Morphology evolution of NaTaO₃ submicrometer single-crystals: from cubes to quasi-spheres

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Surface structure control of functional nano-/micro-crystallites has attracted great attention because many important physicochemical properties depend on their surface. Guided by the supersaturation-dependent surface structure evolution strategy we proposed recently, NaTaO₃ submicrometer crystals with morphologies of cubes, corner truncated cubes, edge and corner truncated cubes, and quasi-spheres can be synthesized by changing the volume ratio of ethylene glycol to water and the amount of NaOH in the composite solvent. Under low supersaturation condition, NaTaO₃ cubic crystals with low energy {100} facets were obtained. As the supersaturation increases, the corners and edges of NaTaO₃ cubic crystals, which possess higher surface energy, were gradually truncated. Surprisingly, quasi-sphere crystallites formed under extremely high supersaturation condition, which is difficult to be explained by the classical crystal growth theories. By analyzing the formation work of two-dimension crystal nuclei, we concluded that the crystal growth tend to be isotropic at extremely high supersaturation, which well explained the formation of the quasi-sphere crystallites.

INTRODUCTION

In the past decade, many efforts have been devoted to controlling the crystal surface structures for specific purpose, since many physicochemical properties of crystals strongly depend on their exposed surface [1–5]. Despite the great success in morphology-controlled syntheses of nanocrystals, our comprehension of the formation mechanism of specific surface of crystals in nanoscale is far from enough. Especially, it is still a great challenge to explore some universal, precise surface-controlling strategies that apply to most crystalline materials from metallic to ionic and even molecular crystals. Establishing the mechanistic proposals on the basis of thermodynamics and kinetics principles and concepts, which are universal for the growth of macroscopic and microscopic crystals, is the first step towards a rational design and systematic approach [6,7]. Recently, based on thermodynamics and the Thomson–Gibbs equation, we concluded that the surface energy of crystal face is in proportion to the supersaturation of crystal growth units during the crystal growth, which can effectively guide the

control of the surface structure of some crystals [8].

NaTaO₃ is a semiconducting metal oxide with perovskite structure and it has important applications in many fields such as photocatalysis and sensing [9–12]. To enhance the performance of NaTaO₃ in the applications, many improvement strategies, by which the bulk or surface structures of NaTaO₃ can be modified reasonably, have been developed to date [9,13–16]. Both photocatalysis and sensing occur on the surface of the functional materials, so the performance of NaTaO₃ can be significantly enhanced through optimizing the surface structure of NaTaO₃ crystals. For example, Jiang *et al.* [17] reported that NaTaO₃ cubic nanocrystals, which possessed very high effective surface area by self-assembling into mesocrystal-like architectures, showed outstanding photocatalytic performance for water splitting. Unfortunately, rare success has been made in rationally engineering specific surface of NaTaO₃ crystals. No matter in macroscopic scale or in nanoscale, NaTaO₃ crystals mostly grow up into cubic or quasi-cubic morphologies enclosed with {100} facets [10,16–18]. This growth habit of NaTaO₃ is inherently determined by the perovskite-type crystals in which {100} facets have the lowest surface energy and lead to the best thermodynamic stability. Therefore it is desirable to study how to synthesize morphology controllable NaTaO₃ crystals with specific surface structures and make it effective in improving the performance of NaTaO₃-based materials.

In this paper, guided by the supersaturation dependent surface evolution strategy, we successfully controlled the growth of perovskite NaTaO₃ crystals via controlling the supersaturation by tuning ratios of ethylene glycol (EG)/water composite solvents and concentrations of NaOH in the reaction solution. It was found that the morphologies of NaTaO₃ crystals evolved from cubes to corner truncated cubes, edge and corner truncated cubes, and finally to quasi-spheres with increasing the supersaturation. Noticeably, the quasi-sphere shape of single crystal particles obtained at high supersaturation condition cannot be explained by the classical crystal growth theories, such as the Wulff con-

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struction theorem. We found that the formation work of two-dimensional crystal nuclei during the crystal growth can well explain the growth of quasi-sphere shape of single crystal.

EXPERIMENTAL

Chemicals

Tantalum (V) oxide (Ta_2O_5 , 99.99%) was purchased from Beijing InnoChem Science & Technology Co., Ltd. Ammonium hydroxide ($\text{NH}_3\cdot\text{H}_2\text{O}$, 25%), hydrofluoric acid (HF, 40%) and ethylene glycol (EG, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH, 96%) was purchased from Guanghua Sci-Tech Co., Ltd. All the reagents were used without further purification.

