

IMPROVEMENT IN PHOTOCATALYTIC ACTIVITY OF TITANIA WITH CARBON COATING

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Abstract

Effect of carbon-coating on photocatalytic activity of titania was investigated, being compared with titania heated without carbon. Three types of titania with different nanosize morphology, particles, tubes, and fibers were used. Heat-treated samples were prepared by annealing at different temperature from 200 to 900 °C in air for 1 h. Carbon-coating on titania powders was achieved by mixing and heating with polyvinylalcohol (PVA) powders in Ar gas flow at either 700 or 900 °C. Photocatalytic activity under UV irradiation was evaluated by discoloring of methylene blue (MB) solution in which photocatalyst powders were dispersed. Photoactivity of samples is thought to depend on crystallinity of anatase phase in powders. Rate constant $-k$ for MB decomposition increases with decrease of full width at half maximum (FWHM) of 101 XRD line, until phase transformation from anatase to rutile occurs. Once the phase transformation takes place, it abruptly decreases for all samples. Since carbon layer on titania suppresses a phase transformation from anatase to rutile as well as particle growth, fine anatase particles with high crystallinity is able to be formed in carbon-coated samples. Consequently, photoactivity of carbon-coated samples is higher than that of titania heated without carbon within a small FWHM of 101 line.

1. Introduction

Release of harmful organic materials into environment is widely recognized as a serious problem for ecosystem. Water pollution such as endocrine disturbing chemicals from industrial effluent and domestic wastewater, and air pollution from motor vehicles, airplanes, and industry fume, are getting worse rather than better on a global scale. In addition, allergic to chemicals, such as sick building syndrome, has been increased recently.

Titania is one of coming environmental catalysts for pollutant and technology for photocatalyst titania has been commercialized as coating agent for building wall, floor of hospital, mirror, window, guardrail and sound abatement shield, and as catalyst for electronic air cleaner. Though, degradation and adsorption rate and photoactivity in visible region of titania are so small that various improvements, including dope of foreign atoms, mounting of different materials, combination of adsorbents, morphological control of titania, have been made an attempt actively. Mounting of nano particles of platinum on titania accelerates charge separations [1]. Substitution of oxygen for nitrogen in titania develops photoactivity in visible region [2]. Activated carbon and hydroxyapatite are used with titania as adsorbents [3-4]. Titania nano tubes and titania nano fibers are prepared under hydrothermal conditions and are applied to photocatalysts and dye-sensitized solar cell [5-6].

Enhancement of photoactivity with carbon-coating has been developed in our group [7-15]. Organic molecules are thought to be adsorbed on thin carbon layer on titania and then they are thought to pass through carbon layer to get to surface of titania. Finally, they are decomposed under UV irradiation at the surface. Some advantages of carbon-coating on titania have been confirmed. First, porous carbon layer on titania adsorbs organic molecules quickly. Second, carbon layer suppresses particle growth and a phase transformation from anatase with highest activity among polymorphs to less active rutile.

In the present paper, three types of titania, granulous, fibrous and tubular particles, were coated with carbon in order to examine effect of carbon-coating on photocatalytic activity of titania by comparing titania heated without carbon. Photocatalytic activity was evaluated by color fading of methylene blue (MB) solution under UV irradiation and was marshaled by FWHM of 101 line for anatase phase, a measure of crystallinity, for all samples.

2. Experimental

2.1 Preparation

Titania nanotubes (TNT) and titania nanofibers (TNF) were prepared through hydrothermal condition as reported by Kasuga et al. [5] and Uchida et al. [16] respectively. The TNT and TNF samples thus obtained were confirmed to be nano tubular and nano fibrous shape respectively by the observation under transmission electron microscope (TEM). TNT and TNF thus prepared were annealed at different temperatures from 100 to 900 °C for 1 h in air. For comparison with TNT and TNF synthesized, commercially available anatase phase ST-01 powders (Ishihara Sangyo Co., Ltd) was also annealed at different temperatures.

