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Nano-sized cube-shaped single crystalline oxides and their potentials; composition, assembly and functions

Kazumi Kato a,⁎, Feng Dang a, Ken-ichi Mimura a, Yoshiaki Kinemuchi a, Hiroaki Imai b, Satoshi Wada c, Minoru Osada d, Hajime Haneda d, Makoto Kuwabara e

a National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Shimoshidami, Moriyama, Nagoya 463-8560, Japan
b Keio University, 3-14-1 Hiyoshi, Kohoku, Yokohama 223-8522, Japan
c University of Yamanashi, 4-3-11 Takeda, Kofu 400-8511, Japan
d National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan
e Kyushu University, 6-1 Kasuga-kouen, Kasuga, Fukuoka 816-8580, Japan

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A B S T R A C T
Nanocrystals, especially with an anisotropic shape such as cubic, are candidates as building blocks for new bottom-up approaches to materials assembly, yielding a functional architecture. Such materials also receive attention because of their intrinsic size-dependent properties and resulting applications. Here, we report synthesis and characteristics of CeO2, BaTiO3 and SrTiO3 nanocubes and the ordered assemblies. The importance of shape as well as size distribution is clarified for the bottom-up development of 3D fine structures. CeO2 nanocube assemblies with enhanced surface of specified crystal planes such as (100) and (111) would open new surface-dominant devices. BaTiO3 and SrTiO3 nanocubes with narrow size distributions and robust diversity in compositions were obtained. BaTiO3 films made up of ordered nanocube assemblies were fabricated on various substrates by evaporation-induced self-assembly method. Regardless of the substrate, the nanocubes exhibited [100] orientations and a high degree of face-to-face ordering, which remained even after heat treatment at 850 °C. The supracrystal films exhibited distinct ferroelectric behaviors.

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1. Introduction

Colloidal nanocrystals exhibit a wide range of size- and shape-dependent properties and have found application in various fields, including optics, electronics, mechanics, drug delivery and catalysis [1–4]. The simple and convenient production of colloidal nanocrystals with controlled size, shape and composition are therefore of key general importance. Current strategies include organic solution-phase synthesis, thermolysis of organometallic precursors, sol–gel processes, hydrothermal synthesis. These unique nanoscale physical properties, their more-robust chemical stability and biocompatibility than the other forms of metal counterparts, metal-oxide nanocrystals being an important class of nanomaterials for biomedicine, catalysis, electronics and optics.

Now a days, new strategies for materials fabrication are fundamental importance in the advancement of science and technology. The nanomaterials form the building blocks for new bottom-up approaches to materials assembly for a range of uses [13,14]; such materials also receive attention because of their intrinsic size-dependent properties and resulting applications [15,16]. Here we would describe the advantages of typical nanomaterials as CeO2, SrTiO3 and BaTiO3 nanocubes and their assemblies [17–28]. We believe our preliminary results provide a route to a variety of building blocks for assembling materials with novel structure and function in nanotechnology.
2. Tunable shape of CeO₂ nanocrystals and ordering manners in the assemblies

2.1. Synthesis of CeO₂ nanocubes using liquid/liquid interface and organic surfactants

CeO₂ has a cubic crystal structure and is attracting a great deal of attention because of its applications in conversion catalysts, three-way catalysts, fuel cells, solar cells, and metal-oxide semiconductor devices [29–32]. Synthesis of ceria materials with a large specific surface area and high oxygen storage capacities has been the focus of much research. Recently, nanostructured CeO₂ particles such as nanowires and mesocrystals have been widely studied. It is well understood that the performance of nanoparticles strongly depends on the morphology and size distribution [33]. It is desirable to obtain nanoparticles with designed morphology and size distribution. Experimental and theoretical studies have indicated the different reactivities of the crystal face of CeO₂. The (100) face is more reactive for the catalytic properties than (111) and (110) faces because of its high surface energy. Yan et al. [34] and Suda et al. [35] observed that the CeO₂ nanocubes exposed by the (100) face obtained the highest oxygen-storage capacity. On the other hand, the (111) face of CeO₂ is stable in the growth of the crystal structure. It is difficult to control the morphology and monodispersibility of CeO₂ nanoparticles under formal reaction conditions. Adschiri et al. [6,36,37] and Yang and Gao [7] investigated the preparation of monodispersed CeO₂ nanocubes bounded by the (100) face by using an organic–inorganic two liquid phase process.

In a typical synthesis process [17], cerium(III) nitrate aqueous solution was added into an autoclave, and then a mixed solution of toluene, oleic acid (OLA), and tert-butylamine was added to the autoclave in open air without stirring. The sealed autoclave was heated at 180–220 °C for adequate periods, and then cooled to room temperature. The upper organic crude solution was centrifuged to separate the CeO₂ nanocrystals. The separated CeO₂ nanocrystals were redispersed into toluene. The molar ratio of OLA:Ce in the synthesis was controlled at 4:1, 8:1, and 10:1. The reaction time ranged from 24 h to 72 h. Ce⁴⁺ was oxidized by the dissolved oxygen in aqueous solution.

Fig. 1 shows the HRTEM images of the polyhedral particles and nanocubes prepared with a molar ratio of OLA:Ce = 8:1 at 180 °C for 24, 36, and 48 h. For the polyhedral particle, a hexagon was observed from the HRTEM image and the FFT of the HRTEM image showed one set of (200) planes and two sets of (111) planes. The morphology of the polyhedral particle could be imaged as the (200) face truncated octahedron as schematically represented in Fig. 1(a) observed from the [100] direction. The HRTEM images of the nanocubes prepared for 36 h and 48 h showed a similar truncated cubic morphology and good crystallinity. Four (200) and (220) planes as well as two sets of (200) and (220) planes were identified from FFT. It indicated the (111) face truncated nanocube as schematically represented in Fig. 1(b) and (c). The morphology of nanocubes did not change through the reaction time.

