

Self-assembly growth process for polyhedral oligomeric silsesquioxane cubic crystals†

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The colloidal self-assembly process for the formation of polyhedral oligomeric silsesquioxane cubic crystals is described; the growth process consists of the formation of spherical particles, one-dimensional particle chains, bundles of chains, and finally, the formation of cubic crystals.

Silsesquioxanes have been the subject of intensive study because of their excellent thermal, mechanical, and electronic properties, which result from their organic–inorganic hybrid nature.¹ They can be used in various industrial applications such as engineering plastics, dielectric materials, additives, and preceramics as well as a model for catalyst supports.² Among the various types of silsesquioxanes, polyhedral oligomeric silsesquioxanes (POSSs) are the best compounds studied so far due to their well defined rigid inorganic silica-like core and easily modifiable organic pendant groups.^{3–8} Recently, POSSs have been recognized as new precursors for low dielectric constant interlayer materials for submicron semiconductor devices.^{9,10} Several techniques, such as vapor deposition and solution coating, have been investigated to obtain POSS interlayer films with lower dielectric properties. POSSs are generally prepared *via* controlled hydrolysis and condensation of trichlorosilanes or trialkoxysilanes.^{3,4} When a typical sol–gel process such as the Stöber process has been employed, spherical particles or gels with partially random structures have been obtained.¹¹ In spite of several novel properties of POSS molecules, low yield and rather tedious synthetic procedures have limited the practical application of these materials. In order to overcome these limitations, several methods for the preparation of POSSs with high yield have been developed.^{3,12,13} Recently, Handke *et al.* reported a new method for preparation of octamethylsilsesquioxane cubes using tetraethoxytetramethylcyclotetrasiloxane as a starting material in THF as a non-aqueous solvent and also investigated their spectroscopic and structural properties.¹⁴ Generally, non conventional sol–gel conditions such as anhydrous solvent, high temperature, or long reaction time are needed to obtain crystalline POSSs. However, it has been known that there are two growth pathways for the formation of large sized crystals and particles: (1) monomer–cluster growth and (2) cluster–cluster growth. The monomer–cluster growth mechanism includes continuous addition of monomers

to initially generated primary particles, while the cluster–cluster growth mechanism follows the formation of secondary particles by the coalescence between primary particles. Although most of the crystalline materials including POSS crystals adopt the monomer–cluster pathway for their growth process, the reaction condition usually decides which growth process would be predominant.

In this study, we present the colloidal growth mechanism of POSS cubic crystals based on observations using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The self-assembly growth mechanism for the formation of 3-dimensional cubic crystals can be summarized by the following assembly processes. First, the nano-sized spherical silica particles are formed through hydrolysis and condensation of silane precursors upon the addition of alkyl-trialkoxysilanes to a basic alcohol solution. Second, these zero-dimensional spherical particles condense to chain-shaped one-dimensional nano-particle arrays. Non-self-assembled primary particles and small POSS molecules still coexist at this stage. Third, pseudo-two-dimensional flower-shaped cluster particles appear from the one-dimensional chain arrays. Finally, the cubic three-dimensional POSS crystals are formed by the self-assembly of the two-dimensional flower-shaped clusters.

In a typical experiment, methyltrimethoxysilane was added to an ethyl alcohol solvent containing ammonium hydroxide as a catalyst. The reaction mixture was stirred at room temperature for 48 hours. Initially, the reaction solution was transparent indicating complete dissolution of silane monomers. As the hydrolysis and condensation reaction proceeded (after 2 hours of the reaction), the solution became opaque indicating the formation of colloidal particles. After stirring for 12 hours, the product started to precipitate from the suspension. Finally, the reaction solution with almost clear supernatant was obtained after 48 hours. In order to investigate the self-assembly growth process, the reaction was quenched after 12 hours by stopping the stirring, and sample aliquots for electron microscope observation were taken after 0, 2, 6, and 48 hours of additional aging, respectively (for complete experimental and sampling conditions, see ESI†). Spherical particles less than 100 nm were observed from SEM and TEM after 12 hours of reaction (0 hours aging time). As can be seen in Fig. 1(a), the SEM image exhibits slightly aggregated particles, while the TEM image (Fig. 1(b)) shows well-dispersed spherical particles. It is probable that the aggregation of particles occurred during the sample drying for SEM analysis and there was still a large amount of unreacted silane monomers with a small amount of POSS molecules formed in the solution. After 2 hours of aging, the second sample aliquot was collected for electron

