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## COMMUNICATION

## Synthesis and formation mechanism of 1D hollow SiO<sub>2</sub> nanomaterials using in-situ formed 1D NaCl crystal templates

Cite this: DOI: 10.1039/x0xx00000x

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Received 5th May 2014

Accepted 00th May 2014

DOI: 10.1039/x0xx00000x

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**One dimensional (1D) hollow silica nanomaterials are, for the first time, successfully prepared using the *in-situ* formed water-soluble NaCl 1D crystals as templates. The formation mechanism of the 1D NaCl crystals and the 1D hollow SiO<sub>2</sub> nanomaterials is systematically studied. This new approach may open up new opportunities in the synthesis of novel anisotropic nanomaterials, the construction of nanodevices, and have potential applications in drug delivery.**

Recently, one dimensional (1D) nanomaterials, including nanotubes, nanobelts, and nanowires, have attracted significant research interest due to their unique mechanical, electrical, and optical properties.<sup>1,2</sup> These intriguing properties of the 1D nanomaterials enabled by the one dimensional structure allow them to be used in a variety of applications, such as high-strength nanocomposites, field-emitting surfaces, nanotransistors, biomaterial delivery tools, sensors, optic devices, energy storage devices, and catalysis materials.<sup>3-12</sup> Among the widely reported 1D nanomaterials, 1D hollow silica nanomaterials have gained special interest arising from their distinct optical, electrical, and mechanical properties.<sup>13</sup> Moreover, 1D hollow silica nanomaterials, possessing a large surface area, are easily combined with other nanomaterials. Also, the 1D hollow silica nanomaterials are highly biocompatible, making them promising in applications in catalysis, drug and gene delivery, and as nanosensors and templates.<sup>14</sup>

Numerous methods, such as surfactant stabilization,<sup>15-18</sup> anodized aluminum oxide (AAO), and vapor phase deposition

templating, have been developed to fabricate silica nanotubes. Surfactant stabilization methods usually require an optimized ratio between the surfactant and tetraethylorthosilicate (TEOS) to obtain size-controllable products, which is a time-consuming trying process, and requires extra washing steps to remove the surfactant due to the toxicity/contamination for further applications. The AAO template method utilizes an AAO membrane with hexagonally arranged pores as a template for the preparation of silica nanotubes.<sup>19</sup> However, this method has a poor control over the diameter and the length of the silica nanotubes. Silica nanotubes can also be synthesized using various metal powders as initiating materials under high temperature and low pressure to grow as 1D nanostructured materials.<sup>20,21</sup> These methods also have technical challenges in controlling the diameter of the silica nanotubes besides the high temperature and low pressure, and expensive equipment that hinders the possibility of large-scale production.

Because on the above, the template-assisted method has become an attractive and popular alternative to overcome these problems. Several 1D inorganic nanomaterials, including Ag nanowires, Au nanorods, CNT, and V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O nanowires, have been employed as templates to synthesize silica nanotubes due to the easy removal of the templates under alkaline or acidic conditions.<sup>17,22-25</sup> These templates can provide binding sites during the silica formation. The thickness of the silica can be controlled by the reaction time, temperature, and/or the concentration of TEOS usually used as a silica precursor. However, the template-based method still has not addressed some of the major challenges, including the handling of toxic organic chemicals or surfactants and the difficulties in controlling their shape and size. More importantly, most of these 1D templates themselves are difficult to synthesize and valuable. The one-time-use nature of these templates makes the cost issue even worse. As an alternative, ionic crystals such as NaCl, usually uniform in geometry and size, have attracted great interest due to their water-soluble and environmentally benign properties. Recently, NaCl nanocubes were used as a template for the facet-selective epitaxial growing of NaYF<sub>4</sub> nanocages.<sup>26</sup> In addition, hollow SiO<sub>2</sub> cubes have been synthesized by a one-step

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

*in-situ* coating on NaCl nanocubes.<sup>27</sup> However, in most cases, it remains a great challenge to obtain 1D silica nanomaterials because of the enormous difficulty in generating 1D NaCl templates.<sup>28-32</sup>

Sodium chloride is one of the most representative examples of water-soluble salts that usually appears in the form of highly regular cubes in both natural and artificial environments.<sup>28,31</sup> Production of NaCl in other shapes and structures has been proven difficult and has seldom been achieved. To the best of our knowledge, there are no reports on the preparation of silica layer-coated NaCl nanowires (NaCl@SiO<sub>2</sub>).<sup>29,30,33</sup>