The formation of nanocubes using organic surfactants has been studied on CeO₂, SnO₂, Fe₂O₃, Mn₃O₄ and Pt so far [6–12,16–18]. Among them, in the cases of CeO₂ with the fluorite structure and SnO₂ with the rutile structure, the crystallographic analysis was successfully conducted to lead better understandings of the development of nanocube shapes. The facets of the synthesized cubic CeO₂ nanocrystals can be determined by HRTEM, operated by directing the incident electron beam perpendicular to the square facet of the cube [7]. The interfringe distances of the dominant 200 lattice fringes of the HRTEM image are 0.269 nm, close to the (200) lattice spacing of the cubic phase of CeO₂ at 0.271 nm. Furthermore, the perpendicular (200) lattice fringes are either parallel to or orthogonal to the edge of the cube, and the occasionally observed (220) fringes (spacing 0.191 nm) run face-diagonally in the cube. Therefore, the six surfaces of the nanocube were terminated with [200] planes. Transformation of the shape of the CeO₂ nanocrystals from truncated octahedral to cubic shape was mostly caused by the suppression of crystal growth on the (001) surface [6]. As the CeO₂ (001) surface is less stable than the (111) surface, the organic ligand molecules were likely to interact preferentially with the (001) surface. This greatly reduced the growth rate of the crystals in the (001) direction and the crystal growth in the (111) direction became predominant. The change in growth direction led to the formation of nanocubes with exposed (001) surfaces. When the amount of decanoic acid as a surfactant was further increased, the CeO₂ nanocrystal size decreased to about 5 nm. The HRTEM image revealed that the nanocrystal shape was a truncated octahedron enclosed by the (111) and (200) planes. These results suggest that, at high organic ligand concentration, the organic ligand molecules can interact not only with the (001) surface but also with the (111) surface, and thus block crystal growth in both directions. Recently, in situ phase contrast high-resolution transmission electron microscopy with spherical aberration correction was applied to analyze cationic reconstruction on the particularly enhanced (100) surface of the
hydrothermally prepared CeO$_2$ nanoparticles [8,9]. The extensive cerium atomic hopping movements were for the first time observed on laterally extended [100] surfaces and to a smaller degree on [111] surfaces after variable times of irradiation. In addition, the formation of cubic shape SnO$_2$ nanocrystals using tetramethyl ammonium hydroxide (TMAH) has been considered with the coordination structure of the outermost Sn cation on the surface [10]. Sn cations in the bulk of tetragonal SnO$_2$ are coordinated by six oxygen anions situated at the vertices of a distorted octahedron. Those exposed on the (110) face have 6-fold and 5-fold coordination of oxygen anions, changing to 5-fold on (100) and (101), and finally 4-fold on (001). From an electrostatic viewpoint, the Sn cations of the (110) face are likely the most stable, whereas those of the (001) face would be the most unstable because of the lowest and highest density of the dangling bonds, respectively. Therefore, the formation of cubic shape SnO$_2$ nanocrystals with terminal (001) and (110) facets suggested that N(CH$_3$)$_4^+$ preferentially caped onto the unstable (001) plane and decreased the surface energy to the level of the stable (110) plane. The crystal face developing mode of SnO$_2$ nanocube in the rutile structure is considered to be a little distinct from those of CeO$_2$ in the fluorite structure and multicomponent oxides of BaTiO$_3$ and SrTiO$_3$ in the perovskite structure, of which both have much higher symmetry.

2.2. Relations between shape and ordering manner of CeO$_2$ nanocube assemblies

Nanofunctional structures are attracting more attention. Unique magnetic, optical, or electric properties could be obtained through the interactions between the special crystal face of nanoparticles in the functional structure, while bulk materials could not obtained. The preparation of long-range ordered self-assembly structure requires nanocrystals with uniform size and morphology.

Surface-stabilized nanoparticles can spontaneously self-assemble into various ordered structures [3,15,16]. The interaction between surface-adsorbed ligands instead of the van der Waals attraction of the nanomolecules promotes the formation of ordered self-assembly structure. Usually, the exposed crystal face and the orientation of nanoparticles in the nanomaterial are difficult to control via the self-assembly methods, and the high concentration of the organic ligand disturbs the formation of the long-range ordered self-assembly structure. A method for the preparation of a self-assembled multilayer with a controlled exposed crystal face and nanocrystals has been introduced [18]. It is known that a surfactant decreases the surface tension of solvent and concentrates on the liquid–gas, liquid–solid, or liquid–liquid interfaces. It is possible that surfactant-stabilized nanocrystals are drawn to the newly formed liquid–gas interface and self-assemble into ordered structure when the liquid–gas interface of the stable suspension of nanocrystals is enlarged in a short period of time. Otherwise, few works reported the successful preparation of ordered structure formed on the enlarged interfaces. It was found that the high concentration of surfactant can accelerate the formation of long-range ordered self-assembly structure. CeO$_2$ nanocrystals with uniform morphologies were used for the preparation of nanocrystals. It is possible to control the physical properties of the self-assembly nanostructures of CeO$_2$ nanocrystals with different crystal faces as the surface. The reaction temperature was changed to control the growth of [001] and [110] directions of CeO$_2$ at the proper concentration of surfactants. CeO$_2$ nanocrystals with a uniform morphology were successfully synthesized. The suspension of CeO$_2$ nanocrystals with a high concentration of OLA was used to prepare the multilayered nanostructures on a rapid enlarged liquid–gas interface. The multilayered self-assembly structures were obtained with a different crystal face as the surface from the suspension of nanocrystals with different morphologies and a relatively broad size distribution.

