Supplementary Information

Synthesis of NaCl single crystals with defined morphologies as templates for fabricating hollow nano/micron-structures

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Experimental Section

Synthesis of NaCl single crystals with certain morphology.

A NaCl-glycerol solution (1.6M) was heated at 140°C, and 0.1ml of the solution was added dropwise to a monohydric alcohol solution (20ml) agitated in ice bath for 5 minutes to obtain white precipitates. The precipitate was collected by centrifugation and washing with ethanol, and then preserved in vacuum for further measurements. The NaCl single crystals with RD morphology can be obtained by using the 2-propanol as solvent, while the NaCl submicro-cubes can be abtained when using the 2-butanol as solvent. The NaCl single crystals with Octahedron morphology were synthesised through aging the as-synthesized NaCl submicro-cubes without washing for 24 h in dry atmosphere.

Synthesis of NaCl with 8-fold flower-like morphology. Experimental section: 1, 3, 5, 7ml of H_2SO_4 solution was mixed with 19, 17, 15, 13ml of ethanol respectively and labeled as H-Ethanol-1,2,3,4 solution, 0.1, 0.2, 0.3 and 0.4ml of NH_4OH solution was mixed with 20ml ethanol respectively and labeled as N-Ethanol-1,2,3,4. A NaCl-glycerol solution (1.6M) was heated at 140°C, and 0.1ml of the solution was added dropwise to the mixed solution (20ml) agitated in ice bath for 5 minutes to obtain white precipitates. The precipitate was collected by centrifugation and washing with ethanol, and then preserved in vacuum for further measurements.

Synthesis of SiO_2 hollow nano/micro-structure particles.

TEOS (0.1ml), $NH_3.H_2O$ (0.05ml) and H_2O (0.05ml) were added into the isopropanol (20 ml) with precipitated RD-NaCl templates with average size of about 1.5um (10mg) step by step, and the reaction took place at 0℃ for 5 h. The

NaCl@SiO_2 core-shell products were collected by centrifugation. The NaCl@SiO_2 composites were calcined in air at 600°C to increase mechanical strength of the amorphous SiO_2. After cooled down to room temperature, then the SiO_2 hollow nano/micro-structure particles can be obtained by washing with water and drying for 24h at 80°C.

Synthesis of TiO_2 hollow nano/micro-strucutre particles

Deionized water (0.2ml) and TBT solution (0.5ml) in isopropanol (5ml) respectively at room temperature were added dropwise into the isopropanol (20ml) with precipitated NaCl templates (10mg) under stirring within 30 min. The mixture was stirred for 1h and then heated to 50 °C for another 1.5 h. The NaCl@TiO_2 composites were calcined in air at 650°C to crystallize the amorphous TiO_2. After cooled down to room temperature, then the TiO_2 hollow nano/micro-structure particles can be obtained by washing with water and drying for 24h at 80°C.

Instrumentation:

Powder XRD measurements were performed on a Philips Xpert. Advance diffractometer using CuK-α1 radiation (λ=0.154056nm). The TEM images were obtained using a JEOL JEM-2010F FETEM. The SEM measurements were conducted using a JEOL S-4800 FESEM.