These three types of titania were coated with carbon in order to improve photocatalytic activity. Carbon-coating was achieved by mechanical mixing of titania powders and polyvinylalcohol (PVA) powders, followed by heating at either 700 or

900 °C for 1 h under Ar gas flow [7-15]. Preparation conditions are listed in Table 1 with their sample code. After carbon coating process, white sample powders turned to be black powders and carbon layer on titania were determined to be a few nano meter layer under TEM observation [7-15].

Table 1. Sample code, preparation conditions, FWHM of 101 XRD line, and rate constant, -k for samples

| Sample code | Heating Temperature (°C) | PVA mixing ratio TiO ₂ /PVA (weight %) | FWHM of 101 XRD line (°) | Rate constant -k (h ⁻¹) |
|-------------|--------------------------|---|--------------------------|-------------------------------------|
| TNT | - | 100/0 | 2.1 | 0.084 |
| TNT-100 | 100 | 100/0 | 2.2 | 0.095 |
| TNT-200 | 200 | 100/0 | 2.0 | 0.072 |
| TNT-300 | 300 | 100/0 | 1.4 | 0.11 |
| TNT-400 | 400 | 100/0 | 0.71 | 0.33 |
| TNT-500 | 500 | 100/0 | 0.58 | 0.41 |
| TNT-600 | 600 | 100/0 | 0.48 | 0.72 |
| TNT-700 | 700 | 100/0 | 0.44 | 0.95 |
| TNT-800 | 800 | 100/0 | 0.40 | 0.74 |
| TP50-700 | 700 | 50/50 | 0.63 | 0.27 |
| TP70-700 | 700 | 70/30 | 0.78 | 0.27 |
| TP90-700 | 700 | 90/10 | 0.47 | 1.3 |
| TP50-900 | 900 | 50/50 | 0.47 | 0.41 |
| TP70-900 | 900 | 70/30 | 0.31 | 1.6 |
| TP90-900 | 900 | 90/10 | 0.31 | 1.8 |
| TNF | - | 100/0 | 1.6 | 0.19 |
| TNF-100 | 100 | 100/0 | 1.6 | 0.21 |
| TNF-200 | 200 | 100/0 | 1.5 | 0.18 |
| TNF-300 | 300 | 100/0 | 1.5 | 0.12 |
| TNF-400 | 400 | 100/0 | 1.1 | 0.16 |
| TNF-500 | 500 | 100/0 | 0.69 | 0.21 |
| TNF-600 | 600 | 100/0 | 0.49 | 0.42 |
| TNF-700 | 700 | 100/0 | 0.38 | 1.2 |
| TNF-800 | 800 | 100/0 | 0.26 | 1.1 |
| FP50-700 | 700 | 50/50 | 0.43 | 0.29 |
| FP70-700 | 700 | 70/30 | 0.41 | 0.44 |
| FP90-700 | 700 | 90/10 | 0.38 | 1.2 |
| FP50-900 | 900 | 50/50 | 0.23 | 3.5 |
| FP70-900 | 900 | 70/30 | 0.22 | 2.1 |
| FP90-900 | 900 | 90/10 | 0.18 | 1.4 |
| ST-01 | - | 100/0 | 1.2 | 0.070 |
| ST-01-100 | 100 | 100/0 | 1.2 | 0.10 |
| ST-01-200 | 200 | 100/0 | 1.1 | 0.074 |
| ST-01-300 | 300 | 100/0 | 0.76 | 0.090 |
| ST-01-400 | 400 | 100/0 | 0.56 | 0.094 |
| ST-01-500 | 500 | 100/0 | 0.44 | 0.20 |
| ST-01-600 | 600 | 100/0 | 0.38 | 0.41 |
| ST-01-700 | 700 | 100/0 | 0.27 | 0.23 |
| ST-01-800 | 800 | 100/0 | 0.18 | 0.084 |
| SP50-700 | 700 | 50/50 | 0.22 | 0.60 |
| SP70-700 | 700 | 70/30 | 0.48 | 1.1 |
| SP90-700 | 700 | 90/10 | 0.60 | 1.3 |
| SP95-700 | 700 | 95/ 5 | 0.68 | 0.50 |
| SP50-900 | 900 | 50/50 | 0.74 | 0.55 |
| SP70-900 | 900 | 70/30 | 0.71 | 1.1 |
| SP80-900 | 900 | 80/20 | 0.74 | 0.27 |
| SP90-900 | 900 | 90/10 | 0.74 | 0.15 |