The OLA-bound CeO$_2$ nanocrystals with a different morphology were prepared at 220, 200, 180, and 160 °C [18]. After the synthesis, the dispersion of CeO$_2$ nanocrystals was centrifuged to remove the impurity for the preparation of multilayered nanostructures. The concentration of OLA in the dispersion was 4 vol%. A copper grid was horizontally placed on a piece of filter paper. One drop of the suspension of CeO$_2$ nanocrystals was placed on the grid perpendicularly. The excess suspension of CeO$_2$ nanocrystals was absorbed rapidly by the filter paper, and the surface of the suspension enlarged rapidly as soon as the suspension was dropped. The CeO$_2$ nanocrystals self-assembled into ordered multilayered structure on the liquid–gas interface and then were deposited on the grid. This process takes only 3 s. Fig. 2 shows the TEM images and size distribution of the nanocrystals used for the preparation of the multilayered nanostructure. The size distribution of the CeO$_2$ nanocrystals was obtained by counting more than 400 particles from TEM images. Nanocubes, truncated nanocubes, and truncated octahedral were obtained at different temperatures. Nanocubes were obtained at 220 °C with a narrow size distribution as shown in Fig. 2(a). The particle size ranged from 5 to 5.8 nm with a size deviation ([d$_{\text{max}}$ – d$_{\text{min}}$]/d$_{\text{average}}$) of 15.1% as shown in Fig. 2(e). The high-resolution TEM (HRTEM) image showed a perfect cubic shape bound by the (200) face. Fig. 2(b) demonstrates that the morphology of the nanocrystals prepared at 200 °C was a (111) face truncated nanocube. The particle size ranged from 4.4 to 5.8 nm with a size deviation of 28.7%. Except for the truncated nanocubes similar to that prepared at 200 °C, polyhedral nanocrystals were also identified. The HRTEM image of the polyhedral nanocrystals in Fig. 2(c) shows a hexagon, and the FFT profiles of the polyhedral nanocrystals showed one set of (200) and (220) planes and two sets of (111) planes. The polyhedral nanocrystal was identified as a (200) face truncated octahedron, and the particle size ranged from 4.6 to 6.2 nm with a size deviation of 31.6%. The morphology of the nanocrystals prepared at 160 °C almost changed to a truncated octahedron as shown in Fig. 2(d). The particle size of the nanocrystals prepared at 160 °C ranged from 3.6 to 5.8 nm with an enlarged size deviation of 55.6%.

Fig. 3 shows the multilayered nanostructures of the CeO$_2$ nanocrystals. The nanocrystals self-assembled into multilayered nanostructures in a short period of time, and the area can be larger than 10 μm × 10 μm with a thickness of about 50 nm. Four kinds of multilayered nanostructures were identified. The distance between the CeO$_2$ nanocrystals in the introduced nanostructures was about 1 nm at high magnification as shown in Fig 3. The length of the OLA molecule can be estimated by the following formula: $\text{L} (\text{nm}) = 0.25 + 0.127n$, where n is the number of carbon atoms in the alkyl chain [38]. The estimated length of the OLA molecule [CH$_3$–(CH$_2$)$_n$CH=CH(CH$_3$)COOH] is about 2.54 nm. Considering the OLA molecule has a double bond with a cis configuration, the effective chain length of OLA can be calculated with the relationship $\text{L}_{\text{eff}} = 0.67 \times \text{L}$, where the $\text{L}_{\text{eff}}$ of OLA should be around 1.7 nm [39,40]. Compared with the observed distance between nanocrystals in the self-assembled structures, the OLA molecule absorbed on the CeO$_2$ nanocrystals must have adopted a tilting configuration or interpenetrated each other. Fig. 3(a) and (b) shows the direct images of the multilayered nanostructure of CeO$_2$ nanocubes at different magnifications. It revealed a face to face square-symmetry structure. The FFT of Fig. 3(a) shows 4-fold symmetry that confirmed the square organization of the nanocubes. The SAED pattern (d = 150 nm) observed along the [100] direction as a zone axis was obtained for this multilayered nanostructure of nanocubes as shown in Fig. 3(a). It means the oriented assembly of nanocubes
along the [100] direction of the CeO$_2$ and (100) face was the exposed crystal face of this structure. The elongated diffraction spots suggested that parts of nanocubes are misoriented along the in-plane direction. The average orientation distribution was about 10 degrees, estimated from the elongated diffraction spots. Fig. 3(c) and (d) show the direct images of the multilayered nanostructure composed of CeO$_2$ truncated nanocubes at different magnifications. The FFT of Fig. 3(c) shows 4-fold symmetry that was identified as a square lattice. The upper particles occupied the middle position of the four lower particles. As shown in Fig. 3(d), the average distance ($a = 8.6$ nm) between the truncated nanocubes was about 1.4 times the diagonal of the nanocube, which corresponded to a face-centered cubic (fcc) structure [37]. The elongated spots and diffraction rings along the [100] direction were observed in the SAED pattern as shown in Fig. 3(c). We can conclude that the truncated nanocubes self-assembled along the [100] direction fundamentally, and some particles assembled randomly in this structure. The average orientation distribution of the truncated nanocubes grew to about 15 degrees compared to that of nanocubes. The main exposed crystal face of this structure was also a (100) face. Fig. 3(e) and (f) shows the direct images of the multilayered nanostructure of the mixture of the truncated nanocube and truncated octahedron at different magnifications. This structure was very distinct from others. The truncated octahedron also entered the multilayered nanostructure and was about 30% in this structure. The variety of shapes of the truncated nanocubes and truncated octahedra was identified from Fig. 3(f). It was surprising that the cubic particles assembled in an edge-to-edge fashion and not in a face-to-face fashion compared with those of nanocubes and truncated nanocubes. The 6-fold symmetry in the FFT of Fig. 3(e) indicated the hexagonal packing assembly, although this structure was mainly composed by truncated nanocubes and the SAED pattern of this structure corresponded to that of the 4-fold symmetry assembly structure of nanocubes. The 4-fold symmetry of (200) and (220) planes in the SAED pattern of Fig. 3(e) reflected the oriented assembly of truncated nanocubes along the [100] direction, and the 2-fold symmetry of the (111) plane was also identified, which indicated the existence of the truncated octahedron. The 2-fold symmetry of the (111) plane indicated the oriented assembly of the truncated octahedron along the [110] direction as shown in the HRTEM images of Fig. 2(c). The average orientation distribution was about 30 degrees. The truncated nanocubes hexagonally assembled via the introduction of the truncated octahedron to fit the (100) face and avoid the (111) face of the truncated octahedron at the bottom layer. The upper truncated nanocubes occupied the middle position of the two lower particles and rotated to fit the crystal face of the truncated octahedron. The rotation of nanocrystals was thought to be decided by the area of the (111) face. It can be determined that the exposed crystal face of this nanostructure became (100) and (111) faces. Fig. 3(g) and (h) shows the direct images of the multilayered nanostructure of the CeO$_2$ truncated octahedron obtained at different magnifications; 6-fold symmetry of (111), (200), and (220) planes was identified from the SAED pattern of Fig. 3(g). It can be concluded that the truncated octahedron basically self-assembled along the [110] direction, and the main exposed crystal face of this nanostructure became a (111) face. The FFT of Fig. 3(g) shows 6-fold symmetry. The upper truncated octahedron occupied the middle position of the three lower particles to fit the (100) and (111) faces of lower particles in this structure. This structure was identified as hexagonal closely packed (hcp) structure [40]. In addition, it was reported that the oriented attachment of CeO$_2$ nanocubes has been controllable by tuning the hydrothermal conditions [41]. Furthermore, enhanced surface properties of CeO$_2$ nanoparticles dominated by specific crystal planes were investigated for application of several catalysts [42,43].

