

Hydrothermal synthesis of brookite type TiO_2 photocatalysts using a water-soluble Ti-complex coordinated by ethylenediaminetetraacetic acid

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Nanocrystalline brookite titanium oxide was prepared by hydrothermal treatment of a water-soluble titanium complex with ethylenediaminetetraacetic acid (EDTA). In this work, we examined the effect of synthesis conditions such as reaction time, titanium concentration and solution pH on the brookite phase formation and its photocatalytic performance. It was found that hydrothermal treatment of the titanium complex may yield anatase and brookite phases, and their ratio can be varied depending on titanium concentration. Single phase brookite could be prepared when titanium concentration in the starting solution was higher than 0.25 mol/dm^3 , while lower concentration favors formation of anatase. Remarkably, brookite could be synthesized from the Ti-EDTA complex in the wide range of pH including both acidic and basic media. The samples prepared from Ti-EDTA complex demonstrated higher photocatalytic activity in terms of NO gas decomposition than the brookite powders synthesized from Ti-glycolate complex or commercial TiO_2 photocatalyst P25. Higher photocatalytic activity of powders obtained from Ti-EDTA complex aqueous solution is explained by higher surface area of smaller but well-crystallized brookite particles that can be achieved when this new titanium complex is employed.

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Key-words : Brookite, Titanium oxide, Hydrothermal method, Water-soluble titanium complex, Ethylenediaminetetraacetic acid, Photocatalyst

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1. Introduction

Titanium dioxide (TiO_2) is an important material showing high photocatalytic activity in terms of degradation of organic contaminants present in water or air,¹⁾ self-cleaning²⁾ and anti-bacterial properties.³⁾ Most of the attention has been received by anatase and rutile polymorphic forms of titanium oxide, which is explained by simplicity of their synthesis. In contrast, properties of brookite, another crystal form of TiO_2 , are examined less systematically because until recently synthesis of brookite, especially in the nanocrystalline form with controlled morphology, has remained as a difficult task.

Brookite can be obtained by thermolysis of TiCl_4 in strongly acidic aqueous media,⁴⁾ by hydrothermal treatment of an amorphous titania prepared by hydrolysis of titanium isopropoxide in the presence of hydrochloric acid⁵⁾ or by a controlled hydrolysis of titanium acetylacetonate complex in ethylene glycol by a variation of solvothermal process.^{1),6)} These synthesis techniques require careful control of the reaction conditions and usually yield multiphase samples with brookite as a primary product. The situation started to change lately after we have proposed a simple synthesis of single phase nanocrystalline brookite by hydrothermal treatment of a new water-soluble titanium complex coordinated by glycolic acid.⁷⁾ This complex molecule contains four titanium atoms interconnected through oxygen atoms of the ligands in the pattern

similar to the atomic arrangement of brookite. The brookite-like architecture built into the complex molecule allows for the direct preparation of this polymorph during hydrothermal treatment under basic conditions. It was found that brookite could exhibit higher photocatalytic activity in terms of NO gas decomposition than that of the commercial TiO_2 photocatalyst P25 (Degussa).^{7),8)} It was expected that further increase of photocatalytic activity might be achieved by decreasing particles size of brookite. Nevertheless, it turned out that titanium glycolate complex in the basic solutions provided very narrow range of conditions when brookite could be synthesized, and it was extremely difficult to vary size and morphology of nanopowders. Therefore, we have continued search for other water soluble complexes of titanium capable of producing brookite by hydrothermal treatment, which may allow for more flexibility in the brookite synthesis.

In this work a stable and water soluble complex of titanium with ethylenediaminetetraacetic acid (EDTA) was used for the first time for synthesis of brookite by a hydrothermal process. Although synthesis and structures of several speciations of titanium-EDTA complexes have been reported in the past years,^{9)–11)} no connection had been revealed between such complexes and brookite phase. It is particularly worth mentioning that brookite in this work could be synthesized from Ti-EDTA complex in a wide range of pH, unlike in the case of titanium glycolate. In addition, the average size of brookite particles obtained by the hydrothermal treatment of Ti-EDTA complex aqueous solution at 200°C for 24 h was $50 \times 20 \text{ nm}$ that was considerably smaller than that of brookite particles prepared from the titanium glycolate complex under basic

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conditions with average size of 120×50 nm. Thus, a higher photocatalytic performance in NO gas decomposition may be expected for such brookite powders.

