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1 **Novel hydrothermal preparation of pure brookite-type titanium(IV) oxide nanocrystal under**  
2 **strong acidic conditions**

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8

9 **Abstract**

10 Titanium(IV) oxide (TiO<sub>2</sub>) nanocrystal with brookite phase was prepared by hydrothermal  
11 treatment of titanate nanotubes under strong acidic conditions (perchloric acid, hydrochloric acid  
12 and nitric acid). The relative fractions of crystal phases (anatase, rutile and brookite) were  
13 strongly dependent on hydrothermal treatment duration and the kind of strong acid used. A high  
14 brookite type TiO<sub>2</sub> content was obtained by hydrothermal treatment under perchloric acidic solution.  
15 Single-phase brookite TiO<sub>2</sub> particles were extracted from as-prepared TiO<sub>2</sub> by a centrifugal  
16 separation procedure, and they exhibited higher photocatalytic activity for acetaldehyde  
17 decomposition than TiO<sub>2</sub> prepared without the separation procedure.

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## 1 **1. Introduction**

2 Titanate nanotubes (TNTs) have attracted much attention because of their unique structure  
3 and simple preparation method, which was reported by Kasuga et al. [1]. Applications of TNT  
4 powders include dye-sensitized solar cells [2], catalyst supports [3,4] and photocatalysts [5]; these  
5 applications exploit the chemical and physical properties of TNT powders, such as their large  
6 specific surface area and tubular structure. Another very important application of TNTs is as a  
7 titanium source for material preparation. Several groups have investigated the structural  
8 transformation of TNTs to titanium(IV) oxide ( $\text{TiO}_2$ ) by thermal, acid and hydrothermal treatment,  
9 and they found that treatment of TNTs under specific conditions results in the formation of  
10 characteristic  $\text{TiO}_2$  nanostructures, e.g., nanorods, nanobelts, nanofibers [6-10]. The main  
11 component of their crystal phase is anatase and/or rutile, while a trace amount of brookite is  
12 sometimes present [9]. Anatase, rutile and brookite are well known to be the crystal phases of  
13 natural  $\text{TiO}_2$ . However, the physical and chemical properties of brookite still remain unclear, in  
14 contrast with those of anatase and rutile, which have been extensively investigated. This is due to  
15 the low availability of single-phase brookite  $\text{TiO}_2$  as a result of it being thermodynamically  
16 metastable.

17 Kominami et al. prepared single-phase brookite  $\text{TiO}_2$  powders for the first time by  
18 solvothermal synthesis in which oxobis(2,4-pentanedionato-*O,O'*)titanium was used as the  $\text{TiO}_2$   
19 precursor and sodium laurate was used as a reagent for controlling the crystal structure [11]. They  
20 subsequently investigated the photocatalytic activity of single-phase brookite  $\text{TiO}_2$  [12,13].  
21 Recently, other groups have also reported single-phase brookite  $\text{TiO}_2$  having several kinds of  
22 characteristic structures, e.g., nanorods and nanotubes [14-18]. However, the photocatalytic  
23 properties of these structures were not investigated in these studies.

24 In the present study,  $\text{TiO}_2$  powders were prepared by hydrothermal treatment of TNTs under  
25 several kinds of strong acidic conditions without using an organic reagent for controlling the crystal  
26 structure, such as sodium laurate. Single-phase brookite  $\text{TiO}_2$  nanocrystals were extracted from  
27 as-prepared  $\text{TiO}_2$ , and the photocatalytic properties of these  $\text{TiO}_2$  powders were investigated.

1

## 2 **2. Experimental**

### 3 *2.1 Sample preparation*

4 One gram of TNT powder (TNT-352, Catalysts & Chemicals Ind. Co., Ltd.) was dispersed in  
5 50 cm<sup>3</sup> of 2 mol dm<sup>-3</sup> of an acid solution (perchloric acid (HClO<sub>4</sub>), hydrochloric acid (HCl), and  
6 nitric acid (HNO<sub>3</sub>)) in a Teflon bottle. After stirring the solution, the Teflon bottle was sealed with  
7 a stainless steel jacket and heated at 200 °C for 1~50 h in an oven. After this hydrothermal  
8 treatment, the supernatant in the bottle was removed. To extract single-phase brookite TiO<sub>2</sub>  
9 powders, centrifugal separation was performed by adding Milli-Q water, centrifuging the  
10 suspension for 30 min at 5000 rpm, and then filtrating the supernatant (not transparent). The  
11 residues obtained both by using and without using the above-mentioned procedure were washed  
12 with an aqueous NH<sub>3</sub> solution (1%) and Milli-Q water several times until the ionic conductivity of  
13 the supernatant was <10 μS cm<sup>-2</sup>.