3. Synthesis of SrTiO$_3$ nanocubes with diversity in composition

3.1. Synthesis of SrTiO$_3$ nanocubes using Ti–O network structure introduced by aqueous Ti complex

Strontium titanate, SrTiO$_3$, as a dielectric compound, is considered to be a suitable material for tunable microwave devices operating at cryogenic temperatures because of its high dielectric constant, large dielectric tunability and low microwave losses [44–46]. SrTiO$_3$ has been investigated as a photocatalyst, such as in the oxidation of hydrocarbons, H$_2$ generation and reduction of CO$_2$ [47,48]. It is well understood that the performance of nanoparticles strongly depends on the morphology and size distribution [33]. The dielectric properties and the polarization of ferroelectric materials are very sensitive to the morphology and size of the system [49–51]. It is desirable to obtain monodispersed nanoparticles with designed morphology and size. Nanosized SrTiO$_3$ nanoparticles can be synthesized by molten salt synthesis [52,53], hydrothermal and related methods [54–57]. On the other hand, few works have reported the synthesis of SrTiO$_3$ nanocubes. Vincenzi et al. reported the formation of SrTiO$_3$ cubic mesostructured particles composed by nanocrystal [58]. Su et al. prepared SrTiO$_3$ nanocubes by using a reverse micelle route [59]. Federico et al. prepared SrTiO$_3$ nanocubes by molten salt method [60]. Sun et al. reported the hydrothermal synthesis of SrTiO$_3$ nanocubes [61]. The synthesis of monodispersed SrTiO$_3$ nanocubes 20 nm in size remained a challenge. The rapid hydrolysis of the Ti precursor is one of the main problems for the control of the morphology and size of SrTiO$_3$ nanoparticles. Bis (ammonium lactate) titanium dihydroxide (TALH) is one of the interesting starting materials as the Ti
precursor, in which all six coordinate positions of the Ti ion are occupied. TALH is stable at room temperature. The high pH hydrolysis of TALH is slower than for other titanium alkoxides. Furthermore, TALH can be concentrated because of the existence of OH in the structure and the ammonium lactate (AL) that is generated by the hydrolysis of TALH can limit the growth of the Ti–O cluster [62]. Recently, a new method using TALH, tetramethylammoniumhydroxide and hydrazine under hydrothermal condition has been reported for the synthesis of SrTiO3 nanocubes by Koumoto et al. [63]. Otherwise, the formation mechanism of the nanocubes and the effect of hydrazine have still not been identified. The hydrazine-assisted synthesis of SrTiO3 nanocubes by tuning strong basic conditions and characteristic behavior of the nanocubes, forwarding the evolution of the nanostructure were investigated [19]. It was found that hydrazine was important for the formation of SrTiO3 nanocubes and that OLA was important to control the size and monodispersibility of SrTiO3 nanocubes. The molar ratio of OLA to hydrazine was important for the morphology control of the SrTiO3 nanocubes.

Fig. 4 shows SrTiO3 nanocubes with a narrow size distribution. The particle size as observed from the TEM image is about 20 nm. The particle size as observed from the TEM image is about 20 nm. The HRTEM image of the nanocubes showed good crystallinity and a sharp edge. It is worth noting that the SrTiO3 particles prepared with Sr:OLA:Hydrazine = 1:2:4 for 48 h could be well dispersed into a nonpolar solvent and self-assembled into an ordered structure deposited on the silicon substrate. The high intensity of the

Fig. 3. TEM images of the long-range ordered self-assemblies of the CeO2 nanocrystals prepared at (a, b) 220 °C, (c, d) 200 °C, (e, f) 180 °C and (g, h) 160 °C. (Reproduced from Ref. [18].)
The (200) peak of SrTiO₃, identified from the XRD pattern of the particles deposited on the silicon substrate, indicated the formation of nanocubes. The DLS result of the dispersion of the nanocubes showed a narrow size distribution. The size of the nanocubes was concentrated from 21 to 25 nm. The small peaks, which ranged from 50 to 70 nm, were thought to be caused by the small aggregates of nanocubes. When the reaction time was elongated to 72 h, large cubic particles over 100 nm were observed. The ED pattern of the large particles showed a single crystal structure. Some small nanocubes attached on the surface of the large cubic particles. The particles have fused to each other and the interfaces of the particles were not identified. It can be seen that the nanocubes mainly aggregated into cubic morphology through the attachment of the (100) face. The observation of the aggregate of nanocubes provided strong evidence that the large cubic particles formed through the oriented aggregation of nanocubes. Fig. 4 shows the aggregated particles composed by nanocubes. It can be seen that the nanocubes have fused to each other in the vertical direction. The ED pattern of the aggregated particles showed a spot like pattern observed from the [001] direction, which indicated that the incomplete hydrolysis of TALH was limited the random aggregation of the nanocubes. The structure of the Ti precursor used for the synthesis of SrTiO₃ could affect the morphology of the synthesized particles in aqueous solution. It is well understood that the SrTiO₃ is formed through the dissolution–precipitation process under hydrothermal conditions. A Ti-based sol forms by the hydrolysis of the Ti precursor. Ti ions dissolve from the Ti-based sol to form the Ti(OH)₄ monomer and the nucleation of SrTiO₃ occurs in solution at a high concentration of NaOH. The Sr species must break the Ti–O bond and incorporate into the Ti–O cluster in this process. It is difficult to control the morphology under hydrothermal conditions especially in an aqueous solution. The ca. 20 nm SrTiO₃ nanocubes were successfully synthesized by controlling the ratio of hydrazine and OLA and by using TALH as the Ti source. The formation of the nanocubes needs the growth and stabilization of the (100) face. The synthesis of the SrTiO₃ nanocubes started from the hydrolysis of TALH. The initial hydrolysis of TALH can be concluded as the following equations [62].

