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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Hydrothermal synthesis of TiO_2 nano-particles using novel water-soluble titanium complexes

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Abstract Hydrothermal treatment of a series of water-soluble titanium complexes resulted in the formation of TiO_2. Rutile, anatase or a mixture of both can be synthesized by varying the ligands. The titania obtained was composed of nano-sized particles with large specific surface areas. These TiO_2 powders exhibited high photocatalytic activity for NO_x decomposition. In particular, they demonstrated higher activity than P25 (Degussa) under visible-light irradiation.

Introduction

Hydrothermal processing, in which water is used as a solvent under higher pressure at higher temperature than its boiling point at 1 atm, has been used for decomposition of organic compounds and synthesis of single crystals. This method is also attractive for ceramics synthesis [1]. Under hydrothermal conditions, the reaction solution develops an anomalous dielectric constant, density and ionic strength which cannot be achieved under ambient pressure and temperatures; these allow unusual reactions to be carried out.

In recent years, TiO_2 semiconductor compound, which is a prospective photocatalytic material, has been synthesized by the hydrothermal method, with the prepared particles showing high photocatalytic activity [2–6]. For synthesis of TiO_2 in aqueous solution, acidic conditions ($pH < 1$) are required to prevent rapid hydrolysis of titanium compounds. As a result, $TiCl_3$ or $TiCl_4$ in hydrochloric acid aqueous solution or $Ti(SO_4)_2$ in sulfuric acid aqueous solution are mainly used [6–8]. However, these acidic solutions are difficult to handle because of their toxic and aggressive nature. Organic compounds such as titanium tetraisopropoxide are also often used, but these titanium compounds can be highly unstable and flammable. Because of these considerations, titanium compounds which are stable and do not undergo hydrolysis across a wide pH range have long been sought. We have succeeded in developing novel water-soluble titanium complexes [9–11] which are less-toxic, stable under both acidic and basic conditions, and tolerate the use of neutral water as a solvent.

In the present study, we demonstrate synthesis of titania by hydrothermal treatment of these complexes and estimate the photocatalytic activity of the resulting materials.

Experimental

Hydrothermal synthesis of TiO_2 powders

Metallic titanium powder (5 mmol) was dissolved in a cooled mixture of 30% NH_3 aqueous solution (5 mL) and 30% H_2O_2 (20 mL). After dissolution of the titanium powder, a hydroxycarboxylic acid containing –OH and

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–COOH groups (citric acid, lactic acid, glycolic acid, malic acid, or tartaric acid) was added to the solution. The amounts of citric acid, malic acid, and tartaric acid used were equimolar to the amount of titanium, while glycolic acid and lactic acid were used in 1.5 or 3 times excess [9–11]. These solutions were dried at 80 °C to form yellow or orange gel-like substances. Upon further drying, the gels transform into dry powders, which could easily be dissolved in pure water to yield transparent aqueous solutions. The pH of the solutions was about 6. A 20 mL sample of each solution ([Ti] = 0.25 M), was sealed in a Teflon-lined stainless steel autoclave with a volume of 50 mL and was heated at 200 °C for 24 h. After the autoclave had cooled down, the precipitates were separated from the solutions by filtration and/or centrifuge. The products were washed with distilled water until the pH of filtrate was around 7, and then dried at room temperature.

Characterization of TiO_2 powders

The samples were characterized by powder X-ray diffraction using Rigaku RINT-2200 diffractometer operating at 40 kV and 30 mA with CuKα radiation (λ = 1.5406 Å). The data were collected in a 2θ–θ scanning mode with the scanning speed of 4° min^{-1} and step size of 0.02°. Phase composition was also confirmed by Raman spectroscopy. The spectra were acquired by Jasco NRS-3300 Raman spectrometer in the backscattering geometry using 532.2 nm wavelength and laser power of 0.1 W for excitation. The incident beam was focused on the sample through the 100× lenses of microscope into the spot of 2 μm size. The particles morphology was examined by transmission electron microscopy (Carl Zeiss Inc. TEM LEO-912 operating at 200 kV). For observations the powders were dispersed in ethanol; then a drop of the liquid was transferred onto the Cu microgrid coated with holey carbon film and allowed for evaporation of the alcohol. All powders were also characterized by diffuse reflectance spectroscopy (DRS) and Brunauer–Emmett–Teller (BET, absorbed gas N_2, at 77 K) specific surface area measurement.