Syntheses of NaTaO_3 Submicrometer Crystals

Commercial Ta_2O_5 was pre-treated by HF aqueous solution (40%) according to the previously reported procedure [19]. Firstly, 0.50 g Ta_2O_5 and 3.0 mL of HF aqueous solution were mixed in a Teflon-lined autoclave with a capacity of 20 mL. Then the autoclave was sealed and heated at 140°C for 60 min to dissolve Ta_2O_5 . After being cooled to room temperature naturally, 20.0 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$ was dropwise added into the resulting mixture, and then white precipitates generated. Finally, the white precipitates were collected by centrifugation, washed by deionized water and ethanol for several times, and dried in oven at 60°C . This product was named as $\text{Ta}_2\text{O}_5\cdot n\text{H}_2\text{O}$ and used as the precursor of NaTaO_3 submicrometer crystals.

NaTaO_3 submicrometer crystals with different morphologies were prepared in the composite solvent of EG and water with different ratios. In a typical synthesis of cubic NaTaO_3 crystals, 0.010 g $\text{Ta}_2\text{O}_5\cdot n\text{H}_2\text{O}$ and 0.40 g (10 mmol) NaOH were dispersed in 1.0 mL of EG and 13.0 mL of deionized water by ultrasonication. Then, the mixture was transferred into a Teflon-lined autoclave of 20 mL, sealed and heated at 200°C for 12 h before it was cooled to room temperature. The precipitates were collected by centrifugation, and washed with deionized water for three times and ethanol for once. Finally, the precipitates were dried in

oven at 60°C overnight. Other samples were prepared by varying the volume ratio of EG to water or the amount of NaOH in the reaction solution.

Characterizations

The morphologies of the products were observed by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, JEOL JEM2100) at an accelerating voltage of 200 kV. The crystalline phase and composition of the products were determined by X-ray powder diffraction (XRD) recorded on a Rigaku D/max X-ray diffractometer (Cu K α radiation, $\lambda = 0.15418$ nm).

RESULTS AND DISCUSSION

According to the Thomson-Gibbs equation, the surface energy of the crystal facets is in proportion to the supersaturation of the crystal growth units during the crystal growth under a supersaturated condition (not under an equilibrium condition) [8]. Therefore, the exposed surfaces and the morphologies of crystallites can be controlled by varying the supersaturation of the crystal growth units. In our previous papers, it was discussed that the introduction of a poor solvent increased the supersaturation [8,20]. Inspired by these preceding reports, we introduced the supersaturation strategy into the controllable growth of NaTaO_3 crystal. Under the solvothermal condition [21,22], a two-step reaction process, involving the dissolution of reactant $\text{Ta}_2\text{O}_5\cdot n\text{H}_2\text{O}$ with NaOH and the formation of the growth units, is needed, as shown in Scheme 1. Firstly, $\text{Ta}_2\text{O}_5\cdot n\text{H}_2\text{O}$ precursor is gradually dissolved with the assistance of NaOH, and then the released Ta^{5+} ions are bonded with hydroxyl ions to form $\text{Ta}(\text{OH})_6^-$ ions. Afterwards, Na^+ ions bind with $\text{Ta}(\text{OH})_6^-$ ions, followed by the dehydration of the whole group to form NaTaO_3 . According to the “like dissolves like” principle, water could be a good solvent for the growth of NaTaO_3 crystals, while the organic solvent EG is a poor solvent. Therefore, the supersaturation of the growth units in the mixed solvent can be facily elevated by increasing the volume ratio of EG to water, thereby leading to the formation of NaTaO_3 crystals with high energy facets.

Fig. 1 shows typical morphologies of the products ob-

Scheme 1 Formation processes of NaTaO_3 growth units. (a) Dissolution of $\text{Ta}_2\text{O}_5\cdot n\text{H}_2\text{O}$; (b) formation of $\text{Ta}(\text{OH})_6^-$; (c) dehydration and nucleation of the growth units.