\[
\begin{align*}
\text{AL(OH)}_3\text{Ti-AL} + \text{H}_2\text{O} & \rightarrow \text{AL(OH)}_3\text{Ti} + \text{HAL} \\
\text{AL(OH)}_3\text{Ti-OH} + \text{HO-TiOH(Al)}_2 & \rightarrow \text{Al(OH)}_2\text{Ti-O-TiAl}_2\text{O}_2\text{OH} + \text{H}_2\text{O} \\
(\text{AL})_2\text{OHTi-OH} + \text{AL-Ti(OH)}_2\text{AL} & \rightarrow (\text{AL})_2\text{OHTi-O-TiOHAL} + \text{HAL}
\end{align*}
\]

After the first step of hydrolysis (Eq. (1)), the hydrolyzed species can react with other TALH molecules by condensation as shown in Eq. (2). Furthermore, the TALH molecules can react with each other through condensation to release HAL and obtain large sized species following Eq. (3). In the hydrolysis of TALH, the incomplete hydrolysis of TALH are thought to limit the growth of the Ti–O clusters. The Sr species such as Sr²⁺ and SrOH⁻ can easily incorporate into the Ti–O structure. The particles were synthesized by adding TALH into the aqueous solution with pH 14 at first with Sr:OLA:Hydrazine = 1:2:4 for 48 h. The high pH value was thought to accelerate the hydrolysis of TALH and the formation of the Ti–O cross-linked structure. Nanoparticles with irregular morphology were obtained, which indicated that the incomplete hydrolysis of TALH was important for the formation of nanocubes.

More importantly, all six coordinate positions of the Ti ion are always occupied in the hydrolysis process. For the stabilization of the (100) face of SrTiO₃, it is known that surfactants selectively absorb on the crystal face with a high density of metal ions. The OLA is thought to selectively absorb on the crystal face with a high density of Sr ions because all six coordinate positions of the Ti ion are occupied. Because the density of the Sr ions on the (100) face is higher than on other crystal faces, the (100) face is stabilized and nanocubes are obtained. Hydrazine is important for the
formation of SrTiO₃ nanocubes. Nairm and Thomas [66] reported the effect of hydrazine in the transformation of nanoparticles to nanowires. They found that the zeta potential of nanoparticles decreased significantly after the addition of hydrazine because hydrazine could replace the organic ligand coordinated to the surface of nanoparticles. The same effect of hydrazine is thought to occur in the synthesis of SrTiO₃.

3.2. Diversity in composition of SrTiO₃ nanocubes doped by rare earth metals for thermoelectric application

In SrTiO₃ perovskite structure, the Sr atoms construct a simple cubic lattice and a TiO₆ octahedron occupies the center of the cubic lattice, in which oxygen is located at the face-center positions. Reflecting this cubic lattice, it is possible to shape nanoparticles of SrTiO₃ into the cubic form, of which the surface is confirmed to be (001) as mentioned above [19]. The (001) surface is crystallographically unpolared stable surface which can be terminated by either TiO₂ or SrO layers. Actually, the regular TiO₆ octahedron is suggested to be disturbed due to surface relaxation near the (001) surface, which is predicted by first principles calculation [67]. Indeed, the Raman spectrum of such nanocubes shows first order Raman scattering despite the fact that the centrosymmetric cubic structure of SrTiO₃ is not Raman active, indicating permanent surface dipole originating in the breakdown of inversion symmetry near the surface [68]. Such a permanent surface dipole modifies the dielectric properties near the surface. The rare earth, RE, doping to the Sr-site is known to tune the distortion of TiO₆ through the chemical pressure [69].

Charged carrier doped SrTiO₃ is regarded as an important material for thermoelectric energy conversion due to the heavy electron mass originating in triply degenerate Ti 3d orbitals. Because such heavy electron mass enhances thermopower, the conversion efficiency from heat to electricity and vise versa drastically improves. Further improvement can be achieved by nanostructuring. For instance, potential barrier generating near the surface modifies energy distribution of charged carrier, which can boost the average energy of carrier leading to enhancement of thermopower [70].

The surface is also crucial in controlling phonon thermal conductivity, which is significantly lowered through boundary scattering. The influence of grain size on the thermal conductivity of SrTiO₃ suggests Kapitza resistance of grain boundary to phonon transfer [71], which also contributes to the enhancement of the efficiency of thermoelectric energy conversion. Such impact of RE doped SrTiO₃ nanocubes on thermoelectric properties can be found elsewhere [20]. Here the diversity in composition and lattice structure of nanocubes doped with RE elements are described.

Nanocubes of RE doped SrTiO₃ were synthesized by a hydro-thermal synthesis method [19,20]. The nominal composition was chosen as REₑ₋ₓSrₓTiO₃ (x = 0, 0.1 or 0.2), in which La, Ce, Nd, Sm, Eu, Gd, Tb or Y was doped as the RE element. Acetic acids of Sr and RE dissolved in distilled water with stirring were used as starting materials for the Sr-site. TALH, hydrazine, and oleic acid were then added to the solutions. Hydrothermal synthesis at 200 °C for 24 h resulted in a white product. The white products were then annealed in vacuum at 500 °C for 1 h to remove polymer surfactant on the surface. We noticed that the color of the product changed to dark gray after the annealing.

The synthesized nanoparticles had cubic shape and were about 20 nm. The size distribution was relatively large compared with that of non-doped SrTiO₃ [19]. No appreciable secondary phase was found below 20 at% RE substitution. We confirmed that the compositions of the products were identical to the nominal composition within a variation of 2 at% by energy dispersive X-ray (EDX) spectroscopy. The lattice constant changed linearly with RE ionic radius as shown in Fig. 5(a). For the smallest RE, Y, the Vegard’s law was verified until 20 at% of substitution. (Fig. 5(b)) This solubility limit of Y is twice that observed in a previous report [72] in which solid state reaction was employed for the synthesis.