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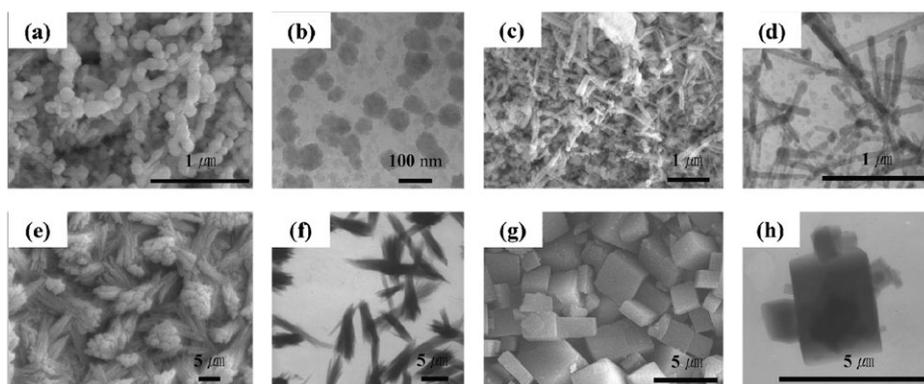


Fig. 1 SEM and TEM images of the products obtained at different aging times during the self-assembly growth process: (a)/(b); 0 h, (c)/(d); 2 h, (e)/(f); 6 h, and (g)/(h); precipitated cubic crystals.

microscopy analysis. The SEM and TEM images of the intermediate product from the second aliquot are shown in Fig. 1(c)

and (d), respectively. One-dimensionally ordered particles are observed while small portions of individual spherical particles still exist in the reaction mixture, as can be seen from the TEM image. The SEM image also shows necklace chain-shaped rods with randomly dispersed spherical particles. After 6 hours of aging, the third sample aliquot was taken and flower-shaped clusters of one-dimensional chains are observed, as shown in Fig. 1(e). The TEM image in Fig. 1(f) also confirms the aggregation of one-dimensional chains. Further aging of the suspension (48 hours) yielded the precipitated products with almost clear supernatant. The precipitated product was identified as cubic polyhedral oligomeric silsesquioxane crystals, as shown in Fig. 1(g) and (h). The exact mechanism of transformation of flower-shaped clusters to cubic crystals is not clear at this stage, but the participation of silane monomers or POSS molecules during the formation cubic crystals cannot be ruled out. The size of the cubic crystals ranged from a few hundred nanometres to a few microns, and most of the products had sharp edges. The total self-assembly process took about two weeks in order to obtain cubic crystals with a constant yield of about 15%. The reaction temperature affected the reaction time for the formation of cubic crystals. The increase in reaction temperature from room temperature to 60 °C produced POSS cubic crystals in less than 8 hours in an ethyl alcohol solvent. The changes in the alkyl chain length of the alcohol solvent also altered the reaction time. When methyl alcohol was used as a solvent, the cubic crystals could be obtained in a short reaction time (<3 hours at 60 °C). The hydrothermal conditions could reduce the reaction time further to less than 1 hour. However, the evolution of growth from nano-sized spherical particles to cubic crystals was not observed in either reaction condition because of the fast growth and precipitation of cubic crystals. The products obtained at high temperature or hydrothermal conditions also exhibited similar cubic morphologies to those obtained at room temperature. In addition, close examination of the SEM images of a minor portion of products obtained from a hydrothermal reaction showed less well-developed edges of the cubic particles. Harsh reaction conditions during a rather short reaction time yielded somewhat ill-defined cubic crystals.

For ethyltrimethoxysilane, the evolution of the growth process could not be observed. When the reaction was carried out at room temperature, no particle formation as a transparent solution was maintained for up to 1 day. The addition of water to this solution produced a gelled product. In order to obtain cubic powders, the reaction solution had to be heated to 60 °C. In this case, more than 6 hours of reaction time was needed before the addition of water to obtain products with octaethylsilsesquioxane cages. However, the product exhibited pseudo-cubic morphologies with less developed cubic edges.

X-Ray diffraction (XRD) patterns of methyltrimethoxysilane-based cubic crystals and ethyltrimethoxysilane-based pseudo-cubic powders were investigated. As can be seen in Fig. 2, both products exhibit well-resolved diffraction patterns, while the positions of the major peaks are shifted to slightly lower angles for ethyltrimethoxysilane-based product compared to those for methyltrimethoxy-based one. The diffraction pattern of methyltrimethoxysilane-based cubic crystals is well-matched with those obtained by Handke *et al.*¹⁴ and Barry *et al.*¹⁵ They used the Rietveld method to obtain theoretical diffraction patterns for octamethylsilsesquioxane and compared them to their experimental results. The exact matching of the diffraction patterns for the products to Handke's result is also a strong indication that the products in this experiment are octamethyl and octaethyl silsesquioxane crystals. The relative intensities between the major diffraction peaks for the cubic crystals are well matched with theoretical peaks, while those for the pseudo-cubic powders are slightly different. This slight difference in relative intensities for the pseudo-cubic powders might be an indication of a less crystalline nature, which is also confirmed by the less sharp edges of the pseudo-cubic powders in the SEM