2. Experimental

2.1 Preparation of water-soluble Ti-complex coordinated by EDTA and synthesis of TiO_2

An aqueous solution of EDTA complex of titanium was prepared in a way similar to the other complexes of titanium with α -hydroxy carboxylic acids in our previous works.^{12)–14)} Titanium powder (5 mmol; Furuuchi Chemical Co., Tokyo) was dissolved in a solution of 30% H_2O_2 (20 cm^3 ; Kanto Chemicals Co., Inc., Tokyo) and 28% NH_3 (aq) (5 cm^3 ; Kanto Chemicals Co., Inc., Tokyo) under constant cooling to room temperature on the water bath. After 2 h, $\text{EDTA} \cdot 2\text{NH}_4$ (20 mmol; Dojindo Laboratories, Tokyo) was added to this solution, and the sample was left for 12 h. Then, the solution was kept at 80°C to eliminate excess of water, H_2O_2 and NH_3 until it turned into a gel-like dry substance. Ti-EDTA complex solution was obtained by dissolving this gel in redistilled water, and this stock solution pH was 6.4. The solution volume was adjusted to 20 cm^3 by water, and it was placed into the 50 cm^3 of a Teflon vessel. This vessel was sealed in a stainless steel autoclave, which was heated at 200°C for 4–120 h in an oven. After the autoclave cooled down to room temperature, the resulting precipitates were separated by filtration or using centrifuge and washed with distilled water till the supernatant became neutral. Finally, the obtained specimens were dried at 100°C . The same procedure was used for experiments with different titanium concentration ($[\text{Ti}] = 0.05\text{--}0.25$ mol/dm^3) and pH adjusted by hydrochloric acid (Kanto Chemicals Co., Inc., Tokyo) or NH_3 (aq.).

2.2 Characterization

The X-ray diffraction (XRD) patterns of samples were collected by a Rigaku RINT-2200 diffractometer with $\text{Cu K}\alpha$ radiation (wavelength: 0.154056 nm) operating at 40 kV–30 mA, at a scanning rate of 2 deg/min in the 2θ range of $20\text{--}50^\circ$. The particle size and morphology were observed by use of a transmission electron microscope (TEM, JEM-2010, JEOL, Ltd.). The samples for TEM analysis were prepared by suspending the powder in ethanol ultrasonically and placing a drop of the solution onto Cu microgrid coated with holey carbon film; the microgrid was kept in an oven at 80°C for the ethanol to evaporate. Raman spectra were recorded using a JASCO NRS-3300 Raman spectrometer. The samples were excited by a green laser (532.2 nm wavelength), which was focused on the sample surface through a lens of a microscope. The power of the laser was 1.7 mW on a sample. The specific surface area of samples was measured using the Brunauer-Emmet-Teller (BET) 5 point method on the basis of nitrogen uptake at 77 K by use of an ASAP2010 equipment (Shimadzu, Ltd.). Before the N_2 adsorption, each sample was heated at 90°C for 1 h and at 200°C for 2 h under vacuum.

2.3 Measurement of photocatalytic activity

The photocatalytic activity was tested by measuring NO gas decomposition ratio. The sample was placed in a hollow space of $20 \text{ mm} \times 15 \text{ mm} \times 0.5 \text{ mm}$ on a glass holder and set in the center of the sealed plastic reactor of 373 cm^3 volume. The gas mixture of NO balanced with N_2 (NO concentration – 1 ppm) and 50 vol% air was flowed into the reactor at a flow rate of 200 cm^3/min . A 450 W high-pressure mercury lamp was used as the light source. A Pyrex jacket around the lamp could cut off wavelength $\lambda < 290$ nm. Between the lamp and the reactor, two cut-off filters ($\lambda < 400$ nm and $\lambda < 510$ nm) could be inserted.

NO and NO_2 concentrations were determined using a NO_x analyzer.¹⁵⁾ For comparison, the photocatalytic activity of the commercial titania powder (P25, Degussa) was also measured.

