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Skeletal Silica Nanoparticles Prepared by Control of Reaction Polarity

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We report skeletal silica nanoparticles using a cubic template whose surface is coated by surfactant. The controlling factors, (a) high acidity of silanol compared to that of surfactant, (b) low affinity between surfactant and organic medium, and (c) high surface energy of vertex and edge of the template, are associated to obtain such structures.

Nanoparticles including hollow,[1] porous,[2] and frame structures exhibit unique characteristics, such as optical properties,[3] and utility as catalyst supports[4] and drug carriers.[5] In order to achieve these properties, precise shape control techniques are required.

Sacrificial templates have been used as an effective technique. Okazaki et al. reported Au frame nanoparticles prepared via selective Au deposition on cubic Ag submicron particles whose entire surface was modified with thiol groups.[6] The Xia research group fabricated Au hollow and frame nanoparticles separately by selective chemical etching of Au/Ag core–shell particles. Removal of Ag template gives cubic Au hollow structure. Further etching promotes removal of Au atoms which are deposited on the face of the hollow particle resulting in Au nanoframe structure with square-shaped windows on each of six faces. They also found that Au frame nanoparticles showed scattering in the visible region depending on their window size.[7] There is much attention to shape control techniques of frame nanoparticles because of their shape-derived properties. The former research utilized thiol functionality to form covalent bonds with Au atom, and it preferentially deposits at the vertexes and edges of cubic Ag templates, while the latter research showed that Au is primarily etched from each face. Both techniques could be explained by increase of surface energy, in the order of face, edge, and vertex. Although this is a simple and useful technique, it is still difficult to control the shape precisely because of decisive factors such as reaction time, scale, and conditions. Furthermore, it is also limited to certain metals.

Previously, inorganic templates for fabrication of hollow nanoparticles have been developed by sol–gel reaction. Cubic-shaped calcium carbonate with calcite crystal structure, as template, was dispersed in ethanol (EtOH) medium. With addition of tetraethoxysilane (TEOS), ammonium hydroxide (NH_4OH), and distilled water, negatively charged silicic acid (SiOH) which is generated by hydrolysis of TEOS adsorbs on positively charged sites of calcite surface to become a thin silica shell. After calcite removal by dilute acid etching, silica hollow nanoparticles were obtained as a replica of the cubic shape from the template.[8] This technique has advantages because the template can be recycled by collection of by-product CO_2 gas and $CaCl_2$ solution in contrast with heat decomposition of organic bead templates.[9]

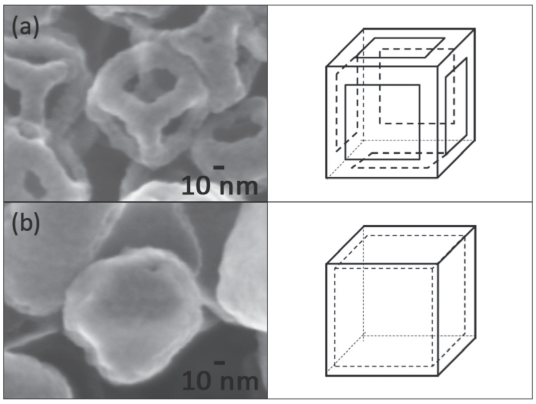

Figure 1. SEM micrographs of silica nanoparticles prepared in (a) EtOH and (b) Dg medium show skeletal and hollow structures, respectively.

Here, we report skeletal structured silica separately from hollow nanoparticles using cubic calcite to whose surface is adsorbed by an organic acid as dehydroabietic acid (DAA). The adsorbed amount of DAA was estimated to be 1 molecule per 1 nm^2 calcite surface. The DAA-adsorbed calcite was suspended in two different media of EtOH and diglyme (Dg). Subsequently, sol–gel reaction induced core–shell particle formation, and silica nanoparticles were obtained after calcite removal by dilute acid etching.

