TiO2 Nanocrystals: Phase Selection and Morphology Control

Ji-Guang Li
National Institute for Materials Science/Advanced Materials Processing Unit, Tsukuba, Japan
Email: LI.Jiguang@nims.go.jp

***Abstract*—TiO_2 nanocrystals of the anatase, rutile, and brookite polymorphs have all been selectively synthesized via oxidation of titanium trichloride under proper conditions. The results showed that phase selection is largely controlled by reaction kinetics, and is influenced by solution pH and solute concentration. Morphology manipulation of the three types of products is also achievable via a careful selection of reaction parameters.**

***Index Terms*—TiO_2 nanocrystals, $TiCl_3$ oxidation, phase selection mechanism, morphology control**

I. Introduction

TiO_2 has three naturally occurring crystalline modifications: anabases, brookite, and rutile. All the three crystal structures are built up of TiO_6 octahedrons, but in different ways. In rutile (tetragonal), two opposing edges of each octahedron are shared to form linear chains along the [001] direction and the TiO_6 chains are then linked to each other via corner connection. Anabases (tetragonal) have no corner sharing, but have four edges shared per octahedron. In brookite (orthorhombic), on the other hand, the octahedrons share 3 edges and also corners [1].

Anabases and rutile are the common polymorphs of synthetic TiO_2 while brookite is the most difficult to obtain in a phase-pure form. Brookite was actually reported to be a high-pressure phase and was classically made from aqueous or organic media as large crystals via hydrothermal treatment at high temperature up to 300 ℃. Even under such harsh hydrothermal conditions, certain amounts of alkaline ions seem indispensable [2,3]. The properties of TiO_2 are closely related to the crystal structure, which makes phase selective synthesis one of the most important issues in academia and in practical application of the material.

Previous work on TiO_2 synthesis almost exclusively started with titanium (IV) compounds, namely tetrachloride ($TiCl_4$) and alkoxides, which are highly sensitive to atmospheric moisture and therefore requires special precautions. We have used titanium trichloride ($TiCl_3$) solution, which is not moisture sensitive and easily manipulatable, as a staring material for TiO_2 preparation [4], and phase pure anatase, brookite, and rutile nanocrystals have all been selected obtained under mild hydrothermal conditions (180 ℃, up to 3 h)

II. Experimental Section

The synthesis of TiO_2 from Ti^{3+} salts requires an oxidation reaction, and the oxidants used in this work are ammonium peroxodisulfate ($(NH_4)_2S_2O_8$), hydrogen peroxide (H_2O_2), perchloric acid ($HClO_4$), and nitric acid (HNO_3). In each case, the $TiCl_3$/oxidant molar ratio was kept constant at unity, and the total volume of the reaction solution was set at 80 mL. Whenever necessary, ammonia water or urea was used as pH adjustors. Hydrothermal treatment was performed without stirring at 180 °C for 3 h. More details of synthesis and characterization may be found elsewhere [4].

III. Results and Discussion

Two categories of results were obtained with this hydrothermal oxidation strategy: (1) only the anatase polymorph was obtainable with ammonium peroxodisulfate as the oxidant, irrespective of solution pH and $TiCl_3$ concentration (denoted as [$TiCl_3$]), and (2) almost identical results were produced when hydrogen peroxide, perchloric acid, and nitric acid were employed as the oxidant. In this case, anatase, brookite, and rutile can all be obtained in a phase pure form, through a careful control of reaction kinetics by varying the solution pH and reactant concentration.

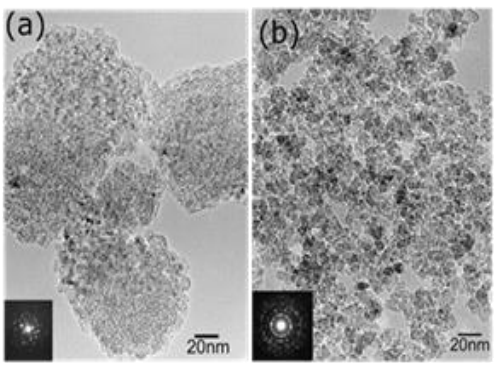

Figure 1. TEM morphologies of the anatase particles synthesized with peroxodisulfate

Manuscript received June 16, 2013; revised August 22, 2013.