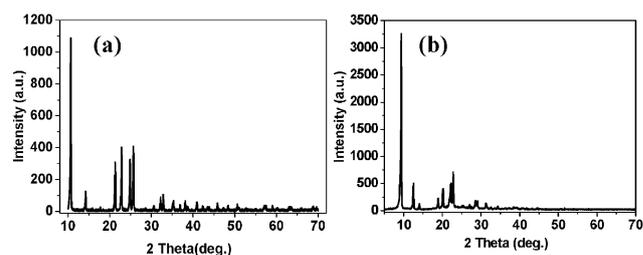


Fig. 2 XRD patterns of (a) methyltrimethoxysilane-based cubic crystals and (b) ethyltrimethoxysilane-based pseudo-cubic powders.

image. In contrast, the XRD pattern of methyltrimethoxysilane-based spherical particles, prepared by a conventional sol-gel process, shows a broad band at 10 degrees and a shoulder at around 20–30 degrees, indicating a random network structure (ESI†). In IR spectra of the methyltrimethoxysilane monomer and methyltrimethoxysilane-based cubic crystals, two peaks at 2954 and 2848 cm^{-1} are observed, which can be assigned to C–H stretching vibrations from methyl and methoxy groups in the silane monomer, respectively (ESI†). On the other hand, cubic crystals have only a C–H stretching vibrational band from methyl groups, indicating the complete condensation of trialkoxy groups. For methyltrimethoxysilane-based cubic crystals, the asymmetric Si–O–Si stretching vibration band from the cage structure is observed at 1144 cm^{-1} .^{16–18} For a random network structure, the Si–O–Si absorption peak usually appears at 1030 cm^{-1} .¹⁷ The absence of a band at 1030 cm^{-1} is a strong indication that the cubic crystals consist only of T_8 units.¹⁶ For ethyltrimethoxysilane-based pseudo-cubic powders, a peak at 1144 cm^{-1} is also observed (ESI†). In comparison, IR spectrum of methyltrimethoxysilane-based spherical particles from a sol-gel process exhibits two peaks at 1144 and 1030 cm^{-1} , indicating that the particles are made of cages and random network structures. More evidence for the cage structure of cubic crystals is the existence of a symmetric Si–O–Si stretching vibration peak at 517 cm^{-1} , which is the characteristic feature of a double ring from the cage structure.¹⁶ This peak is also found in ethyltrimethoxysilane-based pseudo-cubic crystals, while the intensity of the corresponding peak for spherical particles is significantly reduced. In addition, peaks at 774 and 824 cm^{-1} can be assigned to Si–C stretching vibrational and Si–CH₃ rocking modes, respectively.^{16,17} The structures of the cubic crystals and pseudo-cubic powders are also confirmed in Raman spectra (ESI†). For cubic crystals, Si–O–Si bending and O–Si–O bending modes are observed at 420 cm^{-1} , while asymmetric Si–O–Si stretching vibrational and O–Si–O bending modes appear at 1121 cm^{-1} for pseudo-cubic powders. These Raman absorption bands are characteristic features of the cage structure. On the other hand, a peak at 1121 cm^{-1} is not observed for the spherical particles.

The thermal behaviors of three products were also studied (ESI†). The thermogravimetric analysis (TGA) curve for the cubic crystals under an N₂ atmosphere shows an abrupt weight loss of almost 100% at 250 °C indicating that most of the product was sublimed at this temperature. The TGA curve for the pseudo cubic crystals under a N₂ atmosphere also exhibit similar behavior at this temperature, although a small amount of residue is observed after sublimation. It is reasonable to conclude that the crystallinity of pseudo cubic powders is slightly lower than that of cubic crystals. The TGA curve for the spherical particles from the sol-gel process shows a quite different decomposition behavior. The first weight loss starts at room temperature and continues to 500 °C, and the second weight loss appears between 500 and 600 °C. The former is probably due to the loss of encapsulated water molecules and uncondensed silanol groups, and the latter is from the

decomposition of methyl groups on Si atoms in the particles. It was also found that further heating converted the spherical particles to silicon oxycarbide ceramic. The sublimed cubic crystals lost their cubic morphologies resulting in amorphous powder-like materials. The SEM image of the sublimed cubic crystals is shown in the ESI.† TG-IR analysis for the sublimed product at 270 °C also clearly shows that the product maintains its cubic cage structure (ESI†).

In summary, the colloidal self-assembly growth process for POSS cubic crystals was elucidated using SEM and TEM. The growth process consists of (1) zero-dimensional spherical particle formation, (2) one-dimensional chain arrays of spherical particles, (3) bundling of one dimensional rods, and (4) final assembly of bundles into three-dimensional cubes. The methyltrimethoxysilane-based cubic crystals and ethyltrimethoxysilane based pseudo-cubic powders have octaalkylsilsesquioxane cage structures, which can be confirmed by spectroscopic and X-ray diffraction analyses. In addition, the variation of reaction conditions such as reaction temperature and alcohol solvent can reduce the reaction time for the preparation of the POSS crystals.

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