3. Results and discussion

3.1 Conditions for synthesis of brookite-type TiO_2

3.1.1 Hydrothermal reaction time

Figure 1 shows XRD patterns of the samples prepared by the hydrothermal treatment of Ti-EDTA complex aqueous solutions (pH 6.4) at 200°C after different reaction times. Brookite started to form already after 2 h, which can be seen by the appearance of the characteristic peak of brookite at $2\theta = 30.8^\circ$. The systematic variation of this peak intensity with respect to the strongest reflection at $2\theta = 25.3^\circ$, which corresponds to the overlapped peaks from brookite and anatase phases, along the reaction time leads to the conclusion that anatase forms in these samples as the second phase. With increase of reaction time the fraction of brookite gradually increases. However, as one may see from the bar graphs of the ICSD reference data for anatase and brookite in Fig. 1, it is virtually impossible to estimate the fraction of anatase when brookite starts to dominate in the sample by the simple visual comparison of XRD patterns. Therefore, Raman spectroscopy was applied in addition to XRD for characterization of samples phase composition (Fig. 2). Anatase possesses a characteristic peak at 516 cm^{-1} in its Raman spectrum, which can be used to distinguish it from brookite. It is clearly seen in Fig. 2 that this peak of anatase dominated when reaction time was 2 h (Fig. 2(a)). When the hydrothermal reaction time increased, this peak gradually became weaker (Fig. 2(b),(c)) and for synthesis times longer than 6 h, anatase completely disappeared (Fig. 2(d),(e)). Thus, combination of XRD and Raman spectroscopy data show that during hydrothermal treatment of Ti-EDTA complex, formation of anatase is kinetically more favorable; however anatase forms in a rather small amount. In parallel formation of brookite takes place and after longer synthesis times brookite phase starts to dominate, while anatase completely disappears most likely due to incorporation into growing brookite crystallites by a dissolution-recrystallization process.

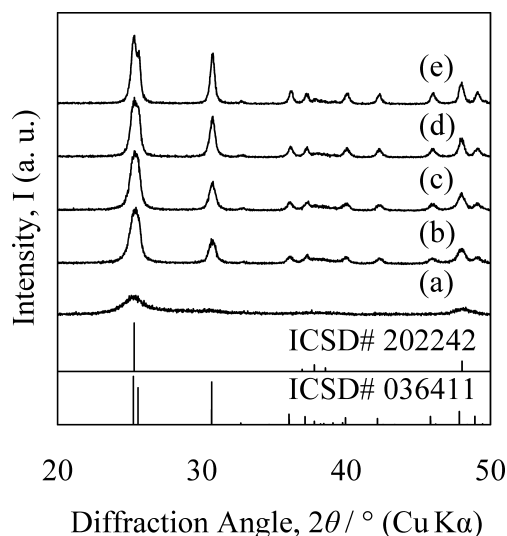


Fig. 1. XRD patterns of the samples prepared by hydrothermal treatment of Ti-EDTA complex aqueous solution (pH 6.4) with titanium concentration of 0.25 mol/dm^3 after the following reaction time: (a) 2 h, (b) 4 h, (c) 6 h, (d) 12 h and (e) 24 h.

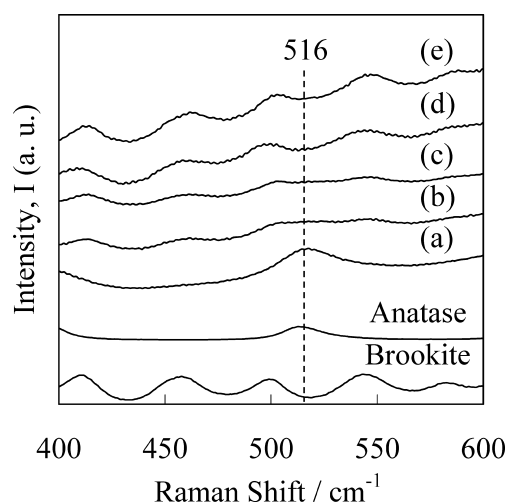


Fig. 2. Raman spectra of the samples prepared by hydrothermal treatment of Ti-EDTA complex aqueous solution (pH 6.4) with titanium concentration of 0.25 mol/dm³ after the following reaction time: (a) 2 h, (b) 4 h, (c) 6 h, (d) 12 h and (e) 24 h.