Figure 1 shows scanning electron microscopic (SEM) micrographs of silica nanoparticles prepared in (a) EtOH and (b) diglyme (Dg) medium. In EtOH medium (Figure 1a), silica skeletal nanoparticles with nanoframes of approximately 20 nm in width and 100 nm in length were observed after calcite removal, while Dg medium (Figure 1b) gives silica hollow nanoparticles similar to our earlier report.[8]

From the above result, it can be seen that calcite with/without DAA coating and different reaction medium strongly affect the silica structures. Figure 2 illustrates schematic diagrams of nanoparticle formation mechanism in (a) EtOH (skeletal) and (b) Dg medium (hollow). When sol–gel reaction starts, SiOH derived from hydrolysis of TEOS begins to displace the adsorbed DAA because the acid dissociation constant (pK_a) of SiOH ($pK_a = 5.70$)[10] is lower than that of DAA ($pK_a = 7.25$).[11]

It is also important to consider the stability of the desorbed DAA in the reaction systems, that is determined by affinity between DAA and organic medium. Dielectric constants (ε) of DAA, EtOH, and Dg are around 2.65,[12] 24.55,[10] and 7.30,[13] respectively. Stability of desorbed DAA is low in EtOH and high in Dg medium.

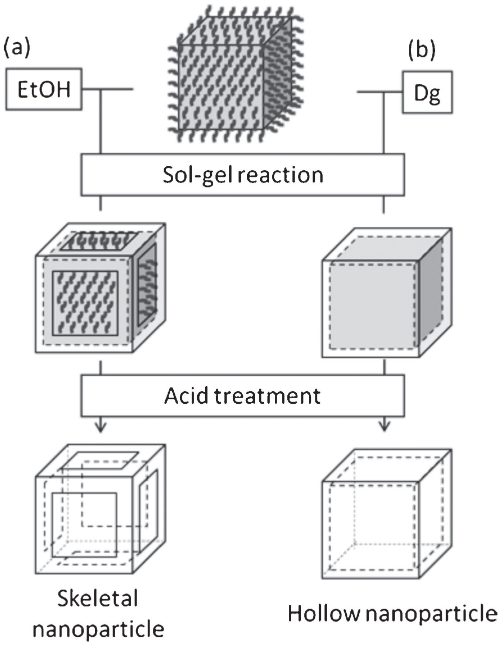

Figure 2. Schematic diagrams of formation mechanism of (a) skeletal and (b) hollow nanoparticles.

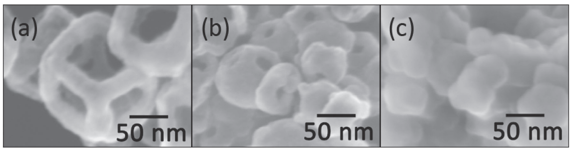

Figure 3. SEM micrographs of nanoparticles prepared using DAA-adsorbed calcite with different size of (a) 80, (b) 50, and (c) 30 nm in EtOH medium.

Based on these properties, displacement of adsorbed DAA with SiOH is not promoted in EtOH medium. Adsorbed DAA molecules at vertexes and edges of calcite surfaces preferentially desorb and SiOH adsorb instead. After calcite removal, silica nanoframe remains as skeletal structure (Figure 2a). On the other hand, Dg medium promotes displacement of adsorbed DAA with SiOH, and hollow nanoparticles form with a thin silica shell (Figure 2b).

In order to obtain skeletal structures, (i) DAA desorption from the vertexes and edges of cubic calcite and (ii) lower stability of the desorbed DAA in EtOH medium seem to be important.

Crystal surfaces are unstable, particularly in vertex and edge positions of cubic calcite, where surface energy is higher than face because of more unsaturated bonds.[14] In order to decrease their surface energy, SiOH with high acidity displaces with DAA which adsorbs on vertexes and edges. Figure 3 shows SEM micrographs of nanoparticles prepared using DAA-adsorbed calcite with different size of (a) 80, (b) 50, and (c) 30 nm in EtOH medium.[15] Skeletal nanoparticles were clearly observed with 80 nm calcite (Figure 3a). With decrease in size to 50 nm (Figure 3b), cubic nanoframe changed to spherical, and large square windows as observed in Figure 3a reduced in size. On further decrease in size to 30 nm, only particulates were observed (Figure 3c) without any skeletal structures, and their hollow interiors were confirmed by transmission electron microscopy (TEM) (result not shown). When surface energies of vertex and edge are high enough in comparison to that of face, SiOH displacement occurs only on vertexes and edges to stabilize calcite surface in EtOH medium. With decrease in size, surface energy becomes high and difference of surface energy among vertex, edge, and face decreases. That is why that the skeletal structures (Figure 3a) approach spherical (Figure 3b) and completely transform to hollow nanoparticles (Figure 3c).