XRD measurement was performed on samples prepared with CuK α ray. A full width at half maximum (FWHM) of 101 line assigned to anatase phase was measured as a parameter for crystallinity of anatase phase.

2.2 Photocatalytic decomposition of methylene blue

Photocatalytic activity of the samples under UV irradiation was measured by color degradation of aqueous solution of methylene blue (MB). Since sample powders prepared had high adsorptivity for MB, sample powders were saturated with MB before measurement of photodecomposition. In the MB aqueous solution of 100 mL with a concentration of 2.94×10^{-4} mol dm⁻³, the sample powder of 0.05 g was dispersed under ultrasonic vibration for 5 min. The solution was kept in the dark under stirring to measure the adsorptivity for MB. Saturation of MB adsorption was confirmed by no change in MB concentration with time in the dark. Then the sample powder was filtered and dispersed again using ultrasonic vibration in MB solution of 300 cm³ with a concentration of 2.94×10^{-6} mol dm⁻³. The solution dispersing the sample powder was irradiated by UV rays, of which strength at 360 nm was about 0.8 mW cm⁻² at the position of the solution surface. Concentration of MB in the solution was measured as a function of irradiation time by sampling the solution of 3 cm³ passing through 0.2 μ m membrane filter, from absorbance at the wavelength of 664 nm with a spectrophotometer. Since the plots of logarithm of relative concentration of MB in the solution $\ln(c/c_0)$ against irradiation time were approximated to be linear, as reported in our previous papers [14-16], the slope of the linear relation, *i.e.*, rate constant *k*, was determined on each sample and used as a measure of the photoactivity for the decomposition of MB in water.

3. Results and discussion

3.1 Crystallinity of samples

XRD patterns of titania nanotube samples with different heating temperature (TNT series samples) and carbon-coated titania nanotube samples heated at either 700 or 900 °C with different PVA mixing ratio (NP series samples) are shown in Figure 1. For TNT series samples, tubular shape keeps up to 350 °C and it collapses to be rod-like particle above 400 °C. XRD lines assigned to anatase phase becomes sharp with increase of heating temperature (Figure 1a) and FWHM of 101 line, a measure of crystallinity, decreases with heating temperature (Table 1). Phase transformation from anatase to rutile is observed at around 800 °C. For NP series samples with the same heating temperature (Figure 1b), XRD lines become sharp with decrease of PVA mixing ratio and those for 900 °C samples are sharper than those for 700 °C samples. A small peaks assigned to rutile phase is observed, but anatase phase in the samples is kept after carbon-coating at 900 °C. This indicates that carbon layer on titania suppresses the phase transformation.

