Available online at www.sciencedirect.com

Journal of Photochemistry and Photobiology A: Chemistry 170 (2005) 177–179

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Visible-light active N-doped TiO_2 prepared by heating of titanium hydroxide and urea

K. Kobayakawa*, Y. Murakami, Y. Sato

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

Received 9 January 2004; received in revised form 31 May 2004; accepted 7 July 2004

Abstract

Nitrogen-doped titanium dioxide (TiO_2) powders were prepared by the heating of titanium hydroxide with urea. The samples had a relatively larger specific surface area of $92 \pm 2\,m^2\,g^{-1}$ and showed visible-light photocatalytic activity of about 550 nm.

Keywords: Visible-light response; Titanium dioxide; Nitrogen doping; Titanium hydroxide; Urea

1. Introduction

Titanium dioxide photocatalysis is now being used in practical applications such as self-cleaning, sterilization, deodorizing and air-cleaning. It is chemically and photochemically stable, but is only excited by ultraviolet light ($\lambda < 390$ nm) so that the light utilization efficiency to solar irradiation and a fluorescent lamp is very low. Therefore, attempts were made to extend the absorption range of titanium dioxide into the visible-light region by the introduction of a donor level by transition metal doping [1,2]. Recently, the creation of a sub-band level was proposed using the N 2p orbital instead of the O 2p orbital by nitrogen doping [3]. It was experimentally confirmed that the states introduced by nitrogen lie close to the valence band edge [4]. The nitrogen doping can be attained by various methods such as the sputtering of TiO_2 in an N_2–Ar atmosphere [3], the heating of TiO_2 powder in an ammonia atmosphere over several hundred degree Celsius [3,5], the hydrolysis of organic and inorganic titanium compounds such as titanium tetraisopropoxide [6], titanium (IV) sulfate [7] and titanium (III) chloride [8] with ammonia water followed heating of the resultant precipitates, and the heating of TiO_2 powder with urea [9]. Among these methods, we are most interested in the last method because the process will provide N-doped TiO_2 fine powders without decreasing their high specific surface area due to the low temperature heating at about 350 °C [9]. The nitrogen doping was postulated to occur by ammonia being liberated during the thermal decomposition of urea and decomposition products [10]. TiO_2 powder is generally prepared by the precipitation of titanium hydroxide ($Ti(OH)_4$) from the hydrolysis of the titanium compound and the following thermal decomposition of $Ti(OH)_4$ to TiO_2. We tried simultaneous N-doping with phase transformation to TiO_2 by heating $Ti(OH)_4$ with urea to save thermal energy. In this study, we prepared N-doped TiO_2 powders by heating $Ti(OH)_4$, prepared by the hydrolysis of titanium tetraisopropoxide, with urea, and evaluated their photocatalytic activity compared to that of samples prepared by the heating of TiO_2 with urea.

2. Experimental

The $Ti(OH)_4$ powder was obtained by the hydrolysis of titanium tetraisopropoxide (TTIP, Wako Pure Chemicals) with water, washing with water, and drying at 120 °C for 60 min.

Simultaneous N-doping with phase transformation by the heating of $Ti(OH)_4$ with urea was carried out as follows.

---

* Corresponding author. Tel.: +81 45 481 5661; fax: +81 45 491 7915.

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2004.07.010

Preliminary experiments using the heating time of 60 min showed that the heating temperature of 350–450 °C was appropriate for the photocatalytic activity and entire thermal decomposition of urea up to 3 g. In this study, we fixed the heating temperature at 400 °C and the heating time for 60 min, and only changed the weight ratio of urea to $Ti(OH)_4$.

One gram of $Ti(OH)_4$ powder was mixed with various amounts of urea granules (Wako Pure Chemicals), heated in a covered crucible in an electric furnace, and then naturally cooled in the furnace. The temperature rate to 400 °C was 15 °C/min. For comparison, N-doped TiO_2 powders were prepared by heating TiO_2 with urea at 400 °C for 60 min.

The XRD and XPS (JEOL, JSP-9010) measurements were carried out to characterize the prepared samples. The specific surface area of the samples was obtained using the BET surface area measuring apparatus at the boiling point of liquid nitrogen. The UV-vis absorption spectra of the samples were measured using a UV-visible spectrophotometer referenced to $BaSO_4$.

A 10 W fluorescent lamp (FL-10) was used as the light source and an optical filter was used to pass visible light ($\lambda > 410$ nm). To evaluate the photocatalytic activity of the samples, we used the photocatalytic oxidation of aqueous KI solution. In this photocatalytic reaction, the photo-generated electron was consumed for the reduction of dissolved oxygen. The prepared samples (25 mg) were dispersed into 25 cm^3 of a 0.1 mol dm^{-3} KI aqueous solution and the amounts of produced I_3^- during 30 min of irradiation were optically determined.

3. Results and discussion

The crystal phase of the prepared powders was anatase. The color of the prepared samples changed from yellowish-white to yellow with the increasing mixing ratio of urea to $Ti(OH)_4$. The UV-vis absorption spectra of the pure TiO_2 (commercially available P25 TiO_2 and TiO_2 sample prepared without urea) and yellow-colored samples prepared using 1 g of $Ti(OH)_4$ are shown in Fig. 1. The absorption edge of the colored samples shifts toward a longer wavelength.

To confirm the N-doping, we measured the N 1s XPS spectra (Fig. 2). The spectra were measured after 60 s of argon sputtering to remove the thermal decomposition products of urea. The XPS peak of N 1s around 397 eV, assigned as atomic nitrogen bonded to titanium from a literature [11] and XPS measurement of TiN powder, was clearly observed for a light brown powder prepared using a large amount of urea such as 10 g (urea/$Ti(OH)_4$ ratio at 2.5) as shown in the figure. This was not observed for the yellowish-white and yellow powders obtained using a small amount of urea