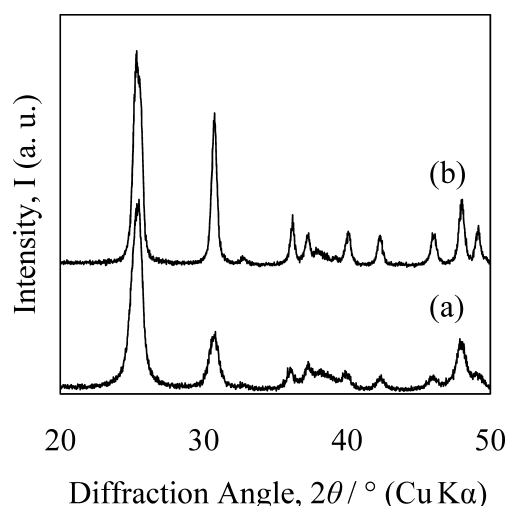


Fig. 3. XRD patterns of the samples prepared by hydrothermal treatment of 0.25 mol/dm³ Ti-EDTA complex aqueous solution at 200°C for 4 h (a) and after hydrothermal post-treatment at 200°C for 120 h (b).

To verify this assumption, we conducted the following additional experiment. The sample containing both anatase and brookite prepared by the hydrothermal treatment of Ti-EDTA complex solution at 200°C for 4 h was ultrasonically suspended in 20 cm³ of redistilled water, and this suspension was sealed in a Teflon-lined stainless steel autoclave for an additional hydrothermal “post-treatment” at 200°C for another 120 h. The XRD patterns of samples before and after the described procedure are compared in Fig. 3. One may clearly see that the intensity of the characteristic peak of brookite at $2\theta = 30.8^\circ$ became stronger after the hydrothermal post-treatment, which indicates an increased fraction of brookite and a smaller amount of anatase in the sample. At the same time, according to the analysis of titanium concentration in the solution by ICP emission spectrometry, the supernatant solution contains less than 1 ppm of titanium and such a small amount cannot account for the disappearance of anatase by simple dissolution. In other words, during the prolonged hydrothermal treatment anatase particles dissolve and titanium

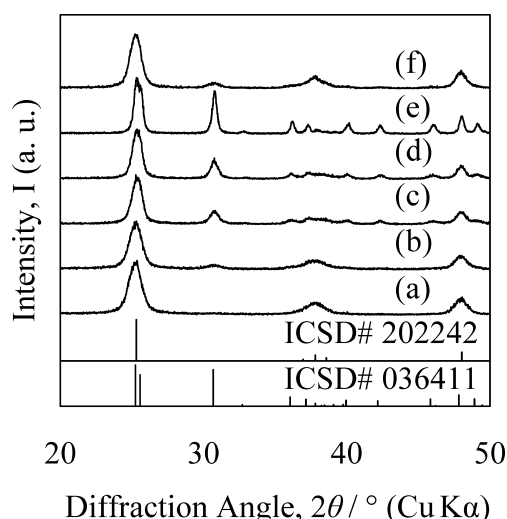


Fig. 4. XRD patterns of the products prepared by hydrothermal treatment of 0.25 mol/dm³ Ti-EDTA complex aqueous solution at 200°C for 24 h with starting pH adjusted by hydrochloric acid or NH₃ (aq) to (a) 2.0, (b) 3.0, (c) 4.0, (d) 5.0, (e) 8.0, and (f) 9.0.

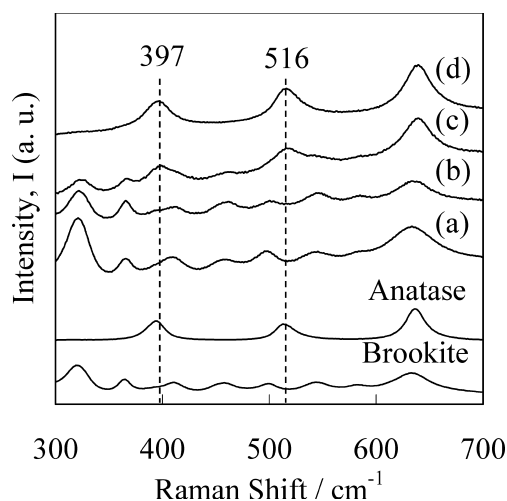


Fig. 5. Raman spectra of the samples prepared by the hydrothermal treatment at 200°C for 24 h of Ti-EDTA complex aqueous solution (pH 6.4) with the following titanium concentration: (a) 0.5 mol/dm³, (b) 0.25 mol/dm³, (c) 0.13 mol/dm³ and (d) 0.05 mol/dm³.

