

## The Sea Urchin-shaped $\text{CaCO}_3$ via Template Mineralization on Surface-functionalized Vaterite Particles by Tiopronin-protected Gold Nanoparticles

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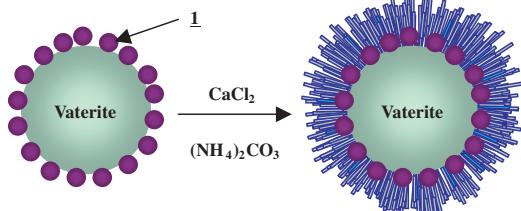
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The sea urchin-shaped particles of  $\text{CaCO}_3$ , i.e., spherical vaterite covered with needle-shaped aragonite, were formed by template mineralization of  $\text{CaCO}_3$  in the presence of the anionic gold nanoparticles modified spherical vaterite in water.

Biomineralization, which produces biological inorganic-organic composites, is a process of the mineral deposition on self-assembled organic templates with the assistance of water-soluble macromolecules.<sup>1,2</sup> Many researchers have focused on in vitro processes of calcium carbonate crystal nucleation, growth, and interface transition with synthetic organic templates such as low-molecular weight additives, linear polymers, and self-assembled monolayers.<sup>3-6</sup> We have studied the crystallization of  $\text{CaCO}_3$  in the presence of anionic poly(amidoamine) dendrimers, which are spherical and proposed as mimics of anionic proteins, and found that the surfaces of metastable vaterite particles were effectively stabilized by the anionic dendrimers.<sup>7</sup> These results motivate us to design “spherical linkers” for surface functionalization of  $\text{CaCO}_3$ . The spherical linkers are rigid and completely defined, and functional groups are unable to attach to the same inorganic surfaces because of the steric hindrance of the spherical structures. The strong bonding to the inorganic surfaces is also expected by a chelate or cluster effect.<sup>8</sup>

Here, we used tiopronin-protected gold nanoparticles (**1**) as spherical linkers to prepare surface-functionalized particles and provided the template mineralization of  $\text{CaCO}_3$  to construct high-ordered structures (Figure 1). The tiopronin-protected gold nanoparticles (**1**) were prepared by the method of Murray et al. reported previously.<sup>9</sup> The gold nanoparticles were purified by dialysis against water two times using cellulose dialysis membrane. The solution was removed under reduced pressure to obtain the gold nanoparticles as black-red powders. Average gold core diameter from a TEM image was 2 nm. The thermal loss of the organic fraction of the nanoparticles was 30 wt % by TGA. The content of tiopronin in (**1**) was calculated to 1.8 mmol/mg. A main advantage of using anionic metal nanoparticles instead of the dendrimers is the ease of preparation. Although a few reports already described crystallization of  $\text{CaCO}_3$



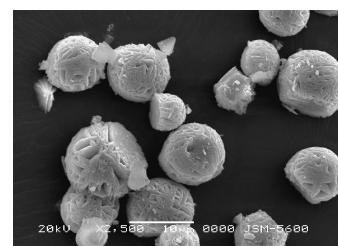
**Figure 1.** Schematic diagram of the sea urchin-shaped  $\text{CaCO}_3$  via template mineralization on tiopronin-protected gold nanoparticles modified spherical vaterite.

by using functionalized metal nanoparticles such as 4-mercaptophenol- and 4-mercaptopbenzoic acid-protected gold nanoparticles,<sup>10,11</sup> surface modification of  $\text{CaCO}_3$  with functionalized nanoparticles has not been achieved. To the best of our knowledge, this is the first report on the nucleation and growth of  $\text{CaCO}_3$  on a surface-functionalized  $\text{CaCO}_3$  with synthetic spherical linkers. We expect that this process helps to understand how to develop the new biomimetic materials and template mineralization mechanism.

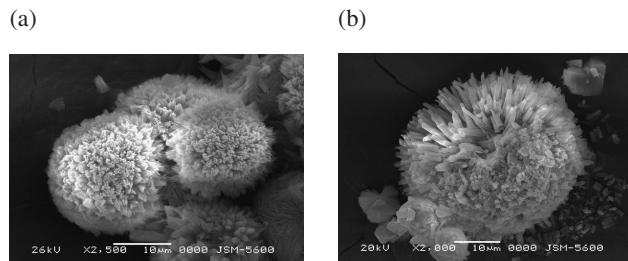
For preparation of the surface-functionalized vaterite particles, each 4.95-mL aqueous solutions of 0.1 M  $\text{CaCl}_2$  and 0.1 M  $(\text{NH}_4)_2\text{CO}_3$  was injected via syringe into 180 mL of water containing 0.13 mg of **1** (pH 7.6) at 30 °C. A slow increase in the turbidity of the solution was observed after incubation for 5–15 min from addition of the calcium reactants. The product was isolated by filtration after incubation for 1 day. The crystalline  $\text{CaCO}_3$  was washed with water to remove the contaminated **1** that were not involved in the crystals. A color of the crystalline was dark-brown, which indicates modification with the gold nanoparticles. The molar ratio of calcium ion to tiopronin on **1** was 0.5.