In this work, we have demonstrated a novel method for the synthesis of 1D hollow silica nanomaterials with structures by using the *in-situ* formed 1D NaCl crystals behaving as effective sacrificial templates. Typically, a certain amount (0.1 ml, can produce 10 mg of NaCl crystals) of NaCl/glycerinum (1.7 mol NaCl dissolved in 1 L glycerinum) solution was added into 20 ml of isopropanol during agitation for 5 min. Consequently, TEOS (0.21 ml), NH<sub>3</sub>·H<sub>2</sub>O (0.14 ml) and H<sub>2</sub>O (0.14 ml) were added into the above solution in sequence. The mixture was then stored at 25 °C for 2 h to allow the reactions to take place. After that, TEOS (0.24 ml), NH<sub>3</sub>·H<sub>2</sub>O (0.1 ml), and H<sub>2</sub>O (0.45 ml) were added one by one and reacted at room temperature for another 4 h (this is the second growth process of SiO<sub>2</sub> coating). The products were collected by centrifugation, washed with deionized water several times, and then dried at 200 °C under air atmosphere overnight. At last, the hollow silica nanobelts were obtained by using the *in-situ* formed water-soluble NaCl nanobelts as templates, for the first time.

As shown in Figure 1, rhombic dodecahedron (RD)-NaCl crystals and RD-NaCl@SiO<sub>2</sub> (Figure 1b) of about 2 μm in length (Figure 1a) were firstly synthesized according to our previous report.<sup>30</sup> After the second SiO<sub>2</sub> coating process, NaCl@SiO<sub>2</sub> nanobelts and hollow RD-SiO<sub>2</sub> particle hybrid materials (see Figure 1c) were obtained. The inset in Figure 1c proves the hollow structure of the RD-SiO<sub>2</sub> particles. Based on the apparent density difference between the NaCl@SiO<sub>2</sub> nanobelts and the hollow RD-SiO<sub>2</sub> particles, the NaCl@SiO<sub>2</sub> nanobelts can be easily separated from the hollow RD-SiO<sub>2</sub> particles through centrifugation. Figure 1d shows typical low-magnification scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (the upper inset in Figure 1d) images of the pure NaCl@SiO<sub>2</sub> nanobelts (with a productivity of > 95%) and NaCl@SiO<sub>2</sub> nanowires. The images reveal that the NaCl@SiO<sub>2</sub> nanobelts are 500–800 nm in width 8–15 μm in length, and 20–80 nm in thickness (see Figure S3). The EDS image (inset in Figure 1d) and XRD pattern (Figure 1f) verify the structure of the NaCl@SiO<sub>2</sub> nanobelts. After the NaCl templates were completely removed by water, the hollow SiO<sub>2</sub> nanobelts retained excellent morphology integrity (Figure 1e). Figure S1a shows the nitrogen adsorption-desorption isotherms. The as-synthesized samples gave only one sharp adsorption-desorption loop near P/P<sub>0</sub> = 1. The Battett–Joyner–Halenda (BJH) pore diameter was estimated to be 3.08 nm in the samples. The Brunauer–Emmett–Teller (BET) surface area was determined to be 19.2 m<sup>2</sup> g<sup>-1</sup> and the volume of the mesopores in the samples was about 34.1 mm<sup>3</sup> g<sup>-1</sup>.

To study the growing mechanism of the hollow SiO<sub>2</sub> nanobelts, we investigated the influence of water and TEOS amount on the formation of NaCl@SiO<sub>2</sub> nanobelts. First, the role of deionized water was investigated. The RD-NaCl@SiO<sub>2</sub> particles of about 2 μm in size were prepared (see Figures 1b and S2a). Subsequently, a fixed amount of TEOS (0.15 ml), ammonia (0.1 ml) and various