Elemental analysis for carbon, hydrogen, nitrogen, and sulfur contents in the samples was carried out by the Elemental Analysis group of IMRAM at Tohoku University. The results of the analysis are presented in Table 1.

Table 1 Carbon, hydrogen, nitrogen, and sulfur concentrations in the titanium dioxide samples prepared by hydrothermal treatment of water-soluble titanium complexes with different ligands

Ligand	C (%)	H (%)	N (%)	S (%)
Citric acid	3.33	0.77	0.44	–
Malic acid	1.22	0.51	0.00	–
Tartaric acid	1.71	0.42	0.23	–
Lactic acid	1.71	0.49	0.00	–
Glycolic acid	0.31	0.26	0.00	–
P25*	0.00	0.18	0.00	0.16

* P25 (Degussa, anatase:rutile = 4:1) is the commercial sample used as a reference

Evaluation of photocatalytic activities for NO oxidation

Samples were placed in a hollow space (20 × 15 × 0.5 mm^3) on a glass holder and set in the center of a sealed plastic reactor of 373 cm^3 volume. A gas consisting of dried air (balanced N_2) and 2 ppm NO was allowed to flow into the reactor (flow rate: 200 cm^3/min, NO_x concentration: about 1 ppm). A 450 W high-pressure mercury lamp was used as a light source. A Pyrex jacket around the lamp was used to cut off wavelengths $\lambda < 290$ nm, and it was cooled by water. Two cut-off filters ($\lambda < 400$ nm: 400 nm filter and $\lambda < 510$ nm: 510 nm filter) could be inserted between the lamp and the reactor. NO and NO_2 concentrations were determined using a NO_x analyzer. For comparison, the photocatalytic activity of the commercial titania powder (P25, Degussa, anatase:rutile = 4:1) was also measured. Figure 1 shows a schematic diagram of the photocatalytic cell [4]. After it had been confirmed that the NO_x concentration was constant at 1 ppm in the darkness, the sample was irradiated with light. NO_x concentration was measured every 10 min at wavelengths of $\lambda > 510$, 400, and 290 nm by removing the 510 and 400 nm filters, respectively.

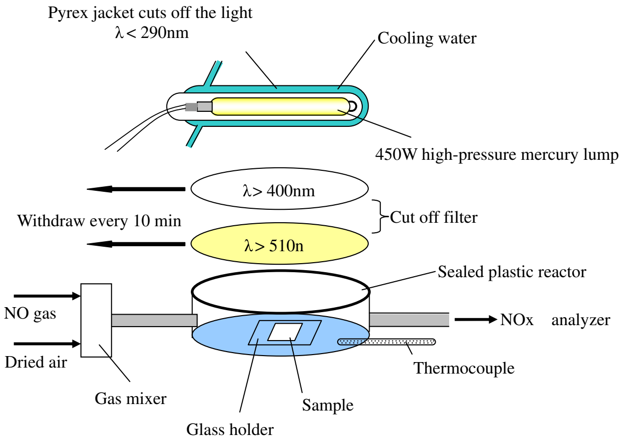

Fig. 1 Experimental apparatus used for photocatalytic oxidation of NO

Results and discussions

Identification of TiO_2 powders

Figure 2 shows the XRD patterns of the powders obtained by hydrothermal treatment of the titanium water-soluble complexes with citric, tartaric, malic, lactic, and glycolic acids. It was confirmed that the samples consisted of rutile and anatase titanium oxide. Single-phase anatase was obtained from the complexes with citric acid, tartaric acid, and malic acid ligands, while a mixture of anatase and rutile was formed from the titanium-lactate complex. Single-phase rutile was obtained starting from the titanium-glycolate complex. These results demonstrate that different titania polymorphs may be selectively synthesized. We also confirmed the phase composition using Raman spectroscopy (Fig. 3). Raman spectra were in a good agreement with the results of XRD measurement as we observed only characteristic peaks [12] of anatase (Fig. 3a–c), rutile (Fig. 3e), and of the mixture of both phases (Fig. 3d).

