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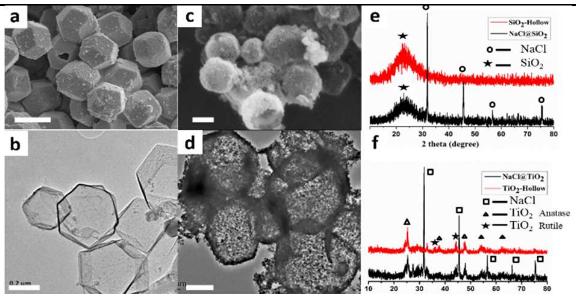

***Photos**: Hollow structured SiO_2, TiO_2 and related XRD before and after the NaCl template removed.*

Synthesis of NaCl Single Crystals with Defined Morphologies as Templates for Fabricating Hollow Nano/micro-structures

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Abstract

Hollow nanostructures have a wide range of applications in nanotechnology. To accurately fabricate such nanostructures, the first and common key step is to synthesize high quality templates with controlled symmetry and geometry, best through a green, efficient, and economical approach. However, it has always been a challenge up to now. In the present work, we report a conceptually new simple approach, i.e., directly synthesizing templates from NaCl solutions. The property of templates can be tailored by selecting appropriate organic solvents and varying the crystal growth conditions. These naturally abundant NaCl single crystal templates are water-soluble, environmental-friendly and uniform in both geometry and size, which hence are ideal for preparing high quality hollow nano/micro structures. The new approachmay have potential to replace the conventional hard or soft template approaches. Furthermore, this work has revealed the formation mechanism of nano/micron NaCl crystals with different size and geometry.

Key words: NaCl water-soluble green templates, SiO_2 hollow structure, TiO_2 hollow structure, NaCl novel morphologies

Introduction

Fabrication of functional materials in the nano-to-micrometer scale has attracted much attention from both scientific and technological perspectives, since such materials exhibit unique and superior properties resulting from the extremely small particle size and well-controlled shape.[1] Among various types of functional nano-materials, the category of hollow structured ones is of special interest especially for such applications as adsorbents, catalysts, sensors, plasmonics, and bio-medical applications for drug delivery or controlled drug release carriers.[2] Conventional synthesis of hollow structures is usually using either the soft or hard template methods. The latter one is based on the use of pre-shaped solid particles of polymeric or ceramic compounds such as polystyrene (PS), $CaCO_3$, or SiO_2, and has found more applications.[3-7] In a typical process of the hard template method, the target material is firstly coated onto a hard template, and the template is selectively removed by firing or chemical etching to leave the target material being hollow shaped. Obviously, removal of template by either firing or etching is technically complicated and costly, and often accompanied by the release of environmental hazards resulting in safety risks.[8]

Therefore, searching for a green and easy-to-removal template method is attractive and challenging.

Sodium chloride (NaCl) is an important material with great abundance. It has existed in most organisms from the ancient time, and also in our ordinary life (taking the table salt as a good example). As is well known from the table salt, the crystallographic shape of natural NaCl is limited only in a highly regular cubic form with facets bounded by {100} surface, which has the lowest surface energy among others.[9] Similarly, NaCl single crystals synthesized in laboratory are seldom of crystal shapes other than cubic, and even the cubic ones have much difficult in down-sizing its size to nanometer scale.[6] This is most probably due to the fact that the order in surface energy in cubic ionic crystals is γ {100}<γ {111}< γ {110}, which makes the {111} and {110} surfaces very unstable under normal conditions. As a result, there has hardly been any report on size and/or morphological controlled synthesis of NaCl single crystals and the deliberate use of them in high-tech related fields.

Despite the universality of NaCl in resource and its easy-to- removal property, to the best of our knowledge, the deliberate use as water-soluble green templates (WSGT) for fabrication of hollow structured functional materials has seldom been reported.[10] This is because it has been extremely difficult to control the size and morphology of the NaCl single crystal during growth. In fact, the $NaYF_4$ nanocages were reported to be able to facet-selective epitaxially grow on NaCl nanocubes.[11] However, the preparation procedure of NaCl nanocube was very complicated and not universal, and the only morphology was stillthe nanocube. Recently it has been reported that the SnO_2 hollow cubes can be synthesized by one-step in-situ coating of NaCl nanocubes.[12] However, except for the non-special morphology, the NaCl nanocubes could only be used in such a very special situation where NaCl involved in the formation reaction of SnO_2, rather than as a universally applicable template. Thus, none of the above-mentioned methods have successfully created single crystals with controlled morphologies. The exploration of universally applicable synthesis method for monodispersed NaCl as WSGT in the fabrication of hollow structured functional nanomaterials is highly significant.

