Preparation of a Nanocrystalline TiO_2 Photocatalyst Using a Dry-process with Acetylene Black

Weiping Tang,* Zaihua Chen, and Shunsaku Katoh
Research Institute for Solvothermal Technology, 2217-43, Hayashi-cho Takamatsu, 761-0301

(Received June 15, 2004; CL-040690)

Well-dispersed anatase-type TiO_2 nanocrystals showing good photocatalytic activity were prepared for the first time by a dry-process involving only the heating of a mixture of titanium tetraisopropoxide and acetylene black.

Photocatalysis has attracted increasing attention because of its application to environmental cleanup.[1,2] An anatase-type TiO_2 is well known as the most effective photocatalyst.[3–7] It shows useful self-cleaning, deodorizing, and antibacterial functions, even under weak UV light. For these applications, TiO_2 is prepared as nanosized crystals to bring out its full abilities. The main drawback is making nanosized crystals by the usual industrial synthesis. So far, TiO_2 nanoparticles have been generally prepared by a sol-gel method or hydrothermal process, which requires a lot of solvents, an environmental hazard in themselves, and complicated preparation processes.[8–11] However, here, we report for the first time a simple method, called a dry-process with acetylene black, for the preparation of anatase-type TiO_2 nanocrystals. The method involves only the heating of a mixture of titanium tetraisopropoxide ($Ti(OCH(CH_3)_2)_4$) and acetylene black, and the products indicate good photocatalytic activity.

TiO_2 nanocrystals were obtained by heating a mixture of $Ti(OCH(CH_3)_2)_4$ and acetylene black with a specific surface area of $300\,m^2{\cdot}g^{-1}$. Acetylene black was purchased from Denki Kagaku Kogyo Co. Ltd. The mixture of $Ti(OCH(CH_3)_2)_4$ (4.3 g) and acetylene black (1 g) was prepared in a dry glove box filled with N_2 gas. The mixture was then taken out, and ground in an automatic mixer at room temperature for 4 h. $Ti(OCH(CH_3)_2)_4$ in the mixture was hydrolyzed during grinding by moisture in the air and gradually become a dried powder because of the formation of hydrated compound. Dried mixture samples were heated at 400, 500, or 600 °C for 8 h in an electronic furnace to obtain TiO_2 nanocrystals. The process involves only the heating of a mixture of titanium tetraisopropoxide and acetylene black. It is superior both environmentally and economically because it did not use any solvents. We call this process a dry-process.

X-ray diffraction (XRD) analyses were carried out using a Rigaku RINT1200 X-ray diffractometer with a graphite monochrometer. TEM observation was carried out on a HITACHI S-4700 transmission electron microscope. A nitrogen adsorption–desorption isotherm at 77 K was obtained by a QUANTACHROME AUTOSORB 1-C apparatus with a sample outgassed for 4 h below 10^{-3} mmHg at 200 °C. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The contents of TiO_2 in all samples were obtained by burning off an aliquot part at 900 °C until it reached a constant weight. The photocatalytic property was evaluated by measuring H_2 gas generated from a 50% ethanol solution ($150\,cm^3$) in which 0.3 g of the final product was immersed. A 300-W-incandescent lamp was used as a light source. The amount of H_2 generated was measured by Shimadzu-type gas chromatography. P-25 (Nihon Aerogel Co. Ltd.) mixed with acetylene black (abbreviated as P-25/AB) was used as a reference sample.

The composition and physical properties of the products are given in Table 1. The products obtained at 400, 500, and 600 °C are black, gray, and white colored powders, containing 94.8, 97.7, and 99.8% of TiO_2, respectively. This indicates that a great part of the acetylene black in the starting mixture was burned off during heating. XRD analysis shows that the product obtained at 400 °C contains a single phase of anatase, while minor rutile as well as anatase phases exist in those heated at 500 and 600 °C. The XRD diffraction strength corresponding to (1 1 0) of the rutile phase and (1 0 1) of the anatase phase is in the ratio of 0.02 to 1, and 0.14 to 1 for the products at 500 and 600 °C, respectively. The size calculated from the half-width of the XRD diffraction peak of (1 0 1) by Scherrer equation is 11, 14, and 21 nm for the products at 400, 500, and 600 °C, respectively, showing an increasing trend with heating temperature. The BET surface area is 157, 71, and $48\,m^2{\cdot}g^{-1}$ for the products obtained at 400, 500, and 600 °C, respectively, showing a decreasing trend with heating.