doi: 10.12720/ijmse.1.1.5-7

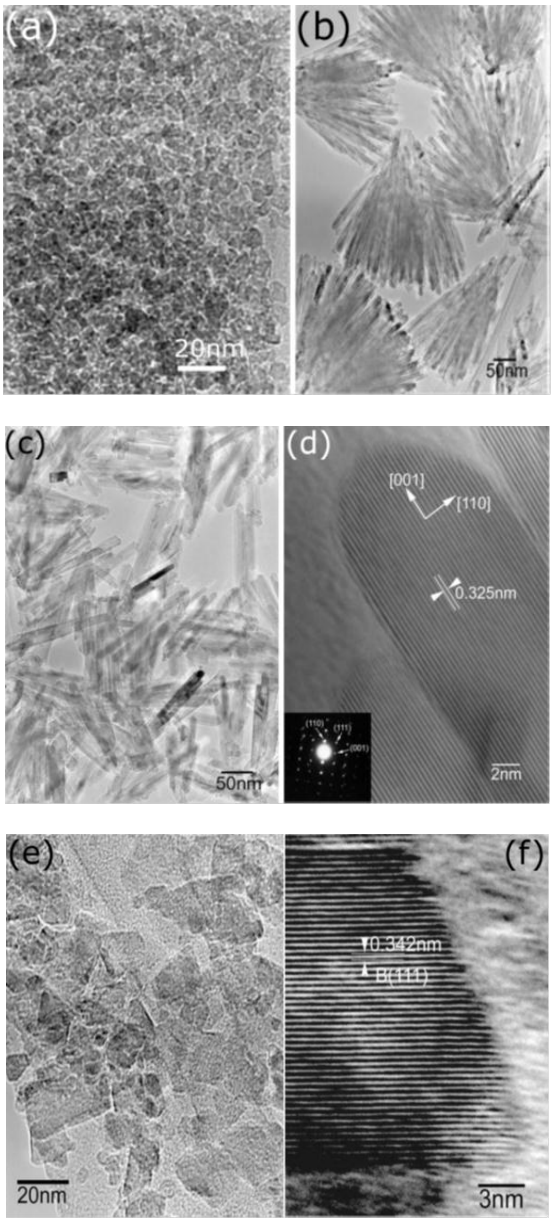

Figure 2. Morphologies of the anatase (a), rutile (b,c,d), and brookite nanocrystallites (d,e). Synthesis conditions are (a): [TiCl3]=0.0625 mol/L, pH=9.0; (b): [TiCl3]=0.9 mol/L, pH<0; (c) [TiCl3]=0.0625 mol/L, pH=0.44; (e) [TiCl3]=0.0625 mol/L, pH=1.32. The powders of (a), (b), (c), and (e) have specific surface areas of 187, 47, 67, and 84 m2/g, respectively. (d) and (e) are lattice images of the sample shown in (c) and (e), respectively.

Fig. 1 shows TEM morphologies of the anatase particles obtained with $(NH_4)_2S_2O_8$ as the oxidant. Spherical aggregates with worm-hole structures were formed under a high [$TiCl_3$] of 0.9 mol/L (pH<0, Fig. 1a). The particles were composed of nanocrystallites sized up to ~4 nm, and the powder has a high specific surface area of 297 m^2/g. With decreasing [$TiCl_3$], more discrete but bigger (though <10 nm) crystallites were formed. Show in Fig. 1b are the anatase crystallites synthesized with 0.15 mol/L of $TiCl_3$ and pH=0.75, from which it can be seen that the crystallites have an average size of ~7 nm. The powder has a specific surface area of 134 m^2/g. The redox reaction between Ti^{3+} and $S_2O_8^{2-}$ generates Ti^{4+} and SO_4^{2-}. Ti^{4+} undergoes strong hydrolysis in an aqueous solution to form $[Ti(OH)_xX_y^m(H_2O)_{6-x-y}]^{4-x-my}$ species due to its high charge/radius ratio (X: a complexing ligand; m: the charge of X). TiO_2 crystallites are then formed via olation and oxolation of the further hydrolyzed species. SO_4^{2-} plays at least two roles herein: (1) strongly complexing the hydrolyzed titanium species due to its high minus charge and orients the $[Ti(OH)_xX_y^m(H_2O)_{6-x-y}]^{4-x-my}$ species in a way favoring anatase nucleation by its large ligand field, and (2) strongly absorbed onto surfaces of the positively charged TiO_2 particles, retarding particle growth via mass diffusion and leading to finer crystallites at a high SO_4^{2-} concentration (Fig. 1a).