A SEM image of the crystal morphology was shown in Figure 2. The obtained product was mostly spherical vaterite with a little rhombohedral calcite. We confirmed the  $\text{CaCO}_3$  crystal phase by X-ray powder diffraction measurement (XRD).<sup>12</sup> The XRD pattern of the product in Figure 2 indicated major reflections corresponding to vaterite (87%) with a little calcite reflections. The content of **1** in the product was 5.4 wt % by elemental analysis. The vaterite particles did not transform into thermodynamically more stable forms in contact with water for more than 1 week. Vaterite is thermodynamically most unstable in the three crystal systems of  $\text{CaCO}_3$ ; calcite, aragonite, and vaterite. In general, vaterite transforms into calcite when in contact with water within 3 days. These results indicate that the vaterite surface was stabilized by **1** to prevent phase transformation to calcite.

The template mineralization was carried out in the presence of the surface-functionalized vaterite particles. The calcium re-



**Figure 2.** SEM image of the surface-functionalized vaterite particles by precipitation condition in the presence of 0.13 mg (**1**).



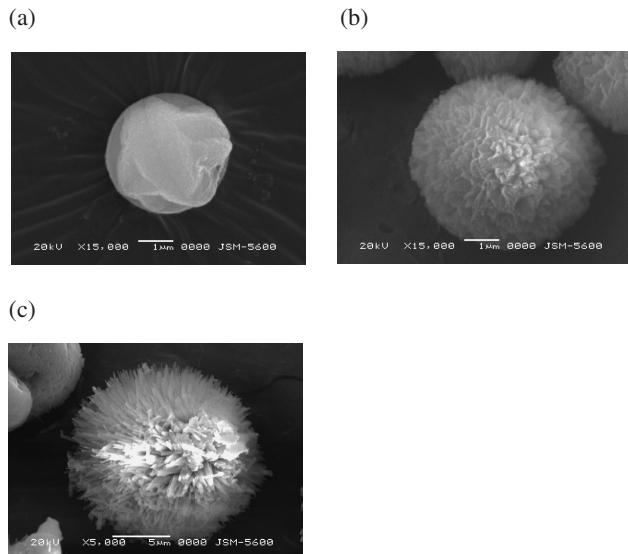
**Figure 3.** SEM images of the products by template mineralization on the surface-functionalized vaterite particles. The amount of the calcium reactant was a) 0.49 mM and b) 0.78 mM, respectively.

actants were injected via syringe into 180 mL of an aqueous solution in the presence of 49 mg of the vaterite particles with 0.013 mg of the additional **1** at 30 °C. The product was isolated after incubation for 1 day. The sea urchin-shaped CaCO<sub>3</sub> with a little rhombohedral calcite was observed by SEM (Figure 3). From the SEM images, needle-shaped crystals on the surface of the vaterite particles appeared to elongate which increasing the amount of the calcium reactants.

In comparison with the XRD pattern of the surface-modified vaterite products, aragonite reflections appeared in the XRD patterns of the products. Intensity of the aragonite reflections increased with an increase in the amount of the calcium reactants. This suggested that the needle-shaped crystals were aragonite. In the absence of the additional gold nanoparticles, only aggregated vaterite particles were obtained. The surface-modified spherical vaterite provided interfacial active sites for nucleation of the second crystalline phase (the needle-shaped aragonite) to produce a hierarchical crystal growth. The presence of **1** in the solution also played an important role for the controlled growth of needle-shaped aragonite on the surface of the gold nanoparticles modified spherical vaterite.

We obtained the same sea urchin-shaped CaCO<sub>3</sub> under the precipitation condition by decreasing the concentration of **1** compared to the product in Figure 2. We injected 4.95-mL aqueous solutions of 0.1 M CaCl<sub>2</sub> and 0.1 M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> via syringe into water containing 0.026 mg of **1** at 30 °C. We monitored the time-dependent crystal growth of the product. The crystals isolated after 10 min incubation (Figure 4a), were brown colored and spherical vaterite with about 3 μm diameter. The spherical vaterite of which polymorph was confirmed by XRD was an aggregate of discs vaterite. After isolation at 20 min incubation, tiny crystals were grown on the surface of the spherical vaterite (Figure 4b). Finally, the sea urchin-shaped CaCO<sub>3</sub> was formed after incubation for 90 min (Figure 4c). Brown color of the sample faded out in the case of the crystalline products isolated after further incubation. The second stage of the formation of the sea urchin-shaped CaCO<sub>3</sub> under in-situ precipitation condition was nucleation and growth of the sharp needle-shaped aragonite on the surface of the gold nanoparticles modified spherical vaterite with about 9 ± 1.3 μm diameter.

We speculate that the remaining **1** and the calcium reactants in the bulk phase are transferred to the rough surface of the va-



**Figure 4.** SEM images of the time-dependent crystal growth of the product in Fig. 3 by isolation of the crystals after incubation for 10 (a), 20 (b), and 90 min (c), respectively.

terite particles for the second nucleation and then competitively grow into sharp needle-shaped aragonite in a restricted space of the vaterite at 30 °C.

The results showed the possibility for new biomimetic composite materials and understanding of biomineralization mechanism. We expect that the functionalized gold nanoparticles would be used as an excellent template for mineralization, because of their ease of preparation.<sup>9</sup>

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