from the solution is consumed by growing brookite crystallites.

3.1.2 pH of the solution

The effect of pH on phase composition of the powders prepared by the hydrothermal treatment of 0.25 mol/dm³ aqueous solution of Ti-EDTA at 200°C for 24 h is summarized in the XRD patterns in Fig. 4. When the solution pH was adjusted to an acidic condition by hydrochloric acid, single-phase anatase was obtained at pH 2.0 (Fig. 4(a)). With the increase of pH the characteristic peak of brookite at around $2\theta = 30.8^\circ$ started to show up (Fig. 4(b)–(d)). In the range of pH between 4.0 and 5.0 (Fig. 4(c),(d)) brookite becomes a major phase; however the characteristic peak of anatase at 517 cm⁻¹ could be still found in the Raman spectra of these samples (not shown). In the basic region when the solution pH was adjusted by adding NH₃ (aq), single-phase brookite was obtained at pH 8.0 (Fig. 4(e)), whereas the synthesis at pH 9.0 yielded anatase as the main phase again (Fig. 4(f)).

3.1.3 Titanium concentration

Figure 5 shows Raman spectra of the samples prepared by the hydrothermal treatment of Ti-EDTA complex aqueous solutions (pH 6.4) at 200°C for 24 h with variable titanium concentrations in the range from 0.05 mol/dm³ to 0.5 mol/dm³. Due to the small amount of samples prepared from the solutions with low titanium concentration, Raman spectroscopy was used to characterize phase compositions. Single-phase brookite was obtained when the starting titanium concentration was in the range of 0.25–0.5 mol/dm³. When the starting solutions of lower concentrations were used for the hydrothermal synthesis the characteristic peaks of anatase at 397 and 516 cm⁻¹ in addition to brookite peaks could be observed in Raman spectra (Figs. 5(c),(d)).

3.1.4 Summary of phase composition of TiO₂

These experimental results described above are summarized in **Table 1**, which presents the phase composition of samples synthesized by the hydrothermal treatment of Ti-EDTA complex aqueous solutions as a function of reaction time, starting titanium concentration and solution pH. It is surprising that Ti-EDTA complex allows for the synthesis of brookite in a very wide range of experimental conditions, while a number of previous reports emphasized that brookite could be obtained only in a narrow range of conditions even when it was detected only as a secondary phase.^{1),4)–6)} We believe that the reason for the brookite formation in such a wide range of conditions when Ti-EDTA complex is used should be closely related to the architecture of these complex species, and their crystal structures are yet to be determined.

Table 1. Phase Composition of TiO₂ Powders Prepared by Hydrothermal Treatment of Ti-EDTA Complex as a Function of Synthesis Time, Titanium Concentration in the Starting Solution and Solution pH

Reaction time / hour	3		4	5	6	7		
	A + B		A + B	A + B	B	B		
Titanium concentration / M			0.05	0.13	0.25			
			A	A + B	B			
pH ^a	2	3	4	5	6	7	8	9
	A	A + B	A + B	A + B	B	B	B	A + B

^a pH 2–5: adjusted by hydrochloric acid, pH 6: original solution, pH 8–9: adjusted by NH₃ aq. A: anatase, B: brookite

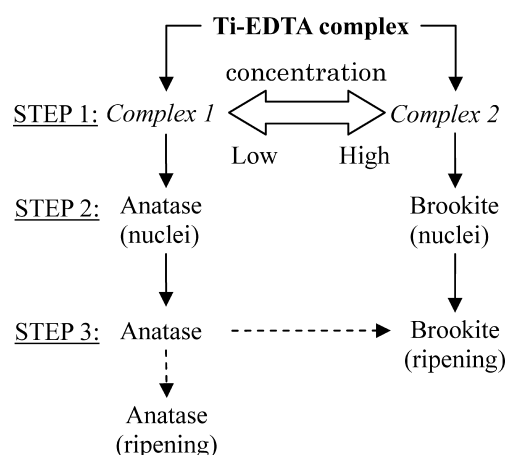


Fig. 6. Schematic sequence of anatase and brookite deposition and phase transformations leading to the final single phase brookite product in the course of hydrothermal treatment of Ti-EDTA complex aqueous solution.

