₂O: H₂O and NaCl on the

- SiO₂ hollow nanobelts.
- (1) After the RD-NaCl@SiO₂ composites with size of about 2um formed (0.1ml NaCl/Glycerinum solution, 0.21 ml TEOS, 0.14ml NH₃·H₂O and 0.14 ml H₂O were added to the solution for the fromation of RD-NaCl@SiO₂ composites), the second coating ratio of TEOS: NH₃H₂O: H₂O are taken from 0.15: 0.1: 0.05 to 0.27: 0.1: 0.65.

	NaCl/Glycerinum solution (ml)	TEOS (ml)	NH ₃ ·H ₂ O (ml)	H ₂ O (ml)	Yields of SiO ₂ 1D hollow materials(mg)	Mophologies
1	0.1	0.15	0.1	0.05	2	Hollow Nanobelts (>90%) and nanotubes
2	0.1	0.15	0.1	0.25	6	Hollow Nanobelts (>90%) and nanotubes
3	0.1	0.15	0.1	0.45	10	Hollow Nanobelts (>90%) and nanotubes
4	0.1	0.15	0.1	0.65	0	No
5	0.1	0.21	0.1	0.45	14	Hollow Nanobelts (>90%) and nanotubes
6	0.1	0.24	0.1	0.45	19	Hollow Nanobelts (>90%) and nanotubes
7	0.1	0.27	0.1	0.45	21	Hollow Nanobelts (>90%) and nanotubes