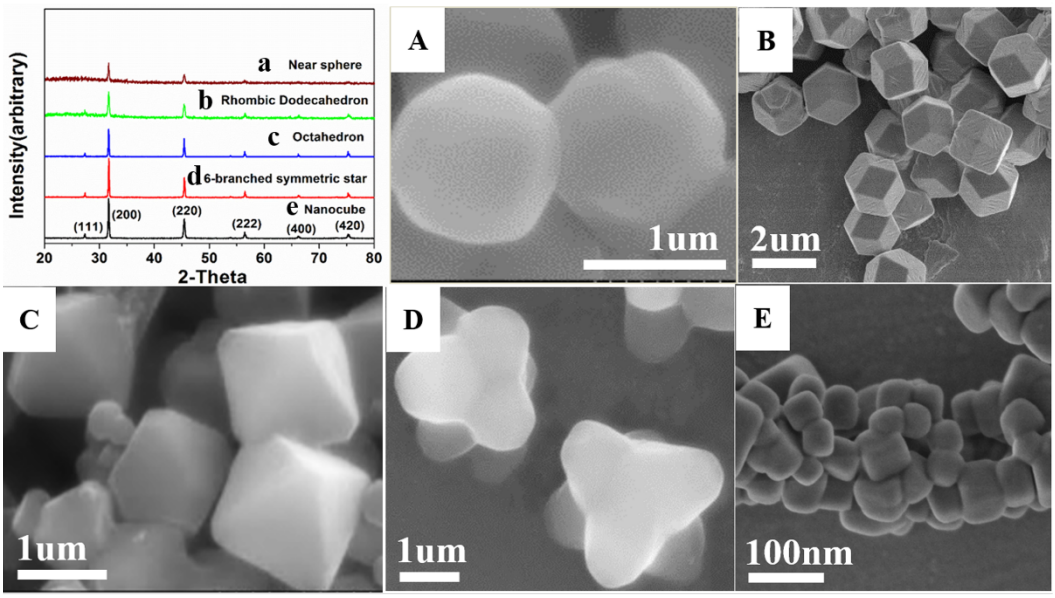

Figure S1. XRD pattern of the as-prepared NaCl with different morphologies: Near sphere (wine red), RD (green), Octahedron (blue), 6-branched symmetric star (red) and Nanocubes (black).

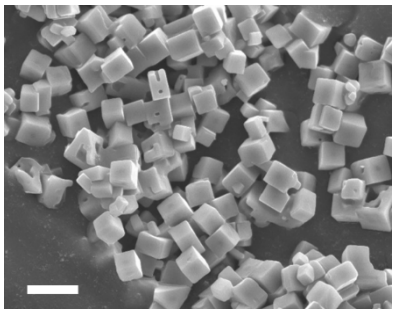

Figure S2. SEM image of the NaCl crystals prepared by adding aqueous NaCl to 2-propanol. Scale bar, 10um.

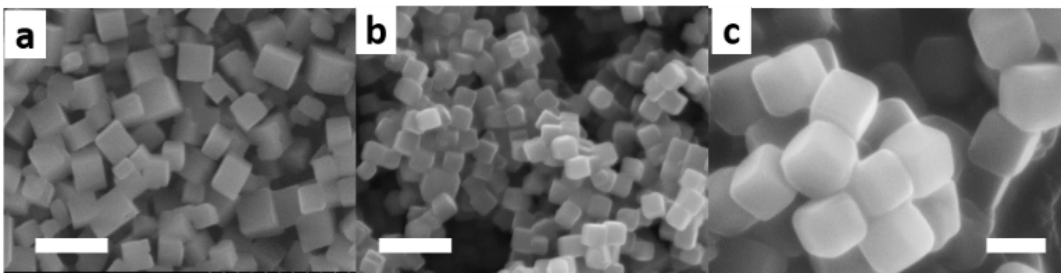

Figure S3. SEM images of the NaCl single crystals prepared in ethanol (a), propanol (b) and butanol (c) solvents as alternative to the 2-propanol. The scale bars in a, b and c are 5um, 3um and 1um respectively.