In this work we have established a versatile method for the synthesis of size and morphology controlled NaCl single crystals by controlled precipitation of NaCl in diluted glycerol solutions. We have succeeded so far in creating NaCl crystals with defined morphologies including the rhombic dodecahedron (RD), octahedron, and submicro-cube. Such NaCl single crystals have been used as novel WSGT to fabricate hollow structured materials. As a remarkable example, the SiO_2 and TiO_2 hollow nanostructures accurately replicate the varied shapes of the NaCl templates.

Results and discussions

The RD-NaCl is used as an example to demonstrate the typical synthesis process. A NaCl-glycerol solution was heated at 140^{o}C, and certain amount of the solution was added dropwise to a 2-propanol solution agitated in ice bath to obtain white precipitates. The obtained precipitate was identified to be face centered cubic NaCl (JCPDF 89-3615) by X-ray diffraction (XRD) (Supplementary Figure S1, ESI†).

Figure 1 shows the morphology of RD NaCl single crystals. It is clearly seen that the NaCl single crystals exhibit an almost perfect rhombic dodecahedra shape with quite uniform size (Figure 1 a and b). The SAED pattern (Figure 1c) reveals the single crystal nature indexed to the [011] zone axis of FCC NaCl,[13] indicating that the crystal is enclosed by {110} basal planes.

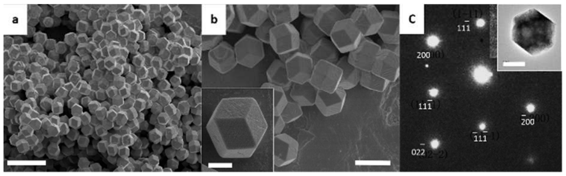

Figure 1. SEM images of RD NaCl (a) and (b, enlarged), and SAED pattern (c) with TEM image inset. The scale bars in a, b and c are 10 um, 3 um and 5 1/nm respectively, and the inset scale bar in b and c are 1 um and 500 nm.

The ionic diffusivity of Na^+ and Cl^- in aqueous solution is extremely high. The fast ion diffusivity and non-directionality lead to formation of the cubic morphology under the conventional conditions. Therefore, in order to obtain non-cubic morphologies, the ionic diffusivity of Na^+ and Cl^- must be drastically reduced. This is realized in this work by using a high-viscosity glycerol instead of water (12070 mPa·s at 0 ^{o}C against 1.787 mPa·s of water). Thus, it becomes possible spatially and temporally to develop other potential orientations during the crystal growth.[14] The effect of glycerol on the crystal growth was confirmed by the fact that numerous trials of adding NaCl aqueous solution to 2-propanol resulted in only cubic-like crystals with larger size about 6 um (Supplementary Figure S2，ESI†).The nucleation time (about 1 second) of NaCl when using NaCl aqueous solution (1.6 M) was much shorter than that (about 20 seconds) using NaCl-glycerol solution (1.6 M) as the source of Na^+ and Cl^-.[15] This confirms that glycerol can drastically reduce the ionic diffusivity of Na^+ and Cl^-, and therefore plays a very important role in formation of NaCl crystals enclosed by {110} surfaces.

From thermodynamics and the well-known Thomson-Gibbs equation, 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. The crystal faces with higher surface energy will appear when the supersaturation of the growth units is increased in the medium. Such inference combines both apparent thermodynamic and kinetic factors that governs the crystal growth process, and has been successfully validated by examples ranging from ionic, molecular to metallic crystals.[26] The formation of RD NaCl crystals enclosed by {110} faces might due to the appropriate supersaturation of NaCl. Hai-xin Lin and co-workers observed that NaCl crystals with higher surface-energy faces, such as {110}, were synthesized through tuning the supersaturation.