14

### 15 *2.2 Characterization*

16 The crystal structures of the TNT or TiO<sub>2</sub> powders were characterized with an X-ray  
17 diffractometer (Rigaku, MiniFlex II) with Cu Kα radiation (λ = 1.5405 Å). The relative surface  
18 areas of the powders (S<sub>BET</sub>) were determined using a surface area analyzer (Quantachrome,  
19 Autosorb-1) in conjunction with the Brunauer-Emmett-Teller (BET) equation. The morphologies  
20 of the TNT or TiO<sub>2</sub> powders were observed using a transmission electron microscope (TEM;  
21 Hitachi, H-9000NAR).

22

### 23 *2.3 Photocatalytic decomposition of acetaldehyde*

24 Photocatalytic activities of TNT or TiO<sub>2</sub> samples were evaluated by photocatalytic  
25 decomposition of acetaldehyde. One hundred milligrams of TNT or TiO<sub>2</sub> powder, which have a  
26 complete extinction of the incident radiation, was spread on a glass dish, and the glass dish was  
27 placed in a 125 cm<sup>3</sup> Tedlar bag (As one). Five hundred parts per million of gaseous acetaldehyde

1 was injected into the Tedlar bag, and photoirradiation was performed at room temperature after the  
2 acetaldehyde had reached adsorption equilibrium. The gaseous composition in Tedlar bag were  
3 79 % of N<sub>2</sub>, 21 % of O<sub>2</sub>, <0.1 ppm of CO<sub>2</sub> and 500 ppm of acetaldehyde, and relative humidity was  
4 ca. 30 %. A light emitting diode (Nichia, NCCU033), which emitted light at a wavelength of ca.  
5 365 nm and an intensity of 1.0 mW cm<sup>-2</sup>, was used as the light source. The concentrations of  
6 acetaldehyde and carbon dioxide (CO<sub>2</sub>) were estimated by gas chromatography (Shimadzu, GC-8A,  
7 FID detector) with a PEG-20 M 20% Celite 545 packed glass column and by gas chromatography  
8 (Shimadzu, GC-9A, FID detector) with a TCP 20% Uniport R packed column and a methanizer (GL  
9 Sciences, MT-221), respectively. In the photocatalytic evaluation, P-25 (Japan Aerosil Co., S<sub>BET</sub> =  
10 50 m<sup>2</sup> g<sup>-1</sup>), which is a well-known commercial TiO<sub>2</sub> photocatalyst with a high photocatalytic  
11 activity, was employed as a standard photocatalyst.

12

### 13 3. Results and discussion

14 The XRD analysis revealed that the crystal phase of the samples was transformed from TNT  
15 into TiO<sub>2</sub> (anatase, brookite and rutile) after over 1 h of hydrothermal treatment of TNT. Figures  
16 1a and b show XRD patterns of samples before hydrothermal treatment and after 50 h of  
17 hydrothermal treatment under HClO<sub>4</sub> solution, respectively. They indicate that a large fraction of  
18 brookite and small fractions of anatase and rutile were formed. The relative fractions of these  
19 crystal phases exhibited a strong dependence on the duration of the hydrothermal treatment.  
20 Figure 2 shows the relative fractions of the crystal phases (*f<sub>A</sub>*: anatase; *f<sub>B</sub>*: brookite; *f<sub>R</sub>*: rutile) as a  
21 function of the duration of the hydrothermal treatment with HClO<sub>4</sub> as the acid. The relative  
22 fractions of the crystal phases were calculated using the following equation [19]

$$23 \quad f_i = k_i S_i / (k_A S_A + k_B S_B + k_R S_R) \quad i = A, B, R,$$

24 where *k<sub>A</sub>* = 0.886, *k<sub>R</sub>* = 1, and *k<sub>B</sub>* = 2.721 [19]. *S<sub>A</sub>*, *S<sub>B</sub>* and *S<sub>R</sub>* are the integrated intensities of peaks  
25 attributed to anatase (101), brookite (121) and rutile (110), respectively. They were estimated by  
26 fitting the XRD patterns in the range of 22~34° with a superposition of five Lorentz functions for  
27 peaks attributed to brookite (120), anatase (101), brookite (111), rutile (110) and brookite (121).