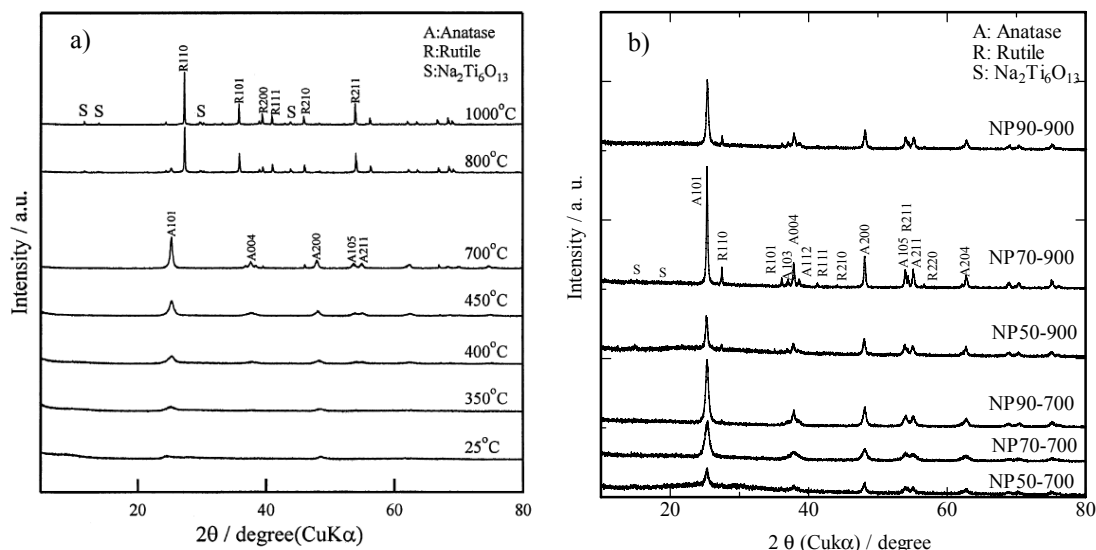


Figure 1. XRD patterns of samples. Titania nanotubes with different heating temperature (TNT series) a) and carbon-coated titania nanotubes with different PVA mixing ratio and heating temperature (NP series) b).

For titania nanofibers (TNF) and ST-01 particles, the same trend in development of crystallinity as TNT is observed and those FWHM of 101 lines are summarized in Table 1.

3.2 Methylene blue decomposition

Changes in relative concentration C/C_0 with irradiation time for TNT series and NP series sample are shown in Figure 2. The slop of the linear relation, rate constant $-k$, represents photocatalytic activity. For TNT series samples, rate constant $-k$ is almost same up to 300 °C and it increases gradually with increase of heating temperature. At around 650 °C value of $-k$ reaches maximum one and then it decreases with increase of heating temperature above 650 °C. The decrease of $-k$ is

reasonably supposed to be caused by phase transformation anatase to rutile. For NP series samples, NP50-700, NP70-700 and NP50-900 with high carbon content has a comparable rate constant $-k$ to TNT-500 and NP90-700, NP90-700 and NP90-900 has the highest among samples. Rate constant $-k$ for the all samples prepared are listed in Table 1.