The proposed supersaturation strategy provides an effective way to control the shape and surface structures of micro/nanocrystals, which is important for both fundamental research and practical applications. [15] Small NaCl submicro-cubes (Figure 2) can be obtained simply by using the 2-butanol as solvent which has one more -CH_2- lipophilic group, as a replacement of 2-propanol, i.e., by adjusting the degree of NaCl supersaturation. The SEM and TEM images (Figure 2a, b) show that NaCl submicro-cubes are of about 120 nm in size. The square spot array of SADE pattern (Figure 2c) confirms that the NaCl submicro-cubes are enclosed by {100} planes with the zone axis of [001].

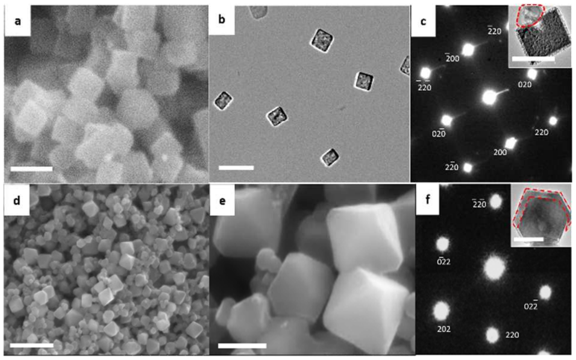

Figure 2. SEM and TEM images of the NaCl submicro-cubes (a) and (b), and the SAED pattern (c) from a single cube recorded along the [001] zone axis. The scale bars in a, b and c are 200 nm, 200 nm and 5 1/nm respectively, and the inset scale bar in c are 100 nm; SEM images of octahedral NaCl (d) and (e, enlarged), and SAED pattern (f) recorded along the [-111] zone axis of a single crystal shown inset. The scale bars in d, e and f are 5 um, 5 um and 5 1/nm respectively, and the inset scale bar in c are 200 nm. The part of NaCl crystal in the red dash line was regrown under the electron beam irradiation [6d].

The formation of monodispersed NaCl submicro-cubes using 2-butanol is a result of the more accelerated crystal growth by 2-butonal than 2-propanol. We observed that the NaCl submicro-cubes could immediately appear when adding the NaCl-glycerol solution into the 2-butanol solution, in comparison to other solutions (e.g., ethanol, butanol, propanol or 2-propanol) where the NaCl crystallization could take dozens of seconds. Since substances with similar polarity can be solvable in each other,[20] the solubility of hydrophilic NaCl in 2-butanol with more lipophilic groups should be lower than in 2-propanol. Therefore, the relative supersaturation in 2-butanol is higher than that in 2-propanol, leading to a much more higher nucleation rate due to the reduced nucleation energy barrier.[21] As is well-known, higher supersaturation results in smaller crystallites during the crystallization. [26] Considering the viscosity of the 2-butanol (3.9 mPa·s at 20 °C) is much higher than that of 2-propanol (2.8mPa·s at 20°C), the ionic diffusivity of Na^+ and Cl^- around the interface between glycerol and the organic molecules like 2-butanol is greatly reduced. The abovementioned two aspects may explain why the Na^+ and Cl^- ions are relatively easier to nucleate than diffuse in favor of the nanocube crystal growth.

Interestingly, we obtained monodispersed single octahedral NaCl crystals by aging the as-synthesized NaCl nanocubes for 24 h in dry atmosphere. To the best of our knowledge, this is the first time for the synthesis of the octahedral morphology of NaCl. Upon aging, most (>85%) of the NaCl cubes were transformed into octahedrons with an average edge length of 450 nm, as shown in SEM images of Figure 2d, e, and the morphology of the rest of the NaCl crystals were truncated octahedron. The SAED pattern in Figure 2f indicates that the NaCl octahedron is a single crystal bounded by {111} facets with the zone axis of [-111], being similar to the octahedral Au nanocrystals enclosed by {111} facets reported elsewhere.[22-24]

The growth mechanism of the octahedral NaCl crystals could be related to the Ostwald ripening process caused by the high activity of nanoparticles.[10] In addition, a small amount of residuals (glycerol, 2-butanol) which are closely contacted to the NaCl nanotubes play an important role in the formation of octahedron. In details, the glycerol acts more likely as a growing medium for larger NaCl particles, and the 2-butanol provide appropriate supersaturation for the {111} higher surface energy of NaCl crystals. [6, 18]

