Formation Mechanism for Hexagonal-Structured Self-Assemblies of Nanocrystalline Titania Templated by Cetyltrimethylammonium Bromide

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Abstract: Hexagonal-structured self-assemblies of nanocrystalline (anatase) titania templated by cetyltrimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$; CTAB) (Hex-ncTiO₂/CTAB Nanoskeleton) were formed after mixing of aqueous solutions containing CTAB spherical micelles and titanium oxysulfate acid hydrate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$) as a titania precursor in the absence of any other additives. Formation mechanism of the Hex-ncTiO₂/CTAB Nanoskeleton was examined in terms of the reaction temperature, titania precursor/CTAB mixing ratio, surfactant type, electrostatic interaction, micelle formation and molecular component. We found that crystal growth of crystalline (anatase) titania (polymorphic crystallization) was promoted with higher temperature and lower titania precursor content in aqueous solutions. In addition, we revealed that the crystalline (anatase) titania was formed in polycation, poly(allylamine hydrochloride ($[CH_2CH(CH_2NH_2)HCl]_n$; PAH), and formamide ($HCONH_2$) solutions. On the other hand, no titania formation was observed in anionic systems such as sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$; SDS) and poly(sodium 4-styrenesulfonate ($[C_8H_7SO_3Na]_n$; PSSS). This indicates that hydrolysis reaction of the titania precursor is initiated by not only cations but also nitrogen atoms in molecules and polymers. Hexagonally structure was formed in only cationic surfactant micellar solutions but not in polycation solutions and formamide.

Key words: hexagonal-structured self-assemblies, nanocrystalline titania, Nanoskeleton, cetyltrimethylammonium bromide, titanium oxysulfate acid hydrate

1 INTRODUCTION

Amphiphilic molecules and polymers are widely used as dispersion stabilizers¹⁻³, pharmaceutical ingredients^{4,5} or biomedical materials^{6,7}. In addition to the such advantages of amphiphilic molecules and polymers, self-assemblies of the amphiphilic molecules and polymers are very useful for mesoporous material synthesis as structure-directing agents and/or templates⁸⁻¹¹. For example, well-ordered hexagonal mesoporous silica structures (e.g., MCM-41, SBA-15) can be synthesized through hydrolysis of

tetraethoxysilane (TEOS) in cetyltrimethylammonium chloride (CTACl) solutions^{12,13} or hexagonal lyotropic liquid crystals afforded by poly(ethylene oxide)-poly(propylene oxide) block copolymers¹⁴⁻¹⁹. Namely, combination of self-assembly with sol-gel chemistry is a promising route for the ordered mesoporous material synthesis. Therefore, the judicious selection of inorganic precursors, amphiphilic molecules and polymers is an important task for designing of mesoporous materials⁸⁻¹⁹.

We have recently found a unique combination;

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cetyltrimethylammonium bromide (CTAB) and titanium oxysulfate acid hydrate ($\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$) as a titania precursor, to form hexagonal-structured self-assemblies of nanocrystalline anatase titania (Hex-ncTiO₂/CTAB Nanoskeleton)^(20,21). The Hex-ncTiO₂/CTAB Nanoskeleton was prepared through a hydrolysis reaction of the titania precursor promoted by CTAB spherical micelles in aqueous solutions at 60°C for 24 h^(20,21). Compared to the reported methods for mesoporous titania synthesis⁽²²⁻²⁷⁾, our system involves unique features and advantages, for example, a facile preparation, utilization of water as a solvent, hexagonal-structure autoformation in solutions (without solvent evaluation), crystallization of titania in aqueous solutions in mild conditions (e.g., at 60°C for 24 h)^(20,21) while crystallization of mesoporous titania normally requires calcinations at high temperature⁽²²⁻²⁷⁾. To realize the full potential of our approach (and to be able to generalize to other systems) we need better insight on the Hex-ncTiO₂/CTAB Nanoskeleton formation.

In this work, we examined the effects of temperature, titania precursor/CTAB mixing ratio, surfactant type, electrostatic interaction, micelle formation and molecular component on the crystal growth, hydrolysis reaction initiation and hexagonally structure formation. We found that temperature and titania precursor/CTAB mixing ratio can control the crystal growth. The hydrolysis reaction of the titania precursor was initiated in cationic surfactant (CTAB), polycation (poly(allylamine hydrochloride); PAH) and formamide solutions but not in anionic surfactant (sodium dodecyl sulfate; SDS) and polyanion (poly(sodium 4-styrenesulfonate); PSSS) solutions. This indicates that interactions between cations (and/or nitrogen atoms) and the titania precursor (TiOSO_4) are attributed to the hydrolysis reaction initiation. Hexagonally structure was formed in only cationic surfactant micellar solutions while no ordered structure was formed in PAH and formamide solutions. So surfactant micelles play an important role for the formation of the hexagonally structure as structure-directing agents and/or templates.