amounts of deionized water (0.05, 0.25, 0.45 to 0.65 ml) were introduced to trigger the growth of the silica cell and the dissolving of the NaCl template (see Table S1). Only a small amount of 1D NaCl@SiO<sub>2</sub> nanomaterials containing both nanobelts (major product) and nanowires (minor product) was obtained when the amount of water added was 0.05 ml (see Figures S2b and S3). The final products contained hollow RD-SiO<sub>2</sub> particles, RD-NaCl@SiO<sub>2</sub> particles, and yolk-shell structured RD-NaCl@SiO<sub>2</sub> particles (see Figure S2f). This indicates that the RD-NaCl crystals encapsulated in the RD-SiO<sub>2</sub> shells were only partially resolved due to the insufficient supply of water. In addition, the dissolved NaCl solution recrystallized into NaCl nanobelt templates, which acted as templates again and coated by SiO<sub>2</sub> shells. Interestingly, the productivity of the hollow SiO<sub>2</sub> nanobelts increased from 2 to 6 to 10 mg when the amount of water increased from 0.05, to 0.25, to 0.45 ml, respectively. (see Figures S2c, d). The yield of hollow SiO<sub>2</sub> nanobelts will reach the highest value at a certain water amount. When the amount of deionized water was increased to 0.65 ml, pure hollow RD-SiO<sub>2</sub> particles were prepared with no appearance of NaCl@SiO<sub>2</sub> nanobelts (see Figure S2e). At this condition, RD-NaCl crystals encapsulated in RD-SiO<sub>2</sub> shells were completely dissolved into solution, and the released NaCl did not recrystallize again into NaCl nanobelts. This may be due to the abundance of water in the reaction system, which allows all of the NaCl to be dissolved in water and in turn, the formation requirement (e.g., oversaturation) of NaCl crystals can not be satisfied. The above phenomenon demonstrates that NaCl nanobelt templates are formed through recrystallization of the released NaCl from the NaCl@SiO<sub>2</sub> structures in an isopropanol-rich solution. Moreover, we also found that the maximum productivity of hollow SiO<sub>2</sub> nanobelts is obtained when an optimized amount of deionized water present in the reaction solution.

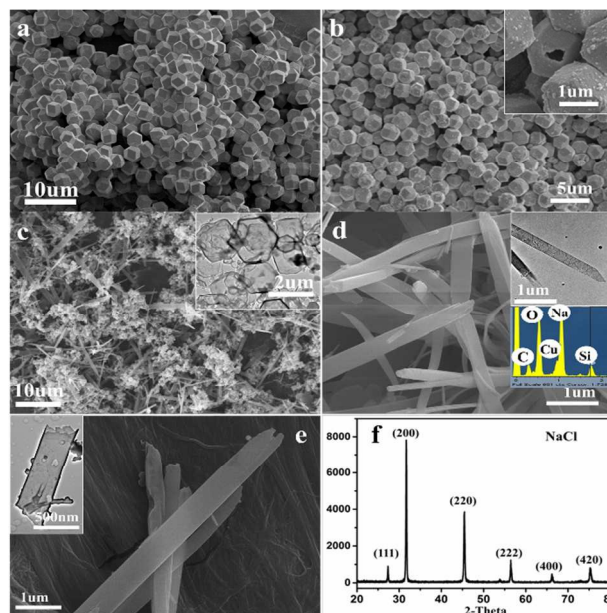


Figure 1. Typical SEM images of the (a) (RD)-NaCl crystals of about 2 μm in size and (b) RD-NaCl@SiO<sub>2</sub> composites; the inset in b shows a NaCl@SiO<sub>2</sub> particle with a broken shell. (c) SEM images of hollow RD-SiO<sub>2</sub> particles and NaCl@SiO<sub>2</sub> nanobelts. The inset in c shows the hollow RD-SiO<sub>2</sub> structure. (d) After centrifugation, pure NaCl@SiO<sub>2</sub> nanobelts were collected, and the inset shows the TEM image of the NaCl@SiO<sub>2</sub> nanobelts. (e) After washing with water

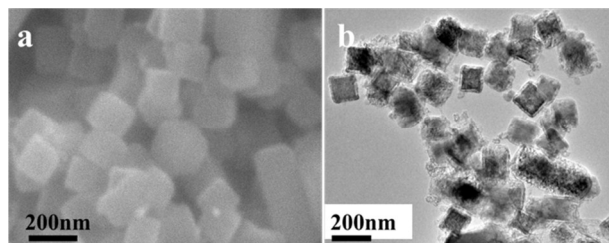


several times, hollow SiO<sub>2</sub> nanobelts were obtained; the inset confirms the hollow structure of the SiO<sub>2</sub> nanobelts. (f) The XRD pattern and EDS image (inset in d) confirm the structure of the NaCl@SiO<sub>2</sub> nanobelts.