Figure 1 SEM images of NaTaO₃ crystals obtained with 10 mmol NaOH and different volume ratios of EG to water: (a) 1/13, (b) 3/11, (c) 5/9, (d) 11/3. Insets are the corresponding SEM images and schematic models.

tained via solvent-dependent experiments, in which the volume ratio of EG to water was varied from 1/13 to 3/11, 5/9, and 11/3, respectively. All the products consist of sub-micrometer particles that are mostly in the size range of 500–800 nm. With the volume ratio of EG to water increasing, the morphology of the particles changes significantly. When the volume ratio of EG to water is 1/13, the as-prepared particles possess a perfect cubic morphology (Fig. 1a). When the volume ratio of EG to water increases to 3/11, the particles remain a cubic shape, but eight corners are obviously truncated, as shown in high-magnification SEM image (Fig. 1b). When the volume ratio of EG to water increases to 5/9, both the corners and edges of the cubic particles are truncated (Fig. 1c). When the volume ratio is higher than 7/7 (e.g. 11/3), the as-prepared products are composed of quasi-spherical particles (Fig. 1d). High magnification SEM image clearly shows that the surface of these particles is smooth, which indicates that the quasi-spherical particles are not built up by secondary particles with smaller sizes. For convenience, the NaTaO₃ crystals with the morphologies of cubes, corner truncated cubes, edge and corner truncated cubes, and quasi-spheres are denoted as Cube, CTC, ETC, and QS, respectively.

The crystalline phase of these products was characterized by XRD, as shown in Fig. 2. It can be seen that all the patterns are well assigned to the pure cubic perovskite NaTaO₃ with a space group of P23 and lattice parameter of $a = 3.8978(2)$ Å after cell refinement. No peaks assigned to Ta₂O₅ appear in the XRD patterns, which indicates that the precursors are completely transformed into NaTaO₃. The narrow and sharp diffraction peaks imply the large particle size and good crystallinity of these products. In addition, it is clear that the ratio of the intensity of the (110) peak to that of the (100) peak changes obviously from Cube and CTC to ETC and QS. The close examination shows that

Figure 2 XRD patterns of NaTaO₃ particles with different morphologies.

the intensity ratio of (100) peak to (110) peak increases from 1.08 for Cube to 1.05, 0.85 and 0.84 for CTC, ETC and QS, respectively. Such a change of relative diffraction intensity results from either the change of crystal structure or preferential orientation of crystallites. In present case, it is associated with the change of the preferred orientation of NaTaO₃ crystals resulted from the change of the percentage of the exposed (100), which is demonstrated by further TEM observations.

More structural information of the as-prepared sub-micrometer NaTaO₃ crystals with different morphologies are provided by TEM characterization (Fig. 3). The regularly arranged diffraction spots in their selected area electron diffraction (SAED) patterns show the single-crystal nature of these NaTaO₃ particles. As shown in low-magnification TEM images (Figs 3a₁–a₄), the four NaTaO₃ particles, all of which are projected from the [001] zone axis, display the projected outlines of varied but well-defined convex polygon. As the corresponding high resolution TEM (HR-TEM) images shown, the interplanar d -spacings of 0.39 nm are clearly recorded in these particles, which correspond to the (100) planes of NaTaO₃. Thus, the flat facets in Figs 3a₁–a₃ should belong to {100} facets and the area of (100) facets gradually decrease from cube to CTC, ETC, and QS, agreeing well with the XRD measurements. It is worthwhile to note that the corners of CTC (marked by dotted boxes in Fig. 3a₂) have a relatively low contrast compared to the center of the particle, indicating that the corners are truncated. For the QS particles, the area of {100} facets becomes very small, and the outline looks nearly round due to the appearance of a dozen facets of different indexes (Figs 3a₄ and S1).

In order to compare the surface energies of these NaTaO₃ crystals, the exposed crystal facets were carefully characterized. The exposed facets can be figured out by

Figure 3 (a) TEM images and (b) HRTEM images of NaTaO₃ cube (*a*₁ and *b*₁), CTC (*a*₂ and *b*₂), ETC (*a*₃ and *b*₃) and QS (*a*₄ and *b*₄) particles. Insets in (b) are the corresponding SAED patterns.

comparatively analyzing the morphology of the single particle with their geometrical models, which were projected from different crystal zone axes. Here we choose ETC as the representative morphology, because at least three facets are included in ETC. Figs 4*a*₁–*e*₁ and Figs 4*a*₂–*e*₂ show the SEM, TEM, HRTEM images, SAED patterns and structural models of a single ETC particle viewed along [111] and [110] zone axis, respectively. The direction of some dominant facets on the surface of the ETC particle in the TEM images are easily inferred through checking the attribution of the lattice fringes in the HRTEM images and analyzing SAED patterns as marked in the images. According to the

Figure 4 (a) SEM images, (b) TEM images, (c) SAED patterns of (b), (d) HRTEM images, and (e) schematic models of the ETC particle viewed along different zone axis: (a–e)₁ [111] and (a–e)₂ [110].