Fig. 2 shows typical morphologies of the anatase, rutile, and brookite nanocrystals obtained with H_2O_2 as the oxidant. Notice the distinctly different particle shapes and sizes: rounded for anatase (~3-10 nm), rod-like for rutile (~10-20 nm in diameter and up to 300 nm in length), and plate-like for brookite (lateral size: ~10-30 nm). Further analysis via HR-TEM indicates that the rutile nanorods grow along the [001] direction (*c*-axis), while the brookite crystals have exposed (111) facets. A thorough investigation has been made to elaborate the correlations between processing parameters and phase structure of the final product [4]. It was concluded that the phase selection of TiO_2 polymorphs largely depends upon reaction kinetics, which is influenced by processing parameters, that is, solution pH and [$TiCl_3$]. It was confirmed that anatase is readily formed under high [$TiCl_3$] and high pH, rutile under highly acidic conditions, while brookite under moderate [$TiCl_3$] and intermediate solution pH.

The phase selection phenomena may also be understood from the specific crystal structures of TiO_2 polymorphs. As aforementioned, anatase, brookite, and rutile have 4, 3, and 2 edges shared per octahedron, respectively. The formation of one edge sharing requires two dehydration reactions among the $[Ti(OH)_xX_y^m(H_2O)_{6-x-y}]^{4-x-my}$ species, while one corner sharing needs only one dehydration reaction. Based upon these facts, the effects of solution pH and [$TiCl_3$] on crystal structure of the final product are discussed as follows:

A. The Effects of Solution Ph (Under Fixed [Ti3+])

(1) The higher the solution pH, the more the OH^- in $[Ti(OH)_xX_y^m(H_2O)_{6-x-y}]^{4-x-my}$, and therefore more chance of edge sharing, favoring anatase crystallization. Oppositely, low pH favors rutile. Brookite is midway between anatase and rutile in terms of the number of shared edges, and therefore needs intermediate pH to stabilize.

(2) Anatase is a metastable phase, and hence rapid aggregation of $[Ti(OH)_xX_y^m(H_2O)_{6-x-y}]^{4-x-my}$ under high pH may promote its crystallization. On the contrary, the very slow hydrolysis under low pH may favor the formation of thermodynamically stable rutile. Besides,

dissolution/recrystallization may take place under low pH, which would also lead to rutile. In this context, the intermediate reaction rate under moderate pH and [$TiCl_3$] may have stabilized the brookite polymorph.

B. The Effects of [Ti3+] (Under Fixed Ph)

High [Ti^{3+}] would lead to a rapid aggregation of $[Ti(OH)_xX_y^m(H_2O)_{6-x-y}]^{4-x-my}$ and thus enhances anatase formation. Significantly decreased growth/nucleation ratio of crystals are expected under extremely low [Ti^{3+}], and therefore finer crystallites will be resulted. Since anatase is more stable at sizes <11 nm [5], the brookite crystals below this critical size may transform to anatase during the hydrothermal treatment. It is thus understandable that brookite tends to form under intermediate [Ti^{3+}] and generally has crystal sizes above 10 nm (Fig. 2e).

The speculation that it is the reaction kinetics and not pressure is crucial to brookite formation was supported by our experimental results obtained under ambient pressure [6]. By reacting in open air a mixed solution of $TiCl_3$ (0.015 mol/L) and urea (0.5 mol/L) at 90 °C for 2 h, phase pure brookite (Fig. 3) of high particle uniformity was directly resulted (Fig. 4a, average particle size: ~154 nm). Here the atmospheric oxygen serves as the oxidant for Ti^{3+}. Again, the primary crystallites of brookite exhibit a thin-plate-like morphology (Fig. 4b). The brookite phase was found stable against annealing up to about 500 °C, and above which a direct transition to rutile would take place [7].

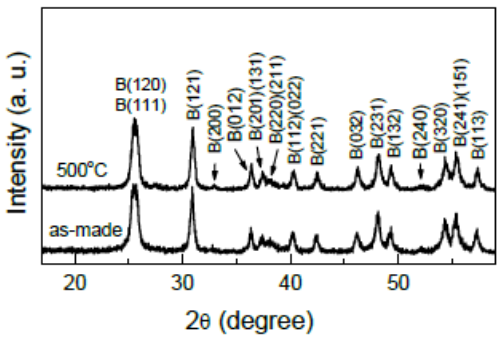

Figure 3. XRD patterns of the as-made brookite powder and that annealed in air at 500°C for 2 h.