In the Raman spectra of the RE doped nanocubes, appearance of forbidden modes was evident as shown in Fig. 6. These were assigned to the ferroelectric soft mode of the TO₂ and TO₄ modes. Basically, the soft modes are Raman inactive. TO₂ predominantly consists of the vibration of Sr against TiO₆ octahedra, and TO₄ of Ti-O stretching. Non-doped nanocube and ceramics are known to similarly show this first-order Raman scattering, which is associated with breakdown of symmetry at the interface; the cubic lattice relaxes into a tetragonal one near the surface or the grain boundary, resulting in it becoming Raman active. In the Raman spectra, it is noticeable that both TO₂ and TO₄ become more evident with RE size. This means that the cubic structure gradually recovers by surface relaxation with smaller RE doping. By the DFT calculation of the surface model, we found that the position of Sr moved largely in the surface region compared with the inside region while the position of oxygen was almost identical to that of the cubic structure. Meanwhile, Ti shifted slightly counter to the direction of Sr movement. The large atomic shift of Sr is thought to originate in the ionic nature in this compound. Importantly, the shift of Sr was larger in the case of La doping than Y doping. The TO₂ mode corresponds to the movement of Sr atoms related to TiO₆ octahedra and is therefore affected by the shift of Sr, so the DFT results imply weak TO₂ mode for small RE, in agreement with the experimental observations. Meanwhile, the TO₄ mode, which corresponds to the Ti-O stretching and is therefore associated with Ti-O distance, is found to be distorted more from the original cubic length in the case of La doping rather than Y doping.
This result also explains the observed experimental trend. So far, it has been confirmed that the thermopower of RE doped nanocubes systematically varied corresponding to the structural variation of the surface, and that of Y doped SrTiO₃ was exceptionally huge, suggesting a high potential of nanocube strategy.

4. Synthesis of BaTiO₃ nanocubes and the supracrystal with ferroelectricity

4.1. In situ growth of BaTiO₃ nanocubes in Ti–O matrix derived by aqueous Ti complex

Barium titanate (BaTiO₃), as a dielectric, is widely used for the preparation of multilayer ceramic capacitors (MLCCs), embedded capacitors in printed circuit boards, positive temperature coefficient of resistance (PTCR) thermostats and electro-optic devices [73–75]. Recent developments aimed for the miniaturization of MLCCs to achieve high capacitance in small size. For BaTiO₃ bulk materials, the largest dielectric properties are obtained at the Curie temperature, Tc, corresponding to the phase transition from tetragonal phase to cubic phase. The strain of the crystal structure induced by phase transition at Tc is thought to be one of the mechanisms for the high dielectric properties. It provides a possible method to obtain high dielectric properties for BaTiO₃ functional nanostructures through the strain of the interface between nanoparticles at room temperature without sintering. Morphology control of nanocrystals has become increasingly important, as many of their physical and chemical properties are highly shape dependent, and the morphology determines the properties and possibility of the formation of functional nanostructures. The cubic morphology is one of the best morphologies for the formation of a close-packed structure and can provide larger interfaces between the contacted nanoparticles than other morphologies. For the synthesis of BaTiO₃ nanocubes, a conventional hydrothermal method cannot provide the required particles size, morphology, and homogeneity [76–78]. When BaTiO₃ particles grow through a dissolution–precipitation mechanism, Ti–O bonds of Ti-based hydrous gel must be broken by Ba⁺⁺ species and rearrange to form the BaTiO₃ structure. Because of the similar surface energy between the crystal faces and the high atomic density of the (110) face, it is difficult to control the growth of the special crystal face of BaTiO₃ [79,80]. Only some works were able to successfully synthesize monodispersed BaTiO₃ nanocubes with well-defined shape and controlled size. O’Brien et al. synthesized monodispersed cubic-like particles of ca. 10 nm by using a complicated Ba–Ti precursor [81]. Caruntu et al. reported the synthesis of monodispersed BaTiO₃ nanocubes of ca. 20 nm by using Ti(OBu)₄ as source material [82]. The formation of nanocubes in these works was based on a dissolution–precipitation mechanism. Recently, the displacement of Ti ions in oxygen octahedral of individual BaTiO₃ nanocubes down to sub-10 nm dimensions was clarified using aberration-corrected transmission electron microscopy (TEM) [83]. It has been reported that the structure of Ti precursor could influence the crystal phase of the synthesized TiO₂ particles [84]. The formation of BaTiO₃ nanocubes depended on the structure of Ti precursor [21], which is similar to the formation of SrTiO₃ [19,63]. TALH is a Ti precursor in which all six coordinate positions of Ti ion are occupied. The hydrolysis of TALH is slow and incomplete. An ordered arrangement of monodispersed BaTiO₃ nanocubes were synthesized in aqueous solution by using TALH as starting material with mechanical stirring under hydrothermal condition. Tert-butylamine (t-butylamine) was used to accelerate the formation of BaTiO₃ phase at a high concentration of OLA. The kinetics of formation of BaTiO₃ nanocubes was observed and the formation of BaTiO₃ nanocubes formed through an in situ growth mechanism was investigated. The presence of superlattice of nanocubes was identified in the formation process [21]. In addition, the recent numerical calculations indicated that the critical size becomes considerably smaller as the degree of adsorbate-induced charge screening increases, because the depolarization energy is reduced [22].