The effect of TEOS amount on the synthesis of NaCl@SiO<sub>2</sub> nanobelts could be deduced from **Figure S4**. Various amounts of TEOS (0.21, 0.24, and 0.27 ml) were added into the system (see in **Table S1**) when the amounts of deionized water and ammonia added were constant at 0.45 ml and 0.1 ml, respectively. Under these conditions, the amount of the secondary recrystallized NaCl nanobelt templates is fixed. As the amount of TEOS increased, the yield of the hollow SiO<sub>2</sub> nanobelts was increased from 14 to 19 and to 21 mg (see **Figure S4a, b**). This suggests that not all of the recrystallized NaCl nanobelt templates are coated by SiO<sub>2</sub> shells when the adding amount of TEOS is insufficient. Those recrystallized NaCl nanobelt templates without the protection of the silica shell were resolved into water phase again. The SiO<sub>2</sub> shells coated on the NaCl nanobelt templates can efficiently protect the NaCl nanobelt templates from being re-dissolved into solution. When the amount of TEOS was increased to 0.27 ml, the yield of hollow SiO<sub>2</sub> nanobelts did not increase apparently. The morphology of the obtained hollow SiO<sub>2</sub> nanobelts under this condition was very poor (see **Figure S4c**). There are many SiO<sub>2</sub> particles attached on the hollow SiO<sub>2</sub> nanobelts. Based on the above results, the maximum yield of hollow SiO<sub>2</sub> nanobelts can be obtained only when the amount of deionized water and TEOS added are exactly appropriate.

Interestingly, among the NaCl@SiO<sub>2</sub> nanobelts and hollow RD-SiO<sub>2</sub> particle hybrid materials, numerous ultrafine NaCl@SiO<sub>2</sub> nanowires with a diameter of about 20–30 nm was observed (**Figure S5**). In order to obtain SiO<sub>2</sub> nanotubes with a diameter of less than 100 nm, the size of each RD-silica shell with around 2 μm should be decreased to the nanometer range.

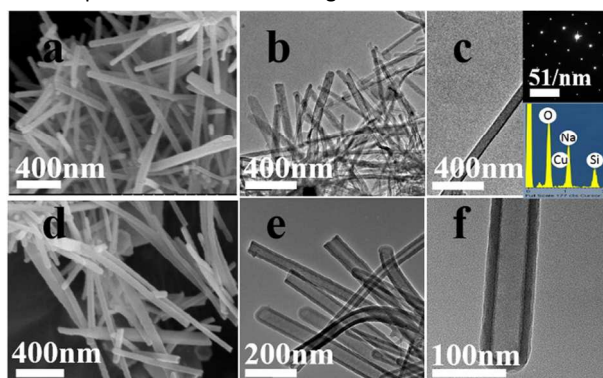
For further confirmation, NaCl@SiO<sub>2</sub> small cubic composites of about 150 nm in size were prepared (**Figure 2a, b**). And then, TEOS (0.4 ml), NH<sub>3</sub>·H<sub>2</sub>O (0.1 ml), and H<sub>2</sub>O (0.45 ml) were added step by step and reacted at room temperature for another 4 h. Then the products were collected by centrifugation, washed with deionized water several times. After dissolving NaCl templates, SiO<sub>2</sub> nanotubes with a diameter of about 60–100 nm were obtained (**Figure 3, S6e, f**).



**Figure 2.** (a) Typical SEM image of the rhombic dodecahedron NaCl cubic crystals with size of about 150 nm and (b) TEM image of the NaCl@SiO<sub>2</sub> cubic composites.

**Figure 3a** shows a typical SEM image of the as-synthesized NaCl@SiO<sub>2</sub> nanowires, which demonstrates that the nanowires are very uniform with diameters predominantly in the range of 60–100 nm and lengths of about 10 μm. TEM images (**Figures 3b and 3c**) confirm the morphology and the size of the as-prepared NaCl@SiO<sub>2</sub> nanowires. The SAED pattern (the upper inset in **Figure 3c**) suggests the single crystal nature of face centered cubic structured NaCl. The EDS image (the lower inset in **Figure 3c**) confirms the elementary