Finally we demonstrate the application of as-synthesized monodispersed NaCl single crystals. One of the most promising applications is the use of the nano/micron NaCl crystals as novel WSGT with well-tailored morphology for fabricating hollow-structures. The SiO_2 hollow nanostructures are successfully developed with various morphologies such as near sphere, 6-fold symmetric star, and RD by using the sol-gel[25] technique to coat SiO_2 on the NaCl templates with different geometries and subsequently removing NaCl by water dissolution. As NaCl is extremely water-soluble, removal of NaCl takes only a few seconds. Considering that NaCl is ubiquitous and almost unlimited in resource, such WSGT approach may set up a basis for the new generation of fabrication technology of hollow micro/nano-structures in favor of environment and multi-functionalities of materials.

Since hydrolysis of tetraethoxysilane (TEOS) requires water, while at the same time the NaCl is extremely water-soluble, it is critically important to control precisely the water content during hydrolysis process. Figure 3a, b show the SEM and TEM images of RD-hollowed SiO_2 structures formed using the WSGT method (Supporting information table 1 and figure S5 (ESI†)have shown the effect of the different ratio of the TEOS, NH_3H_2O and H_2O on coating SiO_2 onto NaCl microcubic crystal templates and their corresponding SEM images.). And the SiO_2 hollow structures with morphologies of spheres and 6-fold symmetric star structures (figure S6, ESI†) can also be obtained by using the NaCl WSGT. All of the morphologies are the replicas of original NaCl templates. The TEM images further show the uniform wall thickness (about 20 nm) of the nanostructure. No secondary solid SiO_2 particles could be observed. The TiO_2 hollow structured particles with morphology of RD can be also synthesized by using the NaCl crystals as the WSGT (Figure 3c, d). The phases of SiO_2 and TiO_2 were confirmed by XRD as shown in Figure 3e, f.

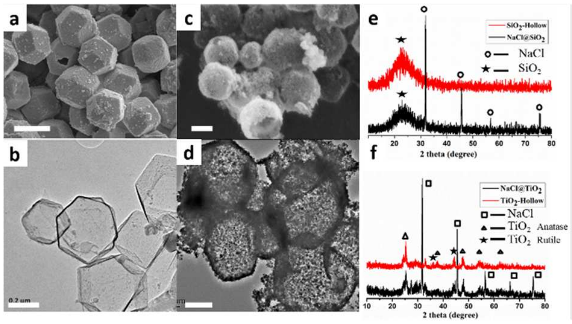

Figure 3. SEM and TEM images of SiO_2 RD-hollow structures (a, b), and TiO_2 hollow structures (c, d) fabricated using the NaCl WSGT. The scale bars in a, b, c, and d are 2um, 0.3um, 1um, 0.6um respectively. (e) XRD pattern of the NaCl@SiO_2 and SiO_2 hollow particles calcinated at 600 ^oC after washing the NaCl template. (f) XRD pattern of the NaCl@TiO_2 and TiO_2 hollow particles calcinated at 650 ^oC after washing the NaCl template.

Conclusions

This study provides insights into the mechanism of the controlled crystal growth via selecting different structures of organic solvents. At the interface of two mixed solvents of which NaCl owns quite different solubility could endow a very unique microenvironment for the nucleation and crystallization, both from kinetic and thermodynamic perspectives. Rather great viscosity of glycerol favored a slow diffusion rate of Na^+ and Cl^- ions. From thermodynamics and Thomson-Gibbs equation, 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. Such a strategy could enlighten the similar synthesis of other water-soluble ionic nanocrystals with controllable and diverse size and morphologies. Such NaCl single crystals were used as a novel WSGT to fabricate SiO_2 and TiO_2 hollow structures with morphologies being their exact replicas. Because of the ubiquitous and environmental friendly nature, the method is expected to become a green alternative to the conventional hard or soft template method for the fabrication of a large group of hollow-structured functional materials, e.g., Al_2O_3, ZrO_2, SnO_2, etc.

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Notes and references

† Electronic Supplementary Information (ESI) available: [The preparation details of NaCl crystals and SiO_2 and TiO_2 hollow structures and other experimental details and characterization data.]. See DOI: 10.1039/c000000x/

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