3.2 Sequence of anatase and brookite deposition and phase transformations between them

The sequence of brookite and anatase formation for different reaction times and for different titanium concentrations in the starting solutions is particularly interesting. Although it is difficult to explain precisely the mechanism of the transformation leading to each particular phase composition, the following simplified explanation presented in **Fig. 6** may be posed. Preparation of Ti-EDTA complex solution results in the equilibrium between several speciations with different molecular structures that exist in the solution in equilibrium. At least two types of complex species should be distinguished whose architecture favors formation of anatase and brookite crystalline phases respectively. This equilibrium in the solution is schematically shown in **Fig. 6** as “STEP 1”, and species leading to anatase and brookite are specified as “Complex 1” and “Complex 2”, respectively. High titanium concentration shifts equilibrium towards Complex 2, once lower concentration results in the higher fraction of Complex 1. After initial stages of hydrothermal process (“STEP 2”), Complex 1 and Complex 2 yield nucleation of anatase and brookite particles, respectively. During the prolonged hydrothermal treatment, “STEP 3”, the fraction of brookite increases due to the continued nucleation from Complex 2 and growth of brookite nuclei at the expense of anatase nuclei dissolution. If brookite is absent, or the number of its nuclei is small, dissolution and recrystallization of anatase becomes a kinetically prevailing process. As a result, solutions with low concentration of titanium lead to formation of anatase as a main product.

In order to explore the possibility of such a scheme presented in **Fig. 6**, we conducted an additional experiment. The sample containing anatase as a major product prepared from Ti-EDTA complex aqueous solution of low concentration (0.13 mol/dm³) at 200°C for 4 h was subjected to a hydrothermal “post-treatment” for 120 h. The XRD patterns of the two samples produced in this experiment are shown in **Fig. 7**. As one may notice, the overall peaks intensities increase and peaks become narrower after the hydrothermal “post-treatment”. Nevertheless, when the phase composition was refined by Rietveld method implemented in the program Quanto,¹⁶⁾ it was found that the starting sample after 4 h of the hydrothermal treatment contained 72.0 ± 0.5%

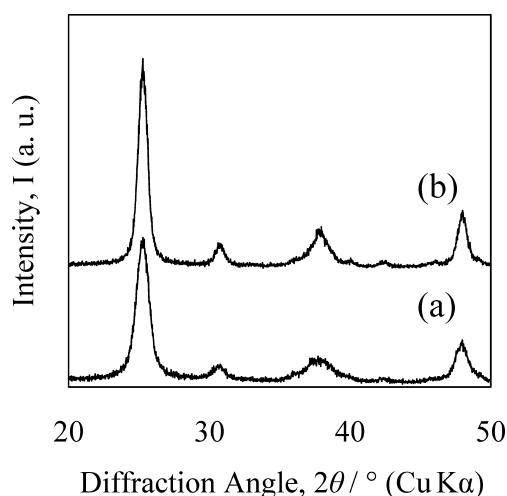


Fig. 7. XRD patterns of the products prepared by hydrothermal treatment at 200°C for 4 h using Ti-EDTA complex aqueous solution with titanium concentration of 0.13 mol/dm³ (a) and after additional hydrothermal post-treatment at 200°C for 120 h (b).

anatase and $27.9 \pm 2.6\%$ brookite, while the sample after the “post-treatment” was composed of $73.4 \pm 0.5\%$ anatase and $26.6 \pm 0.4\%$ brookite. The difference between the compositions of the starting and the final samples does not exceed one standard deviation and strictly speaking, the phase composition should be regarded as the same. Thus, the apparent changes of intensities of diffraction peaks should be ascribed to the improved crystallinity of anatase and brookite, which means that for the sample with predominating anatase nucleation, ripening of anatase crystallites becomes the major process.