SEM image of the ETC particle, it can be inferred that the flat surface should be {100} facets, and the facets perpendicular to directions of observation in Figs 4*a*₁ and 4*a*₂ are {111} and {110} facets, respectively. With the help of the

built ETC models, the above inferences about the predominantly exposed facets on the surface of the ETC particle can be confirmed. The large and flat facets are {100} facets and the curved surface is dominated by {111}, {110} and other high index facets. Based on the above results, we can conclude that the surface of the NaTaO_3 cubes is enclosed by {100} facets, while {111} and {110} facets are exposed, after the corners and edges are truncated gradually. And the NaTaO_3 QSSs are bound with {100}, {111}, {110} and many uncertain high-index facets.

According to the above experimental results, it can be concluded that the corners and edges of cubic NaTaO_3 crystals are gradually truncated and the spherical crystals are eventually formed, just by increasing the volume ratio of EG to water in the mixed solvent. In the presence of surface adsorbates, the above morphology evolution is generally contributed to the capping effect of the specific adsorbates, which can significantly influence the growth rate of each facet. Obviously, this explanation is not acceptable in our case due to the absence of foreign capping agents. According to the supersaturation strategy mentioned above, there should be a direct relationship between the morphology and supersaturation. For the perovskite structure of NaTaO_3 crystals, the order of crystal facet energy of them should be consistent with CaTiO_3 and SrTiO_3 that also have perovskite structure. According to the previous studies, the average surface energies of different facets of perovskite crystals follow the order of $\{111\} > \{110\} > \{100\}$ [23–27]. Thus, NaTaO_3 cubes with low-energy {100} facets prefer to form at low ratio of EG to water (i.e., low supersaturation), which is likely to be a thermodynamic controlled scenario [7]. While, CTC with high-energy {111} facets can be obtained at relatively high ratio of EG to water (i.e., high supersaturation). The morphology evolution of NaTaO_3 crystals from cube to CTC, then to ETC, and finally to spherical surfaces with other high-energy facets is well consistent with the strategy of supersaturation-dependent surface structure evolution [8].

Besides the solubility, the supersaturation can be controlled by the concentration of the crystal growth unit either. In the above reaction mechanism, NaOH plays key

roles in the dissolution of the $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ precursor and the formation of NaTaO_3 growth units. Therefore, the supersaturation of the growth units should increase with the increase of the concentration of NaOH in the reaction solution, so that the morphology of the as-formed NaTaO_3 crystals is accordingly tuned. In our study, the influence of NaOH concentration on the morphology of the products was investigated by fixing the volume ratio of EG to water at 5/9. Fig. 5 shows the representative morphologies of the products obtained with 7.5 mmol, 7.5–20 mmol, and 20 mmol NaOH. More detailed morphology evolution of the products with different amounts of NaOH was summarized in Fig. S2. Typically, when the amount of NaOH is less than 7.5 mmol, the product is not NaTaO_3 but another kind of sodium tantalate with different atomic ratio ($\text{Na}_2\text{Ta}_2\text{O}_6$, ICDD PDF No. 01-70-1155) (Fig. S3). When the amount of NaOH is around 7.5 mmol, perfect NaTaO_3 cubes are overwhelming in the final products, with minor CTCs (insets in the image Fig. 5a). When the amount of NaOH is in the range of 7.5–20 mmol, the dominant products are NaTaO_3 ETC (Fig. 5b). As the amount of NaOH further increases, a large amount of spherical NaTaO_3 crystals form (Fig. 5c). Overall, with the increase of the amount of NaOH, the morphology evolution of the NaTaO_3 products have the tendency from cube to ETC, and to QS finally, which is similar to the trend in the case by changing the volume ratio of EG to water in the mixed solvents.