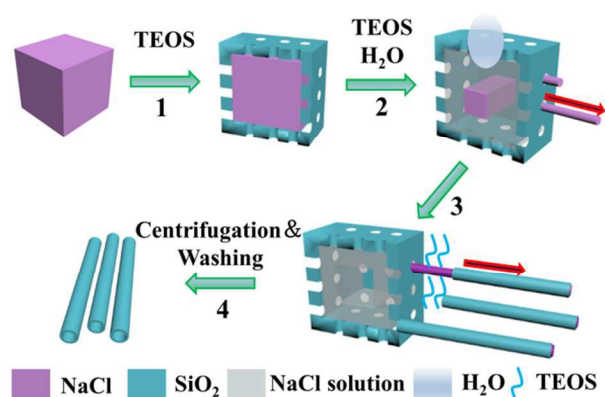
composition of the NaCl@SiO<sub>2</sub> nanowires. The XRD pattern (**Figure S7**) further confirms the elementary composition of the NaCl@SiO<sub>2</sub> nanowires and SiO<sub>2</sub> nanotubes after washing the NaCl template. After removal of the NaCl templates, the hollow SiO<sub>2</sub> nanotubes maintain the original morphology (**Figure 3d**). The TEM images (**Figure 3e, 3f**) confirm that the SiO<sub>2</sub> nanotubes have a uniform shell thickness. Also, the diameter of the NaCl nanowire templates is about 40–60 nm. The as-synthesized samples have only one sharp adsorption–desorption loop near P/P<sub>0</sub> = 1. The BJH pore diameter is determined to be 3.28 nm in the samples (**Figure S1b**). The BET surface area is about 23.2 m<sup>2</sup> g<sup>-1</sup> and the volume of the mesopores in the samples is around 29.1 mm<sup>3</sup> g<sup>-1</sup>.



**Figure 3.** (a) SEM image and (b, c) TEM images show the structure of the NaCl@SiO<sub>2</sub> nanowires. (d) SEM image and (e, f) TEM images of the hollow SiO<sub>2</sub> nanotubes. The insets in c show the SAED pattern and the EDS image of the NaCl@SiO<sub>2</sub> nanowires.

Based on the microstructure evolution process, the formation process of the 1D hollow SiO<sub>2</sub> nanomaterials is schematically illustrated in Scheme 1. The process can be divided into four steps. 1) The NaCl (cubic or RD) crystals were encapsulated into SiO<sub>2</sub> shells. 2) Subsequently, when an appropriate amount of water was added into the system, the NaCl (cubic or RD) crystals were dissolved into solution from the SiO<sub>2</sub> (cubic or RD) shells. Then, the bulk NaCl solution was separated into many 1D NaCl solution by the SiO<sub>2</sub> (cubic or RD) shells and outflowed. At the same time, the 1D NaCl solution was recrystallized into 1D NaCl crystals in the isopropanol-rich solution due to the oversaturation. 3) The hydrolyzed TEOS adsorbed onto the surface of the *in-situ* formed NaCl 1D crystals and formed SiO<sub>2</sub> layers after a period of reaction. 4) 1D hollow SiO<sub>2</sub> nanomaterials were obtained through centrifugation and washing with deionized water several times. These methods were used to separate the 1D hollow SiO<sub>2</sub> nanomaterials from the hollow SiO<sub>2</sub> particles and remove the NaCl crystal templates.

**Scheme 1. Schematic illustration of the formation process of 1D hollow silica nanomaterials using the *in-situ* formed 1D NaCl crystals.**



1D hollow silica nanomaterials with different morphologies, such as nanowires and nanobelts, were successfully fabricated in solution by using the *in-situ* formed 1D NaCl crystals as templates. The 1D hollow silica nanomaterials possess a good biocompatibility, as well as can be easily combined with other nanomaterials. These characteristics endow these structures to be used as building blocks for nanofluidic devices, high-quality nanoreactors for catalysis and confined synthesis, and well-defined containers for drug delivery.<sup>3-12</sup> Furthermore, this work provided insights into the crystal formation of 1D NaCl crystals and the growing mechanism of 1D hollow SiO<sub>2</sub> nanomaterials. Because of the ubiquitous and environmentally friendly nature of the NaCl template here used, this method is expected to become a green alternative to the conventional hard or soft template-based methods in the fabrication of diverse 1D hollow multi-functional materials, e.g., TiO<sub>2</sub>, ZrO<sub>2</sub>, and SnO<sub>2</sub>.

#### Acknowledgements

This study was financially supported by the high-tech project of MOST (2012BAA10B03, 2014AA032802), the national sci-tech support plan the National Natural Science Foundation of China (NSFC, No.: 51272273, 51172265, 51372264), and the Science and Technology Commission of Shanghai Municipality (STCSM, No.: 13PJ1409000, 13NM1402200)

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† Electronic Supplementary Information (ESI) available: [The preparation details of SiO<sub>2</sub> 1D hollow structures and other experimental details and characterization data.]. See DOI: 10.1039/c000000x/

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