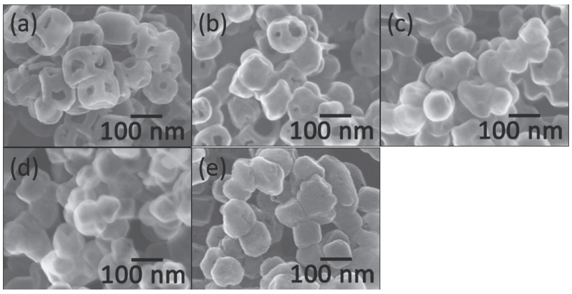

Figure 4. SEM micrographs of nanoparticles prepared in different EtOH/Dg ratio of (a) 100/0, (b) 78/22, (c) 55/45, (d) 29/71, and (e) 0/100, respectively.

In addition, stability of desorbed DAA in the reaction medium was investigated. Figure 4 shows SEM micrographs of nanoparticles prepared in different EtOH/Dg ratio to study the effect of polarity of the reaction system; (a) 100/0, (b) 78/22, (c) 55/45, (d) 29/71, and (e) 0/100 in volume ratio. Corresponding polarities of the systems were calculated as (a) 24.55, (b) 20.76, (c) 16.78, (d) 12.30, and (e) 7.30, respectively. In addition to skeletal structures as observed in EtOH medium (Figure 4a), the number of hollow nanoparticles increased with decrease in system polarity from 20.76 to 16.78 (Figures 4b and 4c). When the polarity reached to 12.30, only hollow particles formed (Figure 4d) similar to Dg system (Figure 4e). In high polarity system, displacement of DAA with SiOH is not promoted. With decrease in system polarity, SiOH displacement proceeds due to increase of stability of desorbed DAA.

In summary, skeletal silica nanoparticles were synthesized using DAA-adsorbed calcite template dispersed in EtOH medium. There are key factors, (i) lower acidity of DAA than that of SiOH, (ii) high surface energy of vertex and edge of the template, and (iii) low affinity between DAA and EtOH, which are associated to control the skeletal structure. According to (i), SiOH adsorbs on the calcite site instead of DAA desorbing. This exchange adsorption preferentially occurs from the vertex and edge of cubic calcite surface by the factor (ii). Control of medium polarity, solute stability of DAA becomes low. Consequently, only the desorbed DAA from vertex and edge can be preferentially stabilized in EtOH media, according to factor (iii). After SiOH adsorbs instead, silica nanoframe forms on vertexes and edges. That is the formation mechanism of silica skeletal nanoparticles.

The skeletal structure of window, nanoframe, and its nanostructure can be controlled by the ratio of TEOS/calcite and sol–gel reaction rate. These desirable structures are expected to exhibit specific properties such as optical materials, drug carriers, heat insulation materials, and catalyst supporters.

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15 Calcite particles were prepared by addition of carbon dioxide gas in calcium chloride solution. After the solution turned white, dehydroabietic acid (DAA) was added to the suspension. The size of calcite was controlled to 30, 50, and 80 nm, by reaction time. Their surface morphologies are shown in Figures S1a–S1c of Supporting Information; SI, which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html. Adsorption of DAA on calcite was confirmed by Fourier transform infrared spectroscopy (FT-IR) in Figure S2a in SI. The calcite nanoparticles were suspended in two different organic media (ethanol (EtOH) and diglyme (Dg)) and sol–gel reaction starts with addition of tetraethoxysilane (TEOS), ammonium hydroxide (NH_4OH), and distilled water. After the reaction completed, the suspension was separated and washed to obtain core–shell particles (see FT-IR spectra in Figure S2b in SI). The core–shell particles were suspended in distilled water, and calcite was removed by addition of hydrochloric acid (HCl) (see FT-IR spectra in Figure S2c in SI). All of the chemicals were purchased from Wako Pure Chemical Industries, Ltd. The skeletal structure was observed by scanning electron microscopy (SEM, JSM-7000F, JEOL Ltd.). Removal of calcite was confirmed by X-ray diffraction (XRD, Ultima IV, Rigaku Corp.), and the hollow interiors were confirmed by a transmission electron microscopy (TEM, 2000-EX, JEOL Ltd.).