1 For the calculation, the ratio of integrated intensities of the three peaks attributed to brookite (120),  
2 (111), (121) was fixed at 10 : 8 : 9, as determined by JCPDS data.

3 In Fig. 2,  $f_B$  and  $f_R$  increase monotonically with an increase in the hydrothermal treatment  
4 duration, and  $f_A$  has a maximum at about 5 h. This indicates that brookite is relatively stable under  
5  $\text{HClO}_4$  conditions, while anatase is metastable and is transformed into the other phases. However,  
6 phase transformation of fine anatase particles (ST-01, Ishihara Sangyo Co.,  $S_{\text{BET}} = 316 \text{ m}^2 \text{ g}^{-1}$ ) to  
7 brookite was not observed after 5 h of hydrothermal treatment under the same conditions. This  
8 result conflicts with the above-mentioned possibility of transforming anatase into brookite.  
9 Another plausible reason might be that  $f_A$  is underestimated because it is difficult to accurately  
10 estimate  $S_A$  in the presence of the brookite phase due to the overlapping of the three peaks that  
11 occur in the range of  $25\sim 26^\circ$ . The reason for this behavior of the anatase phase is currently under  
12 investigation.

13  $\text{TiO}_2$  prepared by 5 h of hydrothermal treatment of TNTs in Milli-Q water or  $2 \text{ mol dm}^{-3}$   
14 aqueous solution of sodium perchlorate had a smaller  $f_B$  than that prepared in  $\text{HClO}_4$  solution.  
15 Some reports have also reported the formation of a large fraction of brookite phase by hydrothermal  
16 synthesis from titanium(IV) tetrachloride ( $\text{TiCl}_4$ ) under  $\text{HCl}$  and  $\text{HNO}_3$  conditions [14,20].  
17 However, 50 h of hydrothermal treatment under  $\text{HCl}$  and  $\text{HNO}_3$  conditions induced small  $f_B$  ( $f_R = 1$   
18 for  $\text{HCl}$ ,  $f_R = 0.53$ ,  $f_B = 0.47$  for  $\text{HNO}_3$ ) in the present study, though relatively large  $f_B$  was observed  
19 for samples prepared by 5 h of hydrothermal treatment ( $f_R = 0.72$ ,  $f_B = 0.28$  for  $\text{HCl}$ ,  $f_A = 0.05$ ,  $f_R =$   
20  $0.12$ ,  $f_B = 0.83$  for  $\text{HNO}_3$ ). These results indicate that a low pH induce the transformation of TNTs  
21 to brookite and the presence of  $\text{ClO}_4^-$  anions suppress the transformation into rutile, while the  
22 presence of  $\text{Cl}^-$  anions promote the transformation into rutile due to the stabilization of rutile  
23 surfaces [21].

24 Figures 1b and c show XRD patterns of  $\text{TiO}_2$  powders that were prepared by 50 h of  
25 hydrothermal treatment without and with centrifugal separation, respectively. The  $\text{TiO}_2$  produced  
26 without centrifugal separation has an appreciable amount of rutile, whereas the XRD pattern of the  
27  $\text{TiO}_2$  produced using centrifugal separation contains no peaks that are attributed to rutile. This

1 indicates that single-phase brookite  $\text{TiO}_2$  was extracted by the separation procedure of the  
2 as-prepared  $\text{TiO}_2$ . Moreover, heat treatment (300 °C, 3 h) of single-phase brookite  $\text{TiO}_2$  induced  
3 no formation of the anatase phase. This result presumably indicates that the single-phase brookite  
4  $\text{TiO}_2$  contains very little amorphous or TNT phases. The primary particle sizes of rutile ( $d_{\text{R}(110)}$ )  
5 and brookite ( $d_{\text{B}(121)}$ ) were estimated from peaks attributed to rutile (110) and brookite (121) in  
6 XRD patterns using the Scherrer equation ( $d = 0.9\lambda/\beta\cos\theta_{\text{B}}$ , where  $\lambda$  is the wavelength of X-rays,  $\beta$   
7 is the full width at half maximum and  $\theta_{\text{B}}$  is the Bragg angle) and found to be 35 nm and 23 nm,  
8 respectively. However, this difference in particle size is not sufficiently large to explain the reason  
9 for the extraction of single-phase brookite  $\text{TiO}_2$ .