It should be also mentioned that the idea about nucleation of different crystalline phases from different metal complex speciations is not unreasonable since it became a well-established fact that both single phase brookite and rutile can be synthesized from the titanium peroxo-glycolate complex under the conditions, which favor formation of tetranuclear and dinuclear complex molecules respectively.¹⁷⁾ We also collected ¹³C-NMR spectra for Ti-EDTA complex solutions. The detailed discussion of the spectra is difficult at this stage, and it will be done elsewhere in combination with analysis of complexes structures. However, it is possible to say that the solution contains multiple types of Ti-EDTA species, which is again in agreement with the proposed simplified model.

3.3 Photocatalytic activities of Brookite-type TiO₂ powders

Transmission electron micrograph (TEM) in Fig. 8 presents typical morphology of the brookite powder prepared by hydrothermal treatment of Ti-EDTA complex for 24 h. The habitus of nano-crystals is quite similar to brookite particles prepared by hydrothermal treatment of titanium peroxo-glycolate complex,⁷⁾ however the size of 50×20 nm is considerably smaller than 120–150 nm particles found when glycolic acid complex is used as a precursor. Therefore, one may expect higher photocatalytic activity of brookite prepared from Ti-EDTA complex.

Figure 9 shows light absorbance spectra of the samples prepared by the hydrothermal treatment at 200°C for 24 h using 0.25 mol/dm³ Ti-EDTA complex aqueous solutions and after an additional calcination of the hydrothermal product at 600°C for 2 h. According to XRD analysis, the sample after annealing was sin-

gle-phase brookite, and average particle size determined from TEM micrographs was 60×40 nm. The powder obtained after the hydrothermal treatment had a strong absorption in the region of visible light (Fig. 9(a)), which arises probably due to organic compounds adhered to particles surface during the hydrothermal treatment. In fact, TG-DTA detected 7% weight loss associated with exothermic peak in the range of 200–500°C (TG-DTA data are not shown). The powder after the calcination of the hydrothermal product exhibited a weaker absorption in visible light range (Fig. 9(b)), which should be expected due to oxidation of organic compounds by annealing. However, such a sample still has an absorption “tail” in the visible light range, that is absent in the case of the reference TiO₂ sample (Fig. 9(c)). This absorption in the visible light range is believed to be due to nitrogen doping into TiO₂ lattice during the hydrothermal synthesis in the presence of nitrogen containing molecules.¹⁴⁾

Figure 10 presents photocatalytic activities in terms of NO gas decomposition ratio by TiO₂ materials prepared by the hydrothermal treatment of 0.25 mol/dm³ Ti-EDTA complex aqueous solutions at 200°C for 24 h and by the same sample after the calcination at 600°C for 2 h. For comparison, activities of

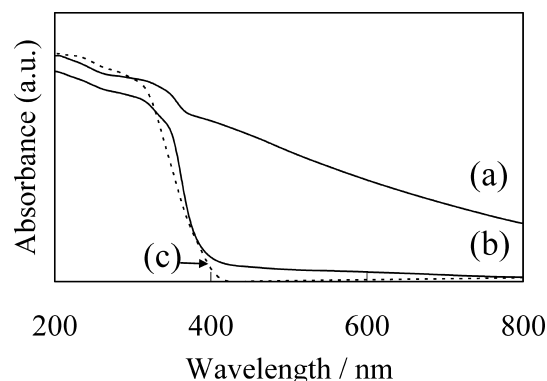


Fig. 9. Diffuse reflectance spectra of samples prepared by hydrothermal treatment of 0.25 mol/dm³ Ti-EDTA complex aqueous solution at 200°C for 24 h (a), after additional annealing at 600°C for 2 h (b) and commercial titania P25 (c).