The above results demonstrate that both the solvents and NaOH influence the supersaturation of the crystal growth units and thus the morphology of NaTaO_3 crystals significantly. Cubes form at relatively small volume ratios of EG to water or low concentrations of NaOH, while spherical single-crystals generate under the conditions of relatively large volume ratios of solvents and high concentrations of NaOH. Scheme 2 depicts the relationship between the morphology of NaTaO_3 crystals and the solvents (horizontal axis) as well as the amount of NaOH (vertical axis), which is summed up according to the systematic experimental results as shown in Figs 1, 5, and S2. When the amount of NaOH is relatively low, NaTaO_3 crystals tend to show as cubic morphology at small volume ratio

Figure 5 SEM images of NaTaO_3 particles obtained at the volume ratio of EG to water of 5/9 and with different amount of NaOH (a) 7.5 mmol, (b) 7.5–20 mmol, (c) > 20 mmol. Insets are SEM images of single particles.

Scheme 2 Morphology evolution of NaTaO₃ particles upon NaOH amounts and volume ratios of EG to water.

of solvents. As the volume ratio of the solvents increases, the morphology of NaTaO₃ crystals gradually evolves into CTC, ETC and QS. It is worthwhile to mention that there should be a very small variation range of NaOH amounts for the transformation from CTC to ETC, or from ETC to QS as marked by dotted wireframes. Therefore, pure CTC or ETC particles are hard to be controlled at these points of volume ratio, which confirms with the results in Fig. 5. With the increase of NaOH amount, the volume ratios of the solvents for forming CTC, ETC and QS decrease along the broken curves. But each one of the solvent ratios have a limit, and the CTC, ETC and QS would not form if the volume ratio of EG to water is below their respective limitation. For example, QS does not form when the volume ratio is lower than 5/9 (Fig. S2). When the volume ratio is 1/13, the truncation degree of edges is the most weak in all ETC products, indicating the volume ratio limitation of ETC formation is slightly less than 1/13. For the NaTaO₃ cubes, they can be prepared in pure water solvent. In a word, NaTaO₃ crystals with clear corners and edges preferentially form at small volume ratios of EG to water and low amount of NaOH, while spherical shape NaTaO₃ crystals easily form at large values of large solvents ratio and the large amount of NaOH.

It should be noted that near spherical surfaces are exposed at very high supersaturation. It seems hard to explain the formation of NaTaO₃ spherical single-crystal simply by the classical Gibbs–Wulff theorem (the Wulff construction), which determines the shape (polyhedron) of crystals in thermodynamical equilibrium condition. Therefore, understanding the formation mechanism of spherical single-crystals nanoparticles is very important. To get deep insight into the formation of such unusual spherical single-crystal, crystal growth kinetics was taken into consideration. The formation work W_{hkl} of two-dimensional crys-

tal nuclei on different specific crystal facets is specifically introduced, which essentially reflects the activation barrier of the crystal growth process on a specific facet. For an ideal crystal growth on single crystal seeds, the crystal growth rate (v_{hkl}) toward the direction normal to the crystal facet is proportional to the formation work W_{hkl} of the two-dimensional crystal nuclei on specific crystal facet, i.e.

$$v_{hkl} \propto \exp\left(-\frac{W_{hkl}}{kT}\right), \quad (1)$$

where (hkl) represent the indices of crystal facet index, W_{hkl} is the formation work, k and T are Boltzman's constant and the absolute temperature, respectively [28].

For every type of crystal lattice, the formation work W_{hkl} of the two-dimensional crystal nuclei gives [28,29]

$$W_{hkl} = \frac{B_{hkl}}{\frac{\Delta\mu}{mN} - A_{hkl}}, \quad (2)$$

where $\Delta\mu$ represents the supersaturation of growth units, m is the atom number, N is Avogadro's constant, A_{hkl} and B_{hkl} are the constants depending on the broken bond work in the crystal lattice. The above two equations were applied to discuss the preferential growth of metals on foreign substrates at different overpotential during electrodeposition [28,29].