Fig. 7 shows TEM, electron diffraction (ED), and fast Fourier transform (FFT) images of the particles synthesized under the fundamental reaction conditions (200 °C, Ba:OLA:butylamine = 1:8:8, NaOH 1 M, 72 h). BaTiO₃ nanocubes with a well-defined cubic morphology ranging from 20 to 50 nm in edge length formed an ordered arrangement (Fig. 7(a)). A spot-like selected area electron diffraction (SAED) pattern (d = 150 nm) along the [001] zone axis was obtained for the ordered aggregates of nanocubes (Fig. 7(b)), which indicated oriented aggregation of nanocubes along the [001] direction. The particle size was in the range from 18 to 50 nm. The direct laser scattering (DLS) method results suggested that the BaTiO₃ nanocubes were well dispersed in toluene. The HRTEM image of a nanocube shown in Fig. 7(c) indicates a high degree of crystallinity. Four (100), (110) and (200) planes as well as two sets of (100), (110) and (200) planes were identified from the FFT profile (Fig. 7(d)) of the HRTEM image. This means that a perfect cubic shape was projected from the [001] direction. In addition to the nanocubes, nanocrystals ranging in size from 3 to 5 nm were also observed; these were highly crystalline with irregular morphologies. In the FT-IR spectrum of the BaTiO₃ nanocubes deposited on the Si substrate, bands in the range of 2500–3300 cm⁻¹ associated with the C–H stretching mode of methyl and methylene groups in OLA appeared. The bands at 1557 and 1418 cm⁻¹ are attributed to the stretching of the carboxylate group, which indicated that the carboxylate group in OLA was chemically bonded to the metal ions on the surface of the BaTiO₃ nanocubes [85,86]. It was found that only OLA was absorbed on the surface of the nanocubes. BaTiO₃ nanocubes with uniform size and morphology were successfully synthesized by changing the molar ratio of OLA to t-butylamine. As shown in Fig. 8, no nanocrystals were identified when the particles were synthesized at 200 °C in 1 M NaOH with the molar ratio of Ba:OLA:butylamine = 1:8:12 for 72 h. The ordered aggregates were composed of perfect nanocubes of ca. 20 nm size with a narrow size distribution. Particle sizes ranging from 16 to 25 nm were confirmed from the DLS results. It is worth noting that the ordered aggregates of nanocubes disappeared with an increase in concentration of t-butylamine but were only formed under a high concentration of OLA. The ordered arrangement of

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BaTiO$_3$ nanocubes was synthesized by using TALH as the Ti precursor with the addition of OLA and t-butylamine. The formation and morphology of the synthesized BaTiO$_3$ nanoparticles and aggregates can be influenced by the structure of the Ti precursor developed in the synthesis process. It is well understood that the BaTiO$_3$ nanoparticles were formed through a dissolution-precipitation process under hydrothermal conditions in aqueous solution\cite{79}. The Ti monomer dissolves from the hydrous gel to form a Ti–O–Ti cross-linked network via dehydration, and nucleation of BaTiO$_3$ occurs in solution at a high concentration of NaOH. Because Ti(OH)$_4$ tetrahedra are the dominant Ti species in the aqueous solution, the Ba species must break the Ti–O bond to be incorporated into the Ti–O cluster, and then rearrange to form the BaTiO$_3$ structure. So far, to the best of our knowledge, there have been no studies reporting precise control of the morphology and size distribution of BaTiO$_3$ particles in aqueous solution under hydrothermal conditions. Based on observations of the kinetics of formation of nanocubes, the BaTiO$_3$ nanocubes were formed through an in situ growth mechanism from the Ti-based hydrous gel and the ordered aggregates of nanocubes were formed in the growth process of the BaTiO$_3$. The in situ growth mechanism of nanocubes can be attributed to the hydrolysis of TALH and the derived structure.

It is worth noting that the BaTiO$_3$ phase could not be obtained without the addition of t-butylamine. It is suggested that t-butylamine stabilizes the hydroxyl group of the Ti octahedra to suppress...
the formation of [TiO₄] building blocks by edge sharing. Only the addition of t-butylamine allowed for the synthesis of BaTiO₃ nanocubes. This is attributed to the strong polarity of t-butylamine. OLA has long hydrophobic C–C chains and hydrophilic –COOH which adsorbs on the interface of the Ti-based hydrogel in aqueous solution. The adsorption of OLA limited the dissolution of the Ti monomer from the hydrogel. The addition of OLA suppressed the growth of BaTiO₃ through the dissolution–precipitation process. For morphology control of BaTiO₃ nanocubes, stabilization of the (100) face needs to be achieved. OLA was considered to be mainly adsorbed on the crystal face with a high density of Ba ions, because all six coordinate positions of the Ti ion are always occupied by hydroxyl groups. Since the density of Ba ions on the (100) face is higher than on other crystal faces, the (100) face is stabilized by the adsorption of oleic acid and consequently (100) dominant nanocubes are formed.

4.2. Development of BaTiO₃ supracrystals and their ferroelectric properties

In order to realize nanotechnology applications, assembly of nanocrystals to form ordered nanostructures should be attained [4,13,14,87]. Nanocrystals with nonspherical and anisotropic shapes, such as cubic, have attracted attention for close packing to directly form ordered architectures. The development of simple and effective methods to create ordered architectures is of great interest. Free-standing, monodisperse BaTiO₃ nanocrystals with a well-defined shape, controllable size and a high degree of compositional homogeneity are essential for opening up new possibilities for assembling individual nanocrystals into functional nanostructures, such as 3D ferroelectric supracrystals. Recently, the high potential of BaTiO₃ nanocubes and assemblies with ordered structures have been demonstrated by several reports [23–28] and thereby the current status of development of advanced future devices would be addressed.

A schematic image of the assembly mechanism is illustrated in Fig. 9. The mechanism of the capillary force-assisted self-assembly is promoted by the convection in the vicinity of the surface of the substrate. Due to the convection, the nanocubes were moved into the liquid film at the surface of the substrate. The lateral capillary force then worked between the nanocubes to connect them to each other when the evaporation of the solvent from the liquid film occurred. When withdrawing the substrate from the nanocube dispersed solution, shear stress was applied at the surface of the substrate. This accelerates convection in the vicinity of the substrate and results in pushing the supply of nanocubes toward the formation of assemblies. In order to fabricate a large area ordered assembly, it is necessary for the assembly rate of nanocubes on the substrate, defined as “formation rate” of the assembly, to be equivalent to the withdrawal rate of the dip coating process [88,89]. The evaporation rate of the solvent should be sufficiently low because the formation rate of the assembly is usually very low. In the method, mesitylene was chosen as the solvent, which has a high boiling point of 165 °C. Thereby, the withdrawal rate could be set as low as 0.01 μm/s and could be made equivalent to the formation rate. As a result, the nanocubes were assembled with a high degree of ordering over a long range.