Table 1. Physical properties and composition of the products

Heating Temperature	Color	Composition/%		Size [b] /nm	S_{BET} [c] $/m^2{\cdot}g^{-1}$
		TiO_2	AB [a]		
400 °C	Black	94.8	5.2	11	157
500 °C	Gray	97.7	2.3	14	71
600 °C	White	99.8	0.2	21	48

[a]Acetylene black. [b]Calculated from the half-width of the XRD diffraction peak of (101) by Scherrer equation. [c]Specific surface area.

The TEM image of the product obtained at 500 °C is given in the left of Figure 1. It shows that the product contains uniform, well-dispersed nanocrystals. The average size of the TiO_2 particles estimated from the TEM photograph is 12 nm; close to the 14 nm calculated from the half-width of the XRD diffraction peak of (1 0 1) by Scherrer equation, as shown in Table 1. The dry-process gives TiO_2 nanocrystals.

The TEM image of the product retains the profile of the acetylene black (Figure 1, right). This result shows that TiO_2 nanocrystals form using acetylene black as a template. The large surface area of acetylene black prevents crystal growth and condensation of TiO_2 nanocrystals. Acetylene black also works a heater and reductor due to self-combustion while heating. This brings about a uniform and rapid heating process and probably produces oxygen-deficient TiO_2 crystals which are visible-light active photocatalysts.

The photocatalytic activity of the products was evaluated by decomposition of an ethanol solution with irradiation by an in-

Copyright © 2004 The Chemical Society of Japan

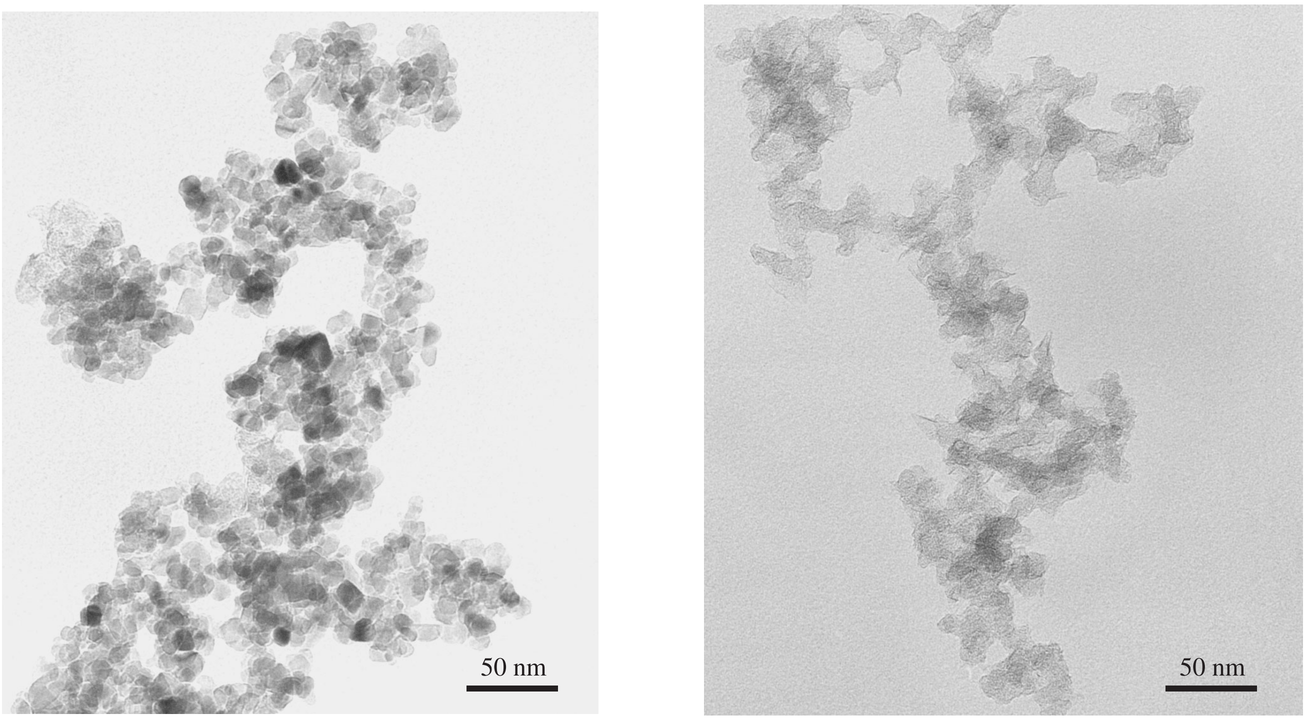

Figure 1. TEM images of the product obtained at 500 °C (left) and acetylene black (right).