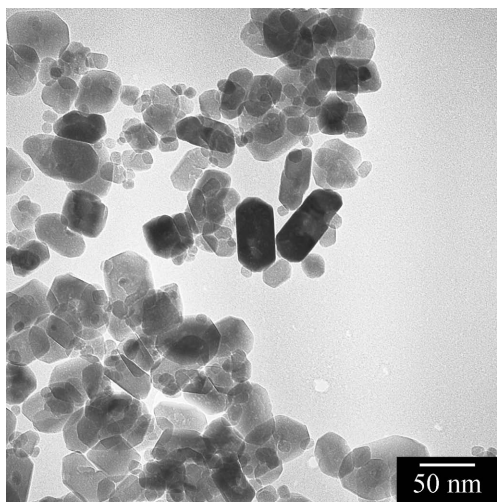


Fig. 8. TEM image of single phase brookite type TiO₂ prepared by hydrothermal treatment of 0.25 mol/dm³ Ti-EDTA complex aqueous solution at 200°C for 24 h.

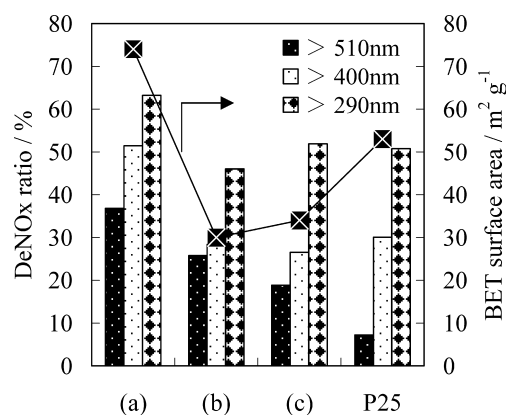


Fig. 10. Photocatalytic activities in terms of NO gas decomposition ratio by brookite samples prepared by hydrothermal treatment of 0.25 mol/dm³ Ti-EDTA complex aqueous solution at 200°C for 24 h (a) after additional calcination at 600°C for 2 h (b), by sample synthesized by hydrothermal treatment of Ti-glycolate complex under basic conditions (c) and by one of the best commercially available TiO₂ photocatalyst P25 (Degussa) (P25).

brookite prepared by a hydrothermal treatment of Ti-glycolate complex under basic conditions and one of the best commercially available TiO₂ photocatalyst P25 are also presented in the same figure. All brookite samples exhibited photocatalytic activities higher than or comparable to that of P25. Especially, the difference with respect to P25 was prominent in the region of visible light irradiation with the wavelength longer than 510 nm, which means that absorbance of visible light revealed in diffuse reflectance spectra in Fig. 9 is important for the improved activity of TiO₂.

One may conclude from Fig. 10 that brookite prepared by hydrothermal treatment of Ti-EDTA complex had a considerably higher activity than that of brookite synthesized from Ti-glycolate complex. This is probably attributed to the fact that the former has a higher surface area, which could be achieved by formation of smaller, but well-crystallized particles when Ti-EDTA complex aqueous solution was employed. It should be also mentioned that the result in Fig. 10 indicated that the detected amount of adsorbed organic compounds on the particles surface did not shadow TiO₂ active sites to the extent, which could degenerate photocatalytic activity in this reaction system. The reproducibility of results was verified by successive photocatalytic activity measurements with the same powder.

4. Conclusions

A water-soluble titanium complex coordinated by ethylenediaminetetraacetic acid (EDTA) was used for the first time for synthesis of nanocrystalline brookite type titanium oxide materials by a hydrothermal process. The effect of synthesis conditions such as reaction time, titanium concentration and solution pH on the brookite phase formation and photocatalytic performance of the materials was investigated. It was found that Ti-EDTA complex allows for the synthesis of brookite in a very wide range of experimental parameters in contrast to a number of previous reports, which emphasized that brookite could be obtained only in a narrow range of conditions. We also observed that synthesis of brookite was accompanied by formation of anatase, which disappeared after longer reaction time. Possible explanation was proposed, which assumes coexistence of two speciations of Ti-EDTA complex in its aqueous solution leading to anatase and brookite phases, followed by disappearance of fine anatase particles in the course of prolonged hydrothermal process due to the dissolution of anatase and recrystallization in the form of brookite. The photocatalytic activities in terms of NO gas decomposition by the samples prepared from Ti-EDTA complex were assessed and they were higher than activities of the brookite phase synthesized from Ti-glycolate complex and commercial TiO₂ photocatalyst P25.

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