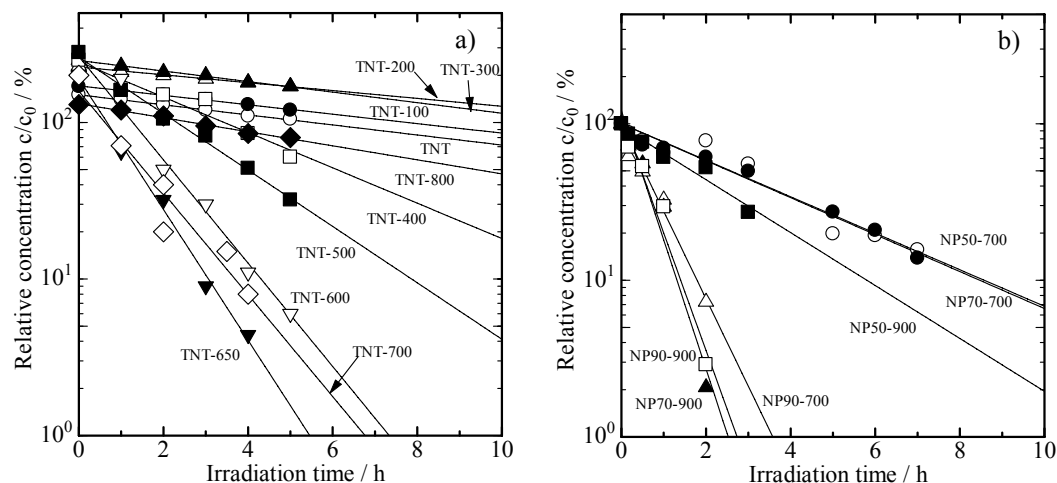


Figure 2. Changes in relative concentration C/C_0 with irradiation time. TNT series a), NP series b).

Dependence of rate constant $-k$ on FWHM of 101 diffraction lines for TNT, TNF and ST-01 are shown Figure 3. For TNT series (open symbols in Figure 1a), $-k$ increases with decrease of FWHM of 101 line and it decreases abruptly around 0.5° but for NP series (closed symbols in Figure 1b), it increases with decrease of FWHM of 101 line. The decrease in TNT series is obviously caused by phase transformation from anatase to rutile. Increment of $-k$ for NP series may continue, until the phase change occurs.

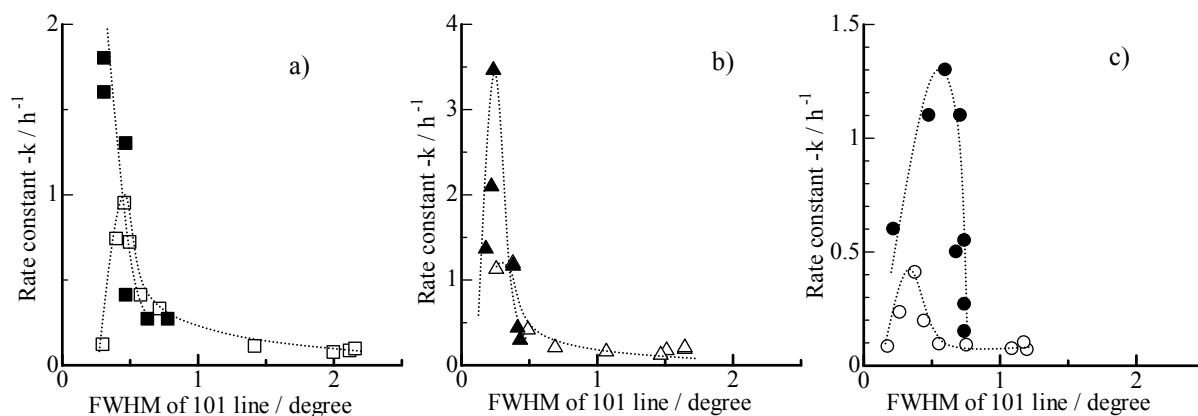


Figure 3. Dependence of rate constant $-k$ on FWHM of 101 diffraction lines. TNT a), TNF b) and ST-01 c). Open symbols are heat treated samples and closed symbols are carbon-coated samples.

For TNF and ST-01 (Figures 3a and 3b), dependence of rate constant $-k$ on FWHM of 101 lines is comparable that for TNT. But absolute value of $-k$ is rather different among three types of titania. This difference in $-k$ is probably due to the difference in the adsorptivity of MB. The samples derived from either TNT or TNF can adsorb large amount of MB on the particles, but adsorptivity of those from ST-01 of the sintered particles is smaller than that of those from TNT and TNF.

4. Summary

Photoactivity of samples is thought to depend on crystallinity of anatase phase. It increases with decrease of full width at half maximum (FWHM) of 101 XRD line, measure of crystallinity, until phase transformation from anatase to rutile occurs. Since carbon layer on titania suppresses a phase transformation from anatase to rutile as well as particle growth, fine anatase particles with high crystallinity is formed in carbon-coated sample. Consequently, photoactivity of carbon-coated samples is higher than that of titania heated without carbon.

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