10 Figure 3 shows TEM images of TNT and  $\text{TiO}_2$  prepared with and without centrifugal  
11 separation. The TNTs had tubular structures with inner and outer diameters of ca. 5 nm and ca. 10  
12 nm, respectively (Fig. 3a).  $\text{TiO}_2$  prepared without centrifugal separation consisted of two kinds of  
13 particle shapes (Fig. 3b), namely large rods (ca. 50 nm by ca. 300 nm) and small particles with an  
14 aspect ratio of ca. 1 (ca. 30 nm), while only small monodispersed particles with a narrow size  
15 distribution were observed in the  $\text{TiO}_2$  prepared with centrifugal separation (Fig. 3c). TEM  
16 observation and XRD analysis indicate that larger rods and smaller particles are attributable to rutile  
17 and brookite nanocrystals, respectively. Thus, the effective particle size of the rutile rods was  
18 larger than  $d_{\text{R}(110)}$  due to the rod structure. This large difference in effective particle sizes explains  
19 why single-phase brookite  $\text{TiO}_2$  was extracted by the centrifugal separation. The  $S_{\text{BET}}$  ( $61 \text{ m}^2 \text{ g}^{-1}$ )  
20 of  $\text{TiO}_2$  prepared with the centrifugal separation procedure was slightly larger than that ( $57 \text{ m}^2 \text{ g}^{-1}$ )  
21 of the  $\text{TiO}_2$  prepared without centrifugal separation because of the low fraction of the rutile phase  
22 with large particle sizes.

23 The TEM image in Fig. 3c suggests that some brookite particles have specific exposed crystal  
24 faces, and lattice fringes were also observed in the TEM images of most of the single-phase  
25 brookite  $\text{TiO}_2$  particles shown in Fig. 3d. The space of lattice fringes (ca. 0.375 nm) indicate that  
26 exposed crystal face was attributed to brookite (101) face. This fringe means that the brookite  
27  $\text{TiO}_2$  particles consisted of a single crystal (i.e., they were not polycrystalline) suggesting that the

1 brookite TiO<sub>2</sub> particles have high crystallinity, which is important for photocatalytic activity.

2 Figure 4 shows the time course of CO<sub>2</sub> evolution of acetaldehyde decomposition over TiO<sub>2</sub>  
3 samples as a function of the photoirradiation time. The prepared brookite TiO<sub>2</sub> had a higher  
4 photocatalytic activity than the other TiO<sub>2</sub> powders. This result is presumably due to the high  
5 crystallinity and relatively large surface area of the prepared brookite TiO<sub>2</sub> [22]. Another plausible  
6 reason for this may be the specific exposed crystal faces, which induce separation of redox sites that  
7 enhances photocatalytic activity [23]. Some reports have revealed that a synergistic effect occurs  
8 for some photocatalytic reactions performed over a mixture of small anatase and large rutile  
9 particles [24]. However, TiO<sub>2</sub> prepared with centrifugal separation (small brookite particles)  
10 exhibited a higher activity than TiO<sub>2</sub> prepared without centrifugal separation (mixture of small  
11 brookite particles and large rutile particles), thus a synergistic effect was not observed in the present  
12 study for powders consisting of a mixture of brookite and rutile TiO<sub>2</sub>. On the contrary, the low  
13 activity of rutile rods with specific exposed crystal faces indicates that recombination rate was  
14 presumably increased by brookite-rutile contacts. The high photocatalytic activity of the  
15 single-phase brookite TiO<sub>2</sub> is attributable to intrinsic photocatalytic properties of brookite TiO<sub>2</sub> that  
16 has a high crystallinity and a large surface area.

17

#### 18 4. Conclusion

19 Hydrothermal treatment of TNT under HClO<sub>4</sub> conditions induced formation of brookite phase  
20 with trace amounts of the other two phases. The results of hydrothermal treatment of TNT under  
21 various conditions indicate that nucleation of brookite phase requires both a suitable pH of the  
22 solution in the dissolution process and the presence of the ClO<sub>4</sub><sup>-</sup> ion to control the formation of  
23 crystal structures in the crystallization process. Single-phase brookite TiO<sub>2</sub> was extracted from  
24 as-prepared TiO<sub>2</sub> by centrifugal separation. It consisted of a single crystal, and exhibited higher  
25 photocatalytic activity, presumably due to its high crystallinity and relatively large surface area.