Stacked structures of BaTiO₃ nanocube assemblies with a high degree of ordering were obtained on various substrates, such as Pt/Si, Pt/MgO, and Pt/SiO₂. Fig. 10 shows typical FE-SEM images of as-assembled films on the Pt/MgO substrate. The assembly area was about several tens of square micrometers. It was found that BaTiO₃ nanocubes were tightly assembled and attached face-to-face on a variety of substrates. FFT images of these assemblies are inset in Fig. 10(a) and (b). Four-fold symmetric patterns were confirmed in all FFT images. This confirmed that highly ordered assemblies of nanocubes were obtained on a variety of substrates. A cross-sectional image of a BaTiO₃ nanocube assembled film on a Pt/MgO substrate is shown in Fig. 10(c). The internal portion of the assembled film is quite dense and has a highly ordered structure. The thickness of the assembly is about 600 nm. The size of the typical ordered region in the nanocube assemblies is about 20 μm².

Fig. 10(d) shows microstructures of a BaTiO₃ nanocube assembled film on a Pt/MgO substrate after heat treatment at 850 °C. The highly ordered structure and shape of the BaTiO₃ nanocube constituents were maintained after heat treatment. The microstructural characteristics of the assemblies are similar on the three types of substrates used. Several pores with cube-like shapes appeared at the surface of the assemblies. These pores are missing nanocubes owing to shrinkage of the films through the heating process.

Surface and cross-sectional HR-TEM images of a BaTiO₃ nanocube assembly fabricated on a Pt/MgO substrate after heat treatment at 850 °C are shown in Fig. 11. The local structures of the surface and the internal portion were determined to be highly ordered and dense. Both electron diffraction patterns of the surface and cross-sectional regions showed perfect 4-fold symmetry and indicated that the assembly had {100} orientation [26–28]. It was again confirmed that a highly ordered structure of nanocubes was maintained during relatively high temperature heat treatment owing to the nanocube packing in a face-to-face manner. The difference in the contrast of each nanocube is due to slight misorientations between them. The stripe-like patterns in some nanocubes may be associated with incoherence in the lattice, which stems from strain generated at the interface, and seems to affect the ferroelectric properties. Otherwise, the connection of each nanocube was confirmed in the high-resolution images. Thus, the assembly of BaTiO₃ nanocubes after heat treatment at 850 °C yielded a unique structure being a quasi single crystal or “supracrystal”.

The $d_{33}$-E loops of BaTiO₃ nanocube assemblies after heating at 850 °C were characterized. BaTiO₃ nanocube assemblies fabricated on Pt/Si, Pt/MgO and Pt/SiO₂ substrates had saturated rectangular shaped ferroelectric hysteresis loops, as shown in Fig. 12. The saturation value of $d_{33}$-PPM was in the range of 10–20 pm/V on various substrates. This value is relatively low compared to that of epitaxial or textured BaTiO₃ thin films, which contained significant strain under stress induced by the substrates. The low value is considered to be due to the fact that the present BaTiO₃ nanocube assemblies are free from the effects of the substrate. Otherwise, as shown in the HR-TEM images in Fig. 11, the nanocubes were slightly rotated and misaligned with each other. These small misfit interfaces in the assembly may affect the piezoelectric properties. The most distinctive feature of the BaTiO₃ nanocube assemblies that differed...
from that of the BaTiO$_3$ single crystal is that the former have many interfaces between the ordered nanocubes. If the interfaces can be completely controlled by tuning the composition and arrangement of nanocubes, the resistivity of the assemblies will be enhanced and the piezoelectric properties can be improved by entirely applying a voltage. An investigation of the relation between the interface and properties is now in progress. Additionally, the $d_{33}$–$E$ curves were shifted to the negative bias of the poling field. The imprint behaviors are considered to stem from the asymmetry of the top and bottom electrodes. By using the cantilever with a high force constant, the interface between the top of the cantilever tip and the surface of the nanocube assembly was improved to have good

![Fig. 10. FE-SEM images of BaTiO$_3$ nanocube assemblies on Pt-coated MgO substrate. (a) and (b) surface images of as-fabricated assemblies with FFT patterns, (c) cross-sectional image of the assemblies, and (d) surface image of the assemblies after heat treatment at 850 °C. (Reproduced from Ref.[27].) ](image1)

![Fig. 11. HR-TEM images and SAED patterns of (a) in-plane and (b) cross sections of BaTiO$_3$ nanocube assemblies after heat treatment at 850 °C. (Reproduced from Refs. [26,27]. Copyright (2013) The Japan Society of Applied Physics.)](image2)
nanocubes, truncated nanocubes, and truncated nanocrystals self-assembled on an nanocube. In contrast, t-butylamine acceler nanocubes, J. Nanocubes, J. Elect. Mater. DOI:http://dx.doi.org/10.1007/ nanocubes was synthesized nanocubes by thermohydrolysis method, with the perovskite structure were fabricated by using nanocubes and related polyhedra prepared by using a liquid–liquid nanocrystal orientation, and is expected to be used for future electronic device applications. Macrocacks induced by shrinkage during the evaporation of solvents should be suppressed for practical device applications. The optimization of substrate materials and surface functions would solve the serious problem to form crack-free assemblies. The nanocube assembly should be characterized to have a lot of interfaces between ordered nanocubes in three dimensions. The interfaces between the nanocubes can be controlled and designed to obtain better electronic properties. The series of studies and systematic analysis in the previous papers on nanocrystals and assemblies pave the way to a new type of crystallography and methodology of thin films leading to a novel device technology, wherein the structure and functionality of assemblies are basically determined by the shape of the constituent nanocrystals.

5. Summary

A rapid approach for preparing the self-assembled multilayered nanostructure of CeO2 nanocubes, truncated nanocubes, and truncated octahedra with a broad size distribution was demonstrated. The high concentration of OLA was the key parameter for the formation of multilayered nanostructure. The orientation of the nanocrystals changed from the [100] direction to the [110] direction in the multilayered nanostructure and decided the exposed crystal face of the multilayer nanostructure that changed from the (100) face to the (111) face. The shape of the building-blocks are found to be dominant for both the structure and properties of the assemblies.

Nanocubes of multicomponent oxides such as SrTiO3 and BaTiO3 with the perovskite structure were fabricated by using TALH, OLA and additives. The diversity in the composition of nanocubes are found to be robust against for doping of RE metals. The work functions on the d33-PFM (pm/V)Detector Laser Pt/TiO2/Si

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