Figure 4 shows TEM images and electron diffraction (ED) patterns of the products. All of the samples consisted of nano-sized particles. Anatase particles of different sizes were obtained depending on the type of ligand used, but all anatase particles had spherical or square shape. The minimum anatase particles were obtained from titanium-lactate complex and its size was about 7 nm, while the sample synthesized using tartrate complex was about 15 nm. Rutile obtained by hydrothermal treatment of titanium-glycolate complex was 50 × 150 nm rod-like shape. The ED patterns confirmed that the obtained samples possessed high crystallinity. Additionally we found that rutile shape could be controlled. Figure 4f shows the particles obtained by hydrothermal treatment of titanium-glycolate complex with excess amount of glycolic acid as an additive. These particles, which were surrounded by anatase, had whisker-like morphology and were different from the particles synthesized without additives. Further studies on the mechanism of particles formation, control of their shape and the dependence of photocatalytic activity on morphology are under way.

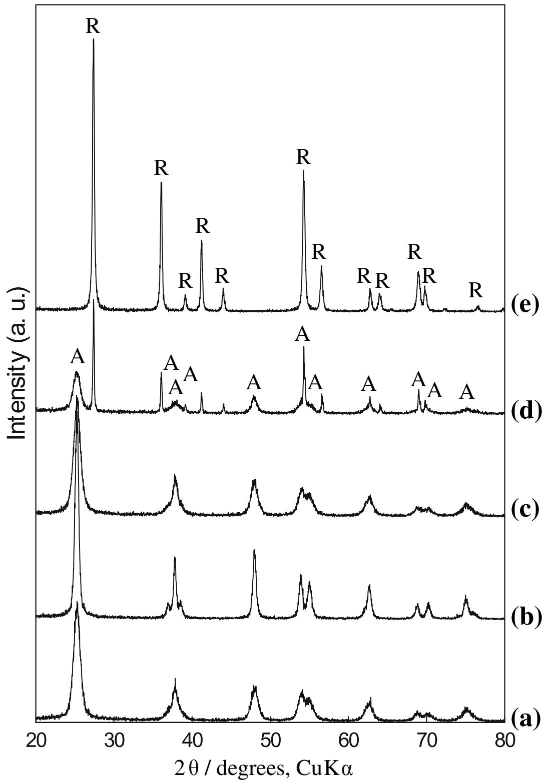

Fig. 2 XRD patterns of the samples obtained after hydrothermal treatment of solutions of titanium complexes containing citric acid (**a**), tartaric acid (**b**), malic acid (**c**), lactic acid (**d**), and glycolic acid (**e**). A: anatase, R: rutile

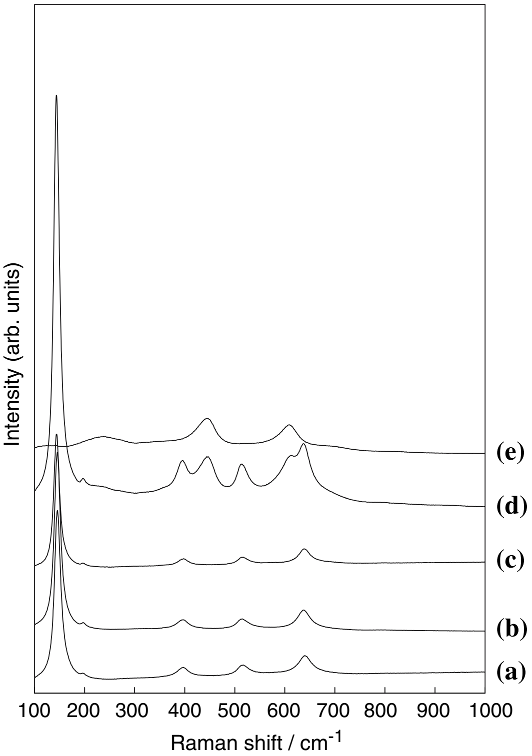

Fig. 3 Raman spectra of the samples obtained by hydrothermal treatment of titanium citrate complex (**a**), titanium tartrate complex (**b**), titanium malate complex (**c**), titanium lactate complex (**d**), and titanium-glycolate complex (**e**)

Photocatalytic activities

Figure 5 shows the NO oxidation ratios of the prepared particles and the commercial photocatalyst P25 under light irradiation. The numbers at the top of Fig. 5 indicate the