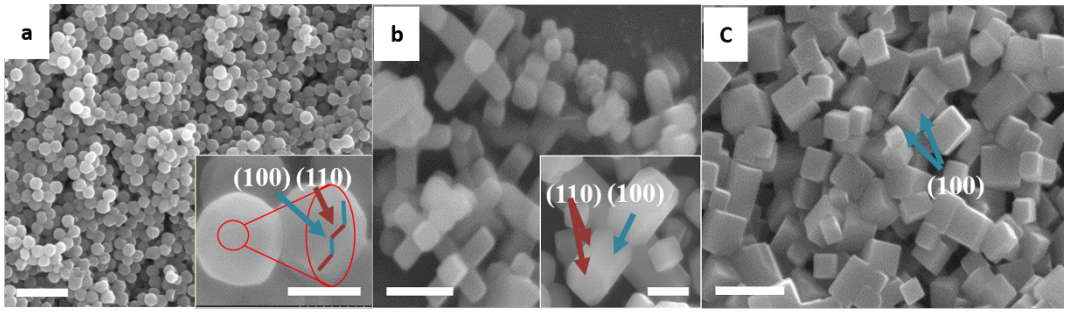

Figure S4. SEM images of the NaCl single crystals with different morphologies obtained by adding different amount of NaCl-glycerol (a) 0.15ml, (b) 0.2ml and (c) 0.3ml into the isopropanol (20ml). The scale bars in a, b and c are 5um, 3um and 10um respectively, and the inset scale bar in a and b are 1um and 2um.

The morphology of NaCl single crystals can be strongly affected by the relative supersaturation of NaCl, which can be modulated by adjusting the amount of NaCl-glycerol solution or the type of solvents used for precipitation. With a fixed NaCl concentration of 1.6 M, for example, the RD NaCl crystals (Figure 1) were obtained by adding 0.1 ml NaCl-glycerol solution to 20 ml 2-propanol solvent. A dramatic change in morphology occurs when increasing the amount of NaCl-glycerol solution. As demonstrated in Figures S5 a, b and c, (ESI†) adding the NaCl-glycerol amount of 0.15, 0.2 and 0.3 ml to the 2-propanol solvent lead to formation of NaCl crystals with near sphere, 6-fold symmetric star, and cube morphologies, respectively.

From thermodynamics and Thomson-Gibbs equation, the morphological change can be attributed to the fact that the surface of crystals can be easily controlled via simply adjusting supersaturation of crystal growth units in the growth medium during the crystal growth process. As a result, the crystal growth along <110> direction will be accelerated, and the {110} surfaces tend to be unstabilized and replaced gradually by the {100} low-energy ones. When increasing the adding amount of NaCl-glycerol solution, the surfaces of the NaCl crystals were enclosed by both {110} and {100} ones. As the crystal grow along six <110> directions, then the near sphere (Figures S5a) and 6-fold symmetric star NaCl crystals (Figures S5b) formed gradually. When the relative supersaturation of NaCl increased to the extremely, the nucleation rate alone <110>

directions were the fastest ones, then {110} surfaces of NaCl were thoroughly substituted by {100} ones, and NaCl cubes formed (Figures S5c).