In view of Equations (1) and (2), it is can be seen that the crystal growth rate normal to a specific crystal facet strongly depends upon the formation work W_{hkl} of the two-dimensional at crystal nuclei on the crystalline seed, which is influenced by the supersaturation of the growth units. At low supersaturation condition (near the equilibrium condition), the formation work W_{hkl} varies inversely with the surface energy of crystal facet [28,29] and thus the crystal facets with low surface energy prefer to be exposed and Wulff construction are validated. With the increase of supersaturation, the sequence of formation work W_{hkl} may change [28,29], resulting in the appearance of high energy crystal facets. At present, the values of A_{hkl} and B_{hkl} in Equation (2) are difficult to be quantified, and thus it is difficult to discuss the morphology evolution from Cube to CTC and ETC by using W_{hkl} . At extremely high supersaturation (i.e., when $\Delta\mu$ is very large), the formation works W_{hkl} of different type of two-dimensional at crystal nuclei (i.e., with different hkl values) become very small and do not differ very much. In this case, various crystal facets should have similar crystal growth rate, which results in the spherical crystals. Therefore, the spherical or quasi-spherical particles are kinetically controlled product, rather than thermodynamically controlled one under high supersaturation growth condition. In our reaction system of NaTaO₃ crystals, large volume ratios of EG to water or

high amounts of NaOH may cause extremely high supersaturation of the growth units of NaTaO₃. In these situations, the formation work W_{hkl} of all the crystal facets of NaTaO₃ crystal is nearly close to each other, leading to the formation of the spherical NaTaO₃ crystals enclosed with multiple facets. As the formation of quasi-spherical crystals can only be explained by the supersaturation strategy, the crystal shape evolution in the present study should mainly depend on the supersaturation.

As well known, particle shape may determine some important physical properties, such as surface plasma, thus many research groups adopted various approaches to prepare spherical single crystalline nanocrystals. Although there were a few successful examples, no formation mechanism of spherical single-crystal from the essence of crystal growth was proposed. The above growth mechanism for spherical single crystalline nanoparticle helps us to understand and design synthetic strategies for preparing spherical single-crystalline nanoparticles. For examples, micro- and nano-spheres of some metals with low melting points were successfully synthesized by quenching melted precursors in solvents [30,31], and single-crystalline spheres of some semiconductors with high melting points were also prepared by the way of laser irradiation [32,33]. In these aforementioned cases, the rapid cooling process can make in extremely high supersaturation of crystal growth units and thus spherical single-crystals can be produced due to the similar formation work W_{hkl} of each facet.

CONCLUSIONS

In summary, the controllable syntheses of NaTaO₃ submicrometer crystals with different specific surface structures were achieved by changing the volume ratio of EG to water in the solvent and/or the amount of NaOH, which directly vary the supersaturation of the growth units. With the increase of the supersaturation, the morphologies of NaTaO₃ crystals change from cubes to CTC, then to ETC, and eventually to QS, in which the surface energies of the crystallite surfaces gradually increase. Finally, we introduced the formation work W_{hkl} of two-dimensional at crystal nuclei to well explain the formation of spherical crystals at extremely high supersaturation.

Received 26 January 2015; accepted 20 March 2015;
published online 10 April 2015

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- Acknowledgements** This work was supported by the National Basic Research Program of China (2011CBA00508 and 2015CB932301) and the National Natural Science Foundation of China (21333008, 21131005, 21171142, and 21473146).
- Author contributions** Chen W designed and performed the experiments and wrote the paper; Kuang Q and Xie Z supervised the theoretical and experimental work. All authors contributed to the general discussion and reviewed the manuscript.
- Conflict of interest** The authors declare that they have no conflict of interest.
- Supplementary information** Experimental details are available in the online version of the paper.

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中文摘要 表面结构决定了晶体材料的许多重要的物理化学性质. 可控制备具有特定表面结构的微纳米晶体, 从而实现对晶体材料性能的改善, 引起了广泛的关注. 本课题组近期相关的研究表明, 晶体生长体系中, 生长单元的过饱和度决定了晶体的表面结构. 基于已有研究结果, 本文通过调节混合溶剂体系中乙二醇和水的相对体积比及NaOH的用量, 改变晶体生长体系中生长单元的过饱和度, 合成了亚微米尺寸的NaTaO₃立方体、削角立方体、削角削棱立方体和准球体. 低过饱和度条件下, 形成的NaTaO₃颗粒是低能{100}晶面裸露的立方体; 随过饱和度的增加, 立方体的角和棱逐渐削去, 裸露表面能更高的晶面; 极高过饱和度条件下, 则形成准球体NaTaO₃颗粒. 这种准球体的形成难以用经典的晶体生长理论加以解释. 通过研究同样受过饱和度影响的二维晶核生成功(W_{hkl}), 发现在极高的过饱和度的条件下, 晶体生长趋于各向同性, 合理地解释了准球体的形成机制.