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## 6 **References**

- 7 [1] T. Kasuga, M. Hiromatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir* 14 (1998) 3163.
- 8 [2] S. Uchida, R. Chiba, M. Tomiha, N. Masaki, M. Shirai, *Electrochemistry* 70 (2002) 418.
- 9 [3] V. Idakiev, Z.Y. Yuan, T. Tabakova, B.L. Su, *Appl. Catal. A* 281 (2005) 149.
- 10 [4] D.V. Bavykin, A.A. Lapkin, P.K. Plucinski, J.M. Friedrich, F.C. Walsh, *J. Catal.* 235 (2005) 10.
- 11 [5] J.C. Xu, M. Lu, X.Y. Guo, H.L. Lia, *J. Mol. Catal. A* 226 (2005) 123.
- 12 [6] H.Y. Zhu, Y. Lan, X.P. Gao, S.P. Ringer, Z.F. Zheng, D.Y. Song, J.C. Zhao, *J. Ame. Chem. Soc.*  
13 127 (2005) 6730.
- 14 [7] C.C. Tsai, H. Teng, *Chem. Mater.* 18 (2006) 367.
- 15 [8] D. Wu, J. Liu, X. Zhao, A. Li, Y. Chen, N. Ming, *Chem. Mater.* 18 (2006) 547.
- 16 [9] J. Nian, H. Teng, *J. Phys. Chem. B* 110 (2006) 4193.
- 17 [10] M. Miyauchi, H. Tokudome, *Appl. Phys. Lett.* 91 (2007) 043111.
- 18 [11] H. Kominami, M. Kohno, Y. Kera, *J. Mater. Chem.* 10 (2000) 1151.
- 19 [12] H. Kominami, J. Kato, S. Murakami, Y. Ishii, M. Kohno, K. Yabutani, T. Yamamoto, Y. Kera,  
20 M. Inoue, T. Inui, B. Ohtani, *Cat. Today*, 84 (2003) 181.
- 21 [13] H. Kominami, Y. Ishii, M. Kohno, S. Konishi, Y. Kera, B. Ohtani, *Cat. Lett.* 91 (2003) 41.
- 22 [14] A. Pottier, C. Chaneac, E. Tronc, L. Mazerolles, J.P. Jolivet, *J. Mater. Chem.* 11 (2001) 1116.
- 23 [15] K. Tomita, V. Petrykin, M. Kobayashi, M. Shiro, M. Yoshimura, M. Kakihana, *Angew. Chem.*  
24 *Int. Ed.* 45 (2006) 2378.
- 25 [16] M. Kakihana, K. Tomita, V. Petrykin, M. Yoshimura, M. Kakihana, *J. Mater. Sci.* 43 (2008)  
26 2158.
- 27 [17] R. Buonsanti, V. Grillo, E. Carlino, C. Giannini, T. Kipp, R. Cingolani, P.D. Cozzoli, *J. Am.*

1 Chem. Soc. 130 (2008) 11223.

2 [18] Q. Deng, M. Wei, X. Ding, L. Jiang, B. Ye, K. Wei, Chem. Comm. (2008) 3657.

3 [19] H. Zang, J. Banfield, J. Phys. Chem. B 104 (2000) 3481.

4 [20] S. Cassaignon, M. Koelsch, J. Jolivet, J. Mater. Sci. 42 (2007) 6689.

5 [21] Q. Huang, L. Gao, Chem. Lett. 32 (2003) 638.

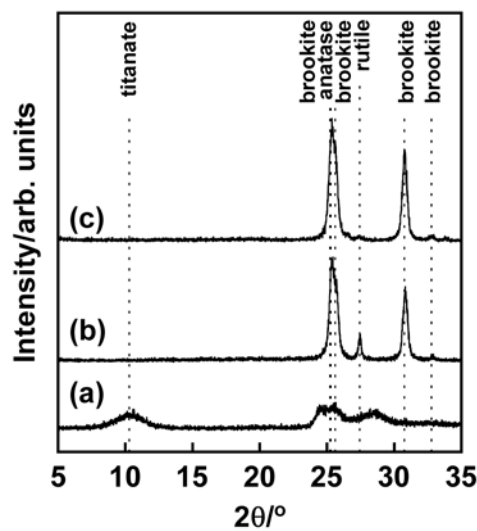
6 [22] H. Kominami, J. Kato, M. Kohno, Y. Kera, B. Ohtani, Chem. Lett. 1996 (1996) 1051.