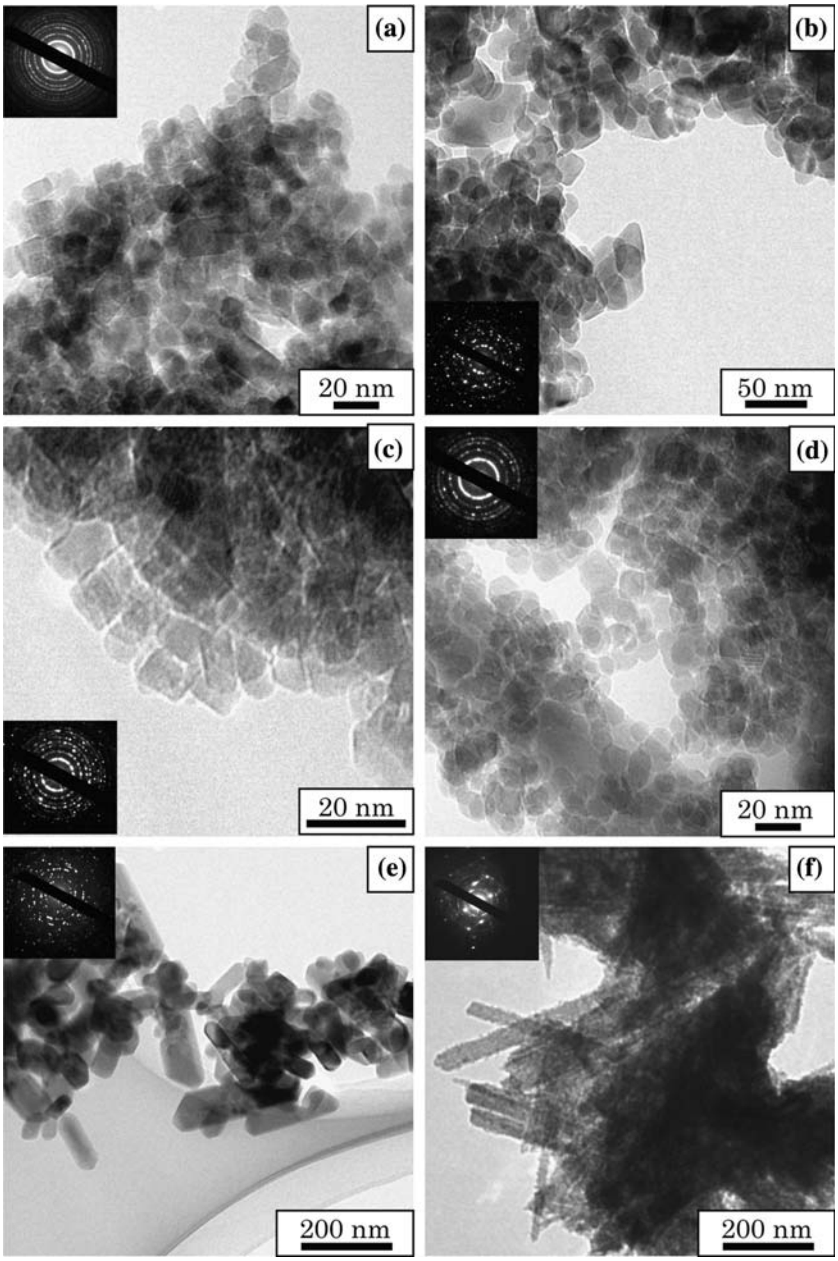

Fig. 4 TEM micrographs and ED patterns of the particles prepared by hydrothermal treatment of the solutions of titanium complexes containing citric acid (**a**), tartaric acid (**b**), malic acid (**c**), lactic acid (**d**), and glycolic acid (**e**), and from titanium-glycolate complex in the presence of glycolic acid excess (**f**)

BET surface area of each sample. NO oxidation ratios were determined based on the following formula:

$$\text{NO oxidation ratio }(\%) = \frac{\text{intial NO}_x\text{ concentration}(1\,\text{ppm}) - \text{final NO}_x\text{ concentration every 10 min}}{\text{intial NO}_x\text{ concentration }(1\,\text{ppm})}$$