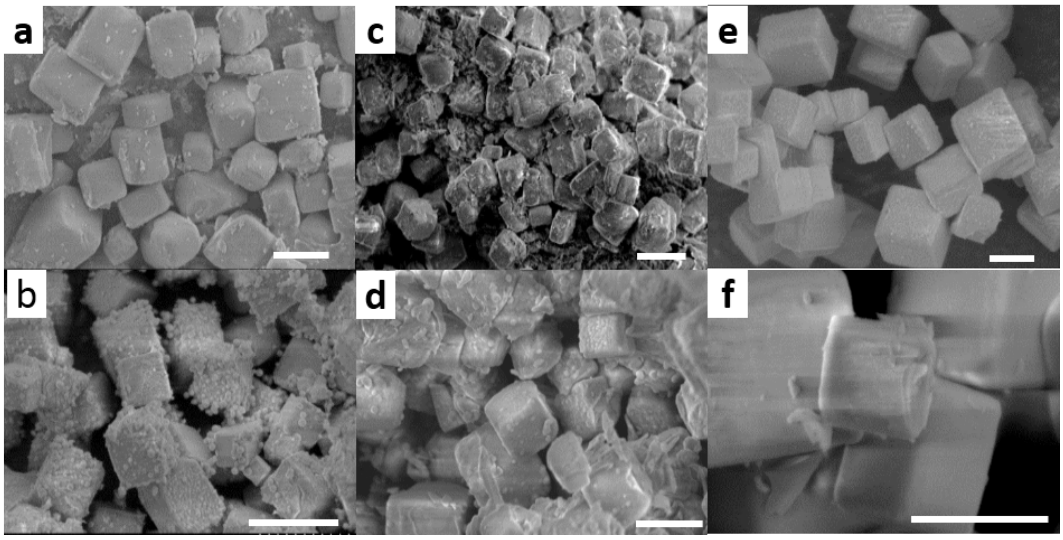

Figure S5. SEM images (a-f) of the NaCl@SiO_2 core-shell products corresponding with the ratios of TEOS: NH_3H_2O: H_2O (1-6) in Table S1. The scale bars in a, b, c, d, e and f are 5um, 10um, 1um, 10um, 5um and 5um respectively

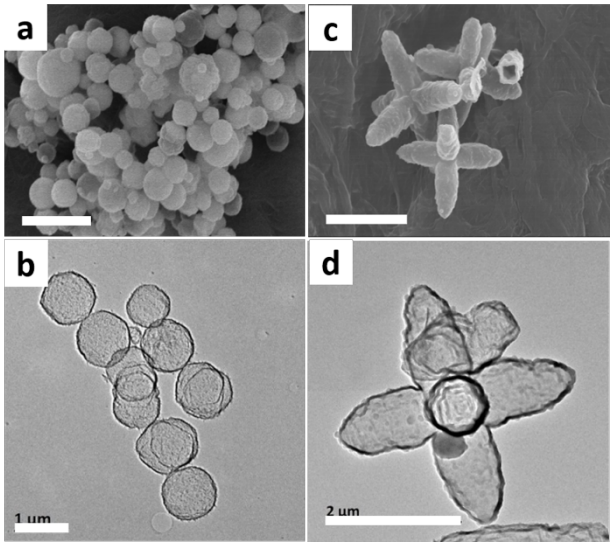

Figure S6. SEM and TEM images of SiO_2 hollow structures with morphologies of spheres (a, b), and 6-fold symmetric star structures (c, d) fabricated using the NaCl WSGT. The scale bars in a, b, c, and d are 2um, 1um, 3um, and 2um respectively.

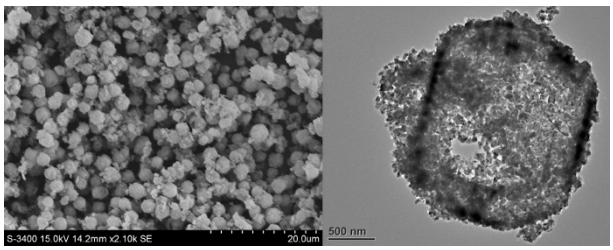

Figure S9. SEM and TEM images of TiO_2 RD-hollow structures fabricated using the NaCl WSGT. The scale bars in a, and b are 20um, and 0.5um respectively.

Table S1

Serial number	NaCl (g)	TEOS (ml)	$NH_3 \cdot H_2O$ (ml)	H_2O (ml)	Products
1	1	0.5	0.5	0.5	a
2	1	1	1	1	b
3	1	0.8	0.4	0.8	c
4	1	0.8	0.8	0.8	d
5	1	0.8	0.4	0.6	e
6	1	0.8	0.4	0.4	f
7	1	0.8	0.4	0.3	Failed
8	1	0.8	0.4	7	Failed

Table S1. The coating ratio of TEOS: NH_3H_2O: H_2O and NaCl[1].

(1) The coating ratio of TEOS: NH_3H_2O: H_2O are taken from 0.5:0.5:0.5 to 0.8:0.4:0.7 while the quality of the NaCl microcubic crystal templates with average size of about 5um are 1g. The as-prepared NaCl@SiO_2 from sample-1 to sample-6 was shown in figure S5. The coating process 7 and 8 were failed for no TEOS hydrolyzing or only silica particles observed confirmed by water dissolution.