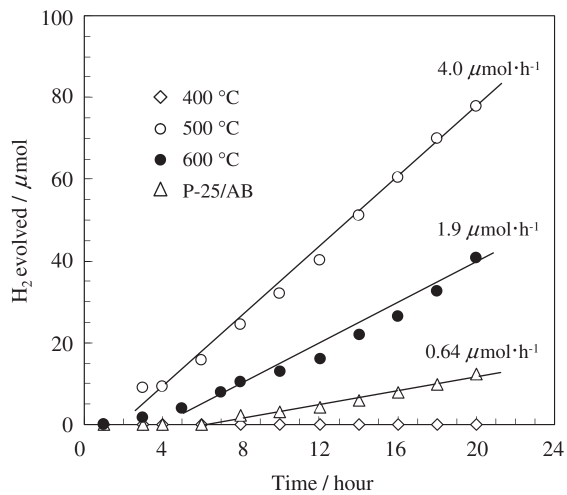

Figure 2. Changes in amount of H_2 generated with irradiation time for the products obtained at 400, 500, and 600 °C, and P-25/AB.

candescent source. The amount of H_2 generated is given in Figure 2. For comparison, the result obtained from P-25/AB having the same contents of TiO_2 (0.293 g) and acetylene black (0.007 g) as the product obtained at 500 °C in this study is also plotted. The products obtained at 500 and 600 °C in this study generated a larger amount of H_2 than P-25/AB. The rate of H_2 generated by the products obtained at 500 and 600 °C is 4.0 and 1.9 $\mu mol{\cdot}h^{-1}$, which is 6.3 and 3.0 times larger than that of P-25/AB (0.64 $\mu mol{\cdot}h^{-1}$), respectively. The results show that the TiO_2 nanocrystals prepared using the dry-process described in this study are an efficient photocatalyst. The photocatalytic ability of the product at 500 °C is higher than that of the product at 600 °C, probably due to the larger surface area of the product at 500 °C. The good photocatalysis of the samples indicates that they are oxygen-deficient TiO_2 nanocrystals. The product at 400 °C did not generate H_2 gas, probably due to its poor crystallization.

In conclusion, anatase type TiO_2 nanocrystals with a unique linear chain-like structure can be prepared using a dry-process with acetylene black as template, and show good photocatalytic activity.

References

1 M. Schiavello, in "Photocatalysis and Environment: Trends and Applications," ed. by M. Schiavello, NATO ASI Series C, Kluwer, Boston (1987), Vol. 234, p 351.
2 A. Mills, R. H. Davies, and D. Worsley, *Chem. Soc. Rev.*, **22**, 417 (1993).
3 H. Uchida, S. Itoh, and H. Yoneyama, *Chem. Lett.*, **1995**, 1993.
4 A. L. Linsebigler, G. Lu, and J. T. Yates, Jr., *Chem. Rev.*, **95**, 735 (1995).
5 M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).
6 D. F. Ollis, E. Pelizetti, and N. Serpone, *Environ. Sci. Technol.*, **25**, 1523 (1991).
7 A. Heller, *Acc. Chem. Res.*, **28**, 503 (1995).
8 B. Tryba, A. W. Morawski, and M. Inagaki, *Appl. Catal., B*, **41**, 427 (2003).
9 C. Guillard, B. Beaugiraud, C. Dutriez, J. M. Herrmann, H. Jaffrezic, N. Jaffrezic-Renault, and M. Lacroix, *Appl. Catal., B*, **39**, 331 (2002).
10 S. Anandan and M. Yoon, *J. Photochem. Photobiol., C*, **4**, 5 (2003).
11 A. Tuel and L. G. Hubert-Pfalzgraf, *J. Catal.*, **217**, 343 (2003).

Published on the web (Advance View) August 21, 2004; DOI 10.1246/cl.2004.1200