Under irradiation with $\lambda > 290$ and 400 nm light, the NO conversion ratios of the synthesized powders are almost the same as that of P25. Under illumination by visible light ($\lambda > 510$ nm), however, all of the prepared specimen exhibited higher photocatalytic activities than P25. Figure 6 shows DRS spectra of the prepared powders. This measurement demonstrated that the obtained samples had absorption in the visible light region, while commercial titania (P25) did not absorb visible light. Elemental analysis results in Table 1 show that carbon and nitrogen

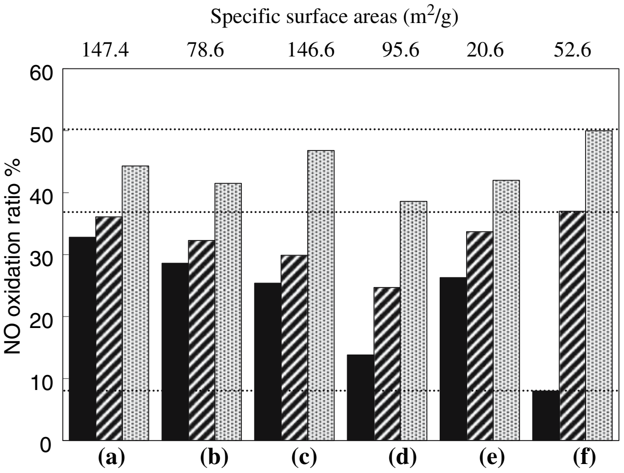

Fig. 5 NO oxidation ratios of the powders synthesized by hydrothermal treatment of solutions of titanium complexes with citric acid (anatase) (**a**), tartaric acid (anatase) (**b**), malic acid (anatase) (**c**), lactic acid (rutile and anatase) (**d**), and glycolic acid (rutile) (**e**) and of commercial photocatalyst P25 (anatase + rutile) (**f**). ⊡: $\lambda > 290$ nm, ▨: $\lambda > 400$ nm, ■: $\lambda > 510$ nm

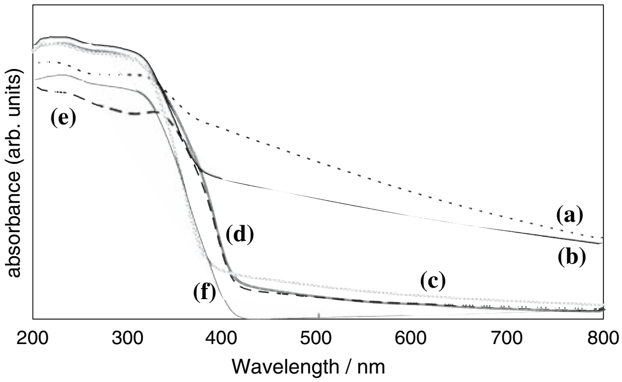

Fig. 6 Diffuse reflectance spectra of the specimen synthesized by hydrothermal treatment of water-soluble titanium citrate complex (anatase) (**a**), tartrate complex (anatase) (**b**), malate complex (anatase) (**c**), lactate complex (rutile and anatase) (**d**), and glycolate complex (rutile) (**e**) and of commercial photocatalyst P25 (anatase + rutile) (**f**)

are not present in P25, while 1–4 wt.% of carbon was detected in the titania nano-powders synthesized by our method. In addition, approximately 0.3 wt.% of nitrogen was found in the titania synthesized from citric acid and tartaric acid complexes. Previous reports have stated that TiO_2 doped with nitrogen and/or carbon shows a visible-light response, with improvement of photocatalytic activity [13, 14]. It is also possible that titania was doped by nitrogen and/or carbon derived from the NH_4^+ counter ion and ligands in our synthesis method. This may be one factor leading to the higher activity of TiO_2 powders in this work when visible irradiation of $\lambda > 510$ nm was used. In addition, our samples had high specific surface areas, and the tendency of surface area increase was rather consistent with the NO oxidation capability of the samples. Thus a large specific surface area is another possible reason for high activity of the TiO_2 nano-powders prepared by hydrothermal treatment of water-soluble complexes of titanium.

Conclusion

Hydrothermal treatment of novel water-soluble titanium complexes resulted in formation of nano-sized rutile and anatase titania. The prepared powders had large specific surface areas and high photocatalytic activities for NO oxidation. In particular, under irradiation with only visible light, the photocatalytic activities of these samples were higher than that of commercial photocatalyst P25.

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