7 [23] T. Ohno, K. Sarukawa, M. Matsumura, New. J. Chem. 26 (2002) 1167.

8 [24] T. Ohno, K. Tokieda, S. Higashida, M. Matsumura, Appl. Catal. A: General 244 (2003) 383.

9

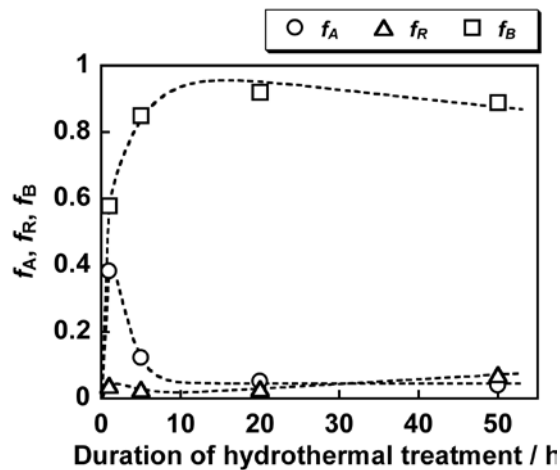
## 10 Figure Captions



11

12 **Figure 1** XRD patterns of (a) TNT and TiO<sub>2</sub> prepared by 50 h of hydrothermal treatment under

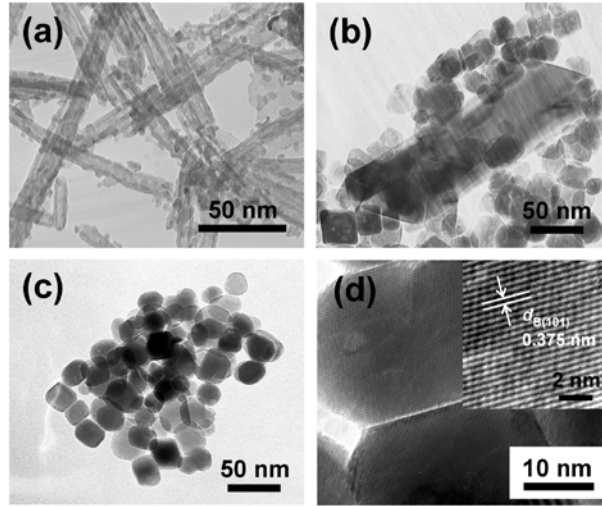
13 HClO<sub>4</sub> solution (b) without and (c) with centrifugal separation.



14

1 **Figure 2** Relative fractions of crystal phases ( $f_A$ : anatase;  $f_B$ : brookite;  $f_R$ : rutile) estimated from  
2 XRD patterns as a function of duration of hydrothermal treatment under  $\text{HClO}_4$  solution.

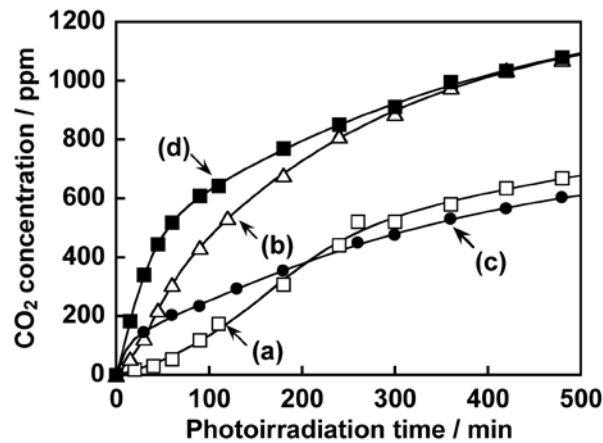
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4

5 **Figure 3** TEM images of (a) TNT and  $\text{TiO}_2$  prepared (b) without and (c) with centrifugal  
6 separation. (d) High-resolution image of image in (c).

7



8

9 **Figure 4** Time course of  $\text{CO}_2$  evolution of acetaldehyde decomposition over  $\text{TiO}_2$  prepared (a)  
10 without and (b) with centrifugal separation, commercial  $\text{TiO}_2$  (c) ST-01 and (d) P-25, as a function  
11 of photoirradiation time.

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