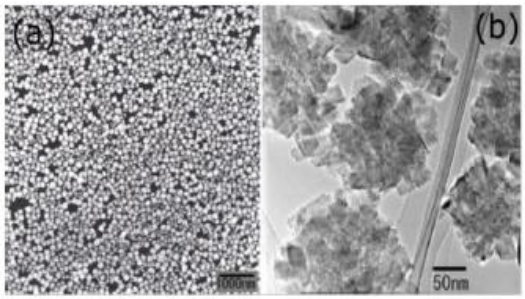

Figure 4. SEM (a) and TEM (b) micrographs showing morphologies of the brookite particle obtained via reacting a mixed solution of TiCl3 and urea in open air.

IV. Conclusion

Phase selective synthesis of anatase, brookite, and rutile nanocrystals have been achieved via oxidation of titanium trichloride solutions under proper conditions. The key factor that governs phase selection was suggested to be reaction kinetics, which is affected by the type of oxidant, solution pH, and solute concentration. It was confirmed that a rapid reaction tends to yield anatase, slow oxidation under low pH leads to rutile, while moderate pH and solute concentration favors brookite crystallization. It was also shown that, with the above mentioned phase selection mechanism, the brookite polymorph of TiO_2 nanocrystals, which is the most difficult to obtain, can even be produced under near ambient conditions via oxidation of $TiCl_3$ solution with the atmospheric oxygen and in the presence of urea for pH adjustment.

References

[1] F. Wells, *Structural Inorganic Chemistry*, Oxford, U.K.: Clarendon Press, 1975.
[2] Y. Zheng, E. Shi, S. Cui, W. Li, and X. Hu, "Hydrothermal preparation of nanosized brookite powders," *J. Am. Ceram. Soc.*, vol. 83, pp. 2634-2636, 2000.
[3] H. Kominami, M. Kohno, and Y. Kera, "Synthesis of brookite-type titanium oxide nano-crystals in organic media," *J. Mater. Chem.*, vol. 10, pp. 1151-1156, 2000.
[4] J.-G. Li, T. Ishigaki, and X. D. Sun, "Anatase, brookite, and rutile nanocrystals via redox reactions under mild hydrothermal conditions: Phase selective synthesis and physicochemical properties," *J. Phys. Chem. C*, vol. 111, pp. 4969-4976, 2007.
[5] H. Zhang and J.-F. Banfield, "Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: Insights from TiO_2," *J. Phys. Chem. B*, vol. 104, pp. 3481-3487, 2000.
[6] J.-G. Li, C. C. Tang, D. Li, and T. Ishigaki, "Monodispersed spherical particles of brookite-type TiO_2: Synthesis, characterization, and photocatalytic property," *J. Am. Ceram. Soc.*, vol. 87, pp. 1358-1361, 2004.
[7] J.-G. Li and T. Ishigaki, "Brookite-rutile phase transformation of TiO_2 studied with monodispersed particles," *Acta Mater*, vol. 52, pp. 5143-5150, 2004.

Ji-Guang Li was born in Shandong province, China. He received his Bachelor Degree in Metallic Materials and Heat Treatment in 1992, Mater Degree in Powder Metallurgy in 1995, and Ph. D. in Materials science in 1998, all from Northeastern University, Shenyang China. After completing his Ph. D. study, He moved to Tsukuba, Japan, in 1999 as an STA Fellow to work at the then National Institute for Research in Inorganic Materials (current the Namiki site of National Institute for Materials Science) under the auspice of the then Science and Technology Agency (STA) of Japan. He became a research scientist at the National Institute for Materials Science (NIMS, Tsukuba, Japan) after the STA Fellowship, and is currently a Principal Researcher at NIMS. He is an author of over 150 peer reviewed papers, 3 book chapters and books, and is a holder of over 20 patents. His primary research interest lies in optically functional inorganic materials, including phosphors, photocatalysts, transparent ceramics and also their controlled synthesis and new fabrication. Dr. Li is a member of the Ceramic Society of Japan. He serves as a reviewer for many international journals, and is on the editorial board of the international journal "New Journal of Glass and Ceramics".