2 EXPERIMENTAL

Hex-ncTiO₂/CTAB Nanoskeleton was prepared through hydrolysis reaction and polymorphic crystallization after mixing of cetyltrimethylammonium bromide ($\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$; CTAB, Aldrich) and titanium oxysulfate acid hydrate ($\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$; Aldrich) as a titania precursor in aqueous solutions, at different temperatures (in the range of 40–60°C) and at the various mixing ratios of the titania precursor/CTAB (in the range of 2–50 molar ratio, CTAB concentration is fixed to be 60 mM). The titanium oxysulfate acid hydrate dissolves in water as titanium(IV) sulfate (Fig. 1)⁽²⁸⁾. Sodium dodecyl sulfate

Fig. 1 Structure of Titanium(IV) Sulfate.

($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$; SDS, Kanto Chemical Co., Inc.) was used to examine the effect of electrostatic interactions between surfactants and the titanium(IV) sulfate on hydrolysis reaction initiation and polymorphic crystallization. Polycation, poly(allylamine hydrochloride) ($[\text{CH}_2\text{CH}(\text{CH}_2\text{NH}_2)\text{HCl}]_n$, average molecular weight $\sim 70,000$; PAH, Aldrich), allows us to evaluate roles of cationic surfactant micelles on the hexagonally structure formation because PAH does not form micelles. For comparison purpose with PAH, polyanion, poly(sodium 4-styrenesulfonate) ($[\text{C}_8\text{H}_7\text{NaO}_3\text{S}]_n$, average molecular weight $\sim 70,000$; PSSS, Aldrich) was tested to prepare titania. The effect of interactions between nitrogen atom in a molecule and titanium(IV) sulfate was investigated using formamide (HCONH_2 , Kanto Chemical Co., Inc.) as a solvent because a formamide molecule contains a nitrogen atom without any ionic parts.

Ordered structure, crystal type and crystallinity of titania that we obtained were characterized with powder X-ray diffraction (XRD) (RINT1100, $\text{CuK}\alpha$ radiation, RIGAKU), small-angle X-ray scattering (SAXS) (SAXSees, Anton Paar, PANalytical) with PW3830 laboratory X-ray generator with a long fine focus sealed glass X-ray tube ($\text{K}\alpha$ wavelength of 0.1542 nm) (PANalytical) and operated at 40 kV and 50 mA, and transmission electron microscopy (TEM) (H-7650, Hitachi High Technology, 120 kV, 3.0 μA), after precipitates (titania) obtained were filtered, washed by water, and dried at 120°C for 10 h under air atmosphere.

3 RESULTS AND DISCUSSION

3.1 Formation of Hex-ncTiO₂/CTAB Nanoskeleton

Hex-ncTiO₂/CTAB Nanoskeleton was prepared with aging for 24 h at 60°C after mixing of the titania precursor and CTAB aqueous solutions (Figs. 2 and 3) following previous reports^(20,21). TEM observation (Fig. 2), SAXS (upper panel of Fig. 3) and XRD (bottom panel of Fig. 3) measurements confirmed formation of Hex-ncTiO₂/CTAB Nanoskeleton. Honeycomb-like structure with pore diameter of ~ 3 nm (upper image of Fig. 2) and long-range lined structure (bottom image of Fig. 2) were observed by TEM. Noticeable three SAXS peaks were assigned to hexagonally structure

Fig. 2 TEM Images of Hex-ncTiO₂/CTAB Nanoskeleton Prepared through Hydrolysis Reaction of the Titania Precursor (3000 mM) and CTAB (60 mM) in Aqueous Solutions at 60°C for 24 h.

($d_{100} : d_{110} : d_{200} = 1 : 1/\sqrt{3} : 1/2$) (upper panel of Fig. 3), and XRD peaks were assigned to crystalline anatase ((101), (004), (200) and (105) facets) (bottom panel of Fig. 3)^{29,30}. The value of d_{100} spacing (~ 4 nm) calculated by Bragg's equation³⁰ was consistent with sum of the pore diameter of ~ 3 nm and framework thickness of ~ 1 nm observed by TEM.

In order to realize the formation mechanism of Hex-ncTiO₂/CTAB Nanoskeleton, SAXS and XRD patterns of TiO₂/CTAB Nanoskeleton were recorded as a function of the elapsed time after mixing of the titania precursor and CTAB in aqueous solutions (Fig. 4). Noticeable three SAXS peaks corresponding to hexagonally structure ($d_{100} : d_{110} : d_{200} = 1 : 1/\sqrt{3} : 1/2$) were observed immediately after mixing of the titania precursor and CTAB in aqueous solutions (0 h) (upper panel of Fig. 4), while no significant XRD peak was observed in the same sample (0 h) (bottom panel of Fig. 4). This indicates that hexagonal-structured amorphous titania (hydrated titania or titanium(IV) oxide)/CTAB Nanoskeleton (Hex-amTiO₂/CTAB Nanoskeleton) with d_{100} spacing of ~ 4 nm was formed immediately after mixing of aqueous solutions containing the titania precursor and CTAB spherical micelles. The SAXS peaks corresponding to hexagonally structure were retained up to 48 h, and following those peaks became broader (upper panel of Fig. 4). On the other hand, the XRD peaks assigned to crystalline

Fig. 3 SAXS (upper panel) and XRD (bottom panel) Patterns of Hex-ncTiO₂/CTAB Nanoskeleton Prepared through Hydrolysis Reaction of the Titania Precursor (3000 mM) and CTAB (60 mM) in Aqueous Solutions at 60°C for 24 h.

anatase ((101), (004), (200) and (105) facets)^{29,30} became more significant and sharper with aging (bottom panel of Fig. 4). These results allow us to propose the formation mechanism of Hex-ncTiO₂/CTAB Nanoskeleton as follows; Hex-amTiO₂/CTAB Nanoskeleton is formed immediately after mixing of the titania precursor and CTAB micellar aqueous solutions, and the amorphous titania (hydrated titania or titanium(IV) oxide) changes to Hex-ncTiO₂/CTAB Nanoskeleton with aging through hydrolysis reaction and polymorphic crystallization (proposed mechanism in Fig. 5).

3.2 Crystal growth and hexagonally structure formation

We realized that the Hex-amTiO₂/CTAB Nanoskeleton initially formed changed to the Hex-ncTiO₂/CTAB Nanoskeleton (with retaining d_{100} spacing of ~ 4 nm) through hydrolysis reaction and polymorphic crystallization with elapsed time (bottom panel of Fig. 4). Namely, crystalline titania was formed through the polymorphic crystallization of the amorphous titania (hydrated titania

Fig. 4 SAXS (upper panel) and XRD (bottom panel) Patterns of Hex-TiO₂/CTAB Nanoskeleton Recorded as a Function of the Elapsed Time after Mixing of the Titania Precursor (3000 mM) and CTAB (60 mM) in Aqueous Solutions at 60°C.

or titanium(IV) oxide) in the Hex-amTiO₂/CTAB Nanoskeleton. Then, in order to evaluate the mechanism on the crystal growth and hexagonal structure formation, time evolutions of SAXS and XRD patterns were monitored at various temperatures (in the range of 40–60°C) and the titania precursor/CTAB mixing ratios (in the range of 2–50 molar ratio). We found that the growth of crystalline (anatase) titania was affected by temperature and the titania precursor/CTAB mixing ratio (Fig. 6). On the other hand, the hexagonal-structure of amTiO₂/CTAB and ncTiO₂/CTAB Nanoskeleton was always formed in the temperature range (40–60°C) and titania precursor/CTAB mixing ratio range (2–50 molar ratio) that we applied in this work (only the results obtained at 60°C and at the titania precursor/CTAB mixing ratio of 50 are shown in Fig. 4). Crystal (200) facet sizes (estimated by Sherrer equation³⁰⁾ of the Hex-ncTiO₂/CTAB Nanoskeleton plotted in Fig. 6 as

Fig. 5 Proposed Mechanism of Hex-ncTiO₂/CTAB Nanoskeleton Formation.

a function of time showed that the crystal growth was enhanced with higher temperature (with order of 40 < 50 < 60°C). The crystal growth of nanocrystalline titania at 25°C was much slower than at 40°C (the result is not reported here). This indicates that temperature is one of the factors to control the crystal growth of titania (and/or hydrated titania) in the Hex-amTiO₂/CTAB Nanoskeleton. This is reasonable because the hydrolysis reaction and polymorphic crystallization of titania precursor (and/or hydrated titania) are enhanced at higher temperature^{22–27)}. In addition, crystal growth of the titania (and/or hydrated titania) is promoted with lower titania precursor content in solutions (with order of the titania precursor/CTAB mixing ratios = 50 < 30 < 10 molar ratio). This is most likely

Fig. 6 Effects of Mixing Ratio of the Titania Precursor/CTAB (=10 (○), 30 (■) and 50 (●) molar ratio) on Crystal Growth of Hex-ncTiO₂/CTAB Nanoskeleton at 40 °C (top panel), 50 °C (middle panel) and 60 °C (bottom panel). Crystal (200) facet sizes estimated by Sherrer equation plotted as a function of time.

due to the different acid (H₂SO₄) concentrations afforded by the titania precursor content in solutions. The titania precursor (TiOSO₄·xH₂SO₄·xH₂O) that we used in this experiments contains H₂SO₄, so the acid concentration is changed by the titania precursor content in solutions. Indeed, pH values of the titania precursor solutions were 1.10, 0.82 and 0.66, at titania precursor concentrations of 600, 1800 and 3000 mM, respectively. Namely, weaker acid conditions due to the lower titania precursor content in solutions most likely promote the crystal growth of titania (and/or hydrated titania) in the Hex-amTiO₂/CTAB Nanoskeleton because the hydrolysis reaction of titanium(IV) sulfate is normally initiated with the addition of base solutions^{28,31}. These findings suggests that formation of the Hex-ncTiO₂/CTAB Nanoskeleton is attributed to two hydrolysis reaction; (i) hydrolysis promoted by CTAB immediately after mixing of the titania precursor and CTAB in aqueous solutions, which contributes to the formation of hexagonal-structured self-assemblies of amorphous titania (Hex-amTiO₂/CTAB), and (ii) hydrolysis promoted by temperature and acid/base balance that contributes to the growth of amorphous titania to crystalline titania.

3.3 Hydrolysis reaction initiation and hexagonally structure formation

We now considered that formation of the Hex-ncTiO₂/CTAB Nanoskeleton is attributed to the (i) hydrolysis promoted by CTAB immediately after mixing of the titania precursor and CTAB in aqueous solutions, and (ii) hydrolysis with aging promoted by temperature²²⁻²⁷ and acid/base balance^{28,31}. The effects of temperature and acid/base balance on the hydrolysis reaction are well known in crystal growth of titania^{22-28,31}. However, the hydrolysis reaction promoted by CTAB involves questions because the CTAB aqueous solution itself is not base (pH value of the CTAB aqueous solution that we used in this experiment is ~7). In general, titania (precipitate) is hardly formed in acid solutions due to the slow hydrolysis reaction of titanium(IV) sulfate in acid solutions^{28,31}. Indeed, the hydrolysis reaction and the resulting titania precipitate were not observed in the TiOSO₄·xH₂SO₄·xH₂O aqueous solution for a couple days (Fig. 7f). This is most likely due to the strong acid solution (with pH < 1). However, white precipitate (titania) appeared immediately after mixing of the titania precursor (TiOSO₄·xH₂SO₄·xH₂O) and CTAB aqueous solutions (Fig. 7a). As described in previous section, the white precipitate was composed of Hex-amTiO₂/CTAB Nanoskeleton. This obviously indicates that CTAB promotes the hydrolysis reaction of titanium(IV) sulfate even in strong acid solutions.

Then, we examined the effects of electrostatic interaction on the hydrolysis reaction initiation to evaluate roles of CTAB on hydrolysis initiation, because an electrostatic

Fig. 7 Solutions Obtained after Mixing of the Titania Precursor ($\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$) with (a) CTAB_{aq} , (b) SDS_{aq} , (c) PAH_{aq} , (d) PSSS_{aq} , (e) Formamide and (f) Water, respectively.

interaction between surfactants and inorganic precursors contribute to the polymorphic crystallization and formation of ordered structure (e.g., hexagonal, cubic, lamellar structures)^{8,12,13,22-27}. Anionic surfactant, SDS micellar aqueous solution was tested to prepare titania because titanium(IV) sulfate has positive charge. However, titania (precipitate) did not form in SDS aqueous solutions (Fig. 7b). In addition to the anionic (SDS) micellar system, we also tested polyanion, PSSS aqueous solutions for titania formation, but this also did not work for titania formation (Fig. 7d). These indicate that the electrostatic interaction is not directly contributed to the hydrolysis reaction initiation in the case of the titania precursor ($\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$). This suggests that cationic group in a CTAB molecule has particular roles to initiate the hydrolysis reaction. So we tested titania formation in polycation, PAH aqueous solutions. Indeed, white precipitation appeared immediately after mixing of the titania precursor and PAH aqueous solutions (Fig. 7c), and crystalline anatase titania was obtained with aging for 24 h at 60°C in PAH aqueous solutions (bottom panel of Fig. 8). This supports the contribution of cation group to the hydrolysis reaction initiation.

Fig. 8 SAXS (upper panel) and XRD (bottom panel) Patterns of Titania Precipitate Prepared through Mixing of the Titania Precursor (3000 mM) and PAH (2 wt%) in Aqueous Solutions at 60°C for 24 h.

Here, one more question arise; which is a main contributor between cationic groups or nitrogen atoms in CTAB and PAH to the hydrolysis reaction. In order to address this question, we used formamide that involves nitrogen atom in a molecule but no ionic part. White precipitation was also obtained by just dissolving of the titania precursor ($\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$) in formamide (Fig. 7e), and the resulting titania precipitate was crystalline (anatase) titania (bottom panel of Fig. 9). These findings indicate that nitrogen atoms themselves in molecules (polymers) play an important role for the hydrolysis reaction initiation, in the case of $\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ aqueous solutions. This also suggests that nitrogens in molecules provide a particular reaction site (e.g., base condition) or react directly with titanium(IV) sulfate. Furthermore, we found that hexagonally structure is formed in only CTAB micellar solutions but not in polyanion (PAH) or formamide solutions (upper panel of Figs. 3, 8 and 9). No noticeable SAXS peaks originating from ordered structure such as hexagonally structure were observed in the case of polyanion (PAH) or for-

Fig. 9 SAXS (upper panel) and XRD (bottom panel) Patterns of Titania Precipitate Obtained through the Reaction of Titania Precursor (3000 mM) with Formamide at 60°C for 24 h.

mamide solutions (upper panel of Figs. 8 and 9). We also confirmed formation of Hex-ncTiO₂/C_nTAB using alkyltrimethylammonium bromides (C_nH_{2n+1}N(CH₃)₃Br; C_nTAB, *n* = 12, 14, 16 and 18) (this result will be reported elsewhere). So we realized that micelles are required for the hexagonally structure formation in our system. The hexagonally structure formation from spherical micelles during the hydrolysis reaction and polymorphic crystallization is most likely related to the condensation (phase transition) of surfactant self-assemblies caused by the interaction, complexation and/or reaction between C_nTAB and titanium(IV) sulfate⁸⁻¹³. As described above, nitrogens in molecules (e.g., C_nTAB) provide a particular reaction site (e.g., base condition) or react directly with titanium(IV) sulfate. So the interaction, complexation and/or reaction between C_nTAB and titanium(IV) sulfate would produce a condensed phase of C_nTAB-titanium(IV) sulfate complexes in solutions. The white precipitate that we obtained immediately after mixing of the titania precursor and C_nTAB in aqueous solutions would be the condensed phase in solu-

tion. Namely, the hexagonally structure formation is most likely due to the condensation by the complexation (reaction) of titanium(IV) sulfate with C_nTAB micelles.

4 CONCLUSIONS

Formation mechanism of Hex-ncTiO₂/CTAB Nanoskeleton was examined in terms of temperature, titania precursor/CTAB mixing ratio, electrostatic interactions (charge), micelle formation and molecular component. Temperature and the titania precursor/CTAB mixing ratio contribute to the crystal growth but not to the hexagonally structure formation. The electrostatic interactions caused by molecular (micelle) charge did not contribute to the hydrolysis reaction initiation directly in the case of TiOSO₄·xH₂SO₄·xH₂O as a titania precursor. On the other hand, small molecules and polymers containing nitrogens can promote the hydrolysis reaction initiation and polymorphic crystallization, while the hexagonally structure was not formed in the absence of micelles. This suggests that amphiphilic molecules containing nitrogens to form micelles are one of the candidates as structure-directing agents for the titania precursor (TiOSO₄·xH₂SO₄·xH₂O) to build the hexagonal-structured crystalline anatase titania Nanoskeleton.

Our findings that we reported here provided better insight for fabrication of the ordered-structure materials, nucleation and crystal growth using water-soluble inorganic precursors such as TiOSO₄·xH₂SO₄·xH₂O. Judicious selection of amphiphilic molecules (as structure-directing agents and/or templates) and inorganic precursors should enable to tune the ordered-structure of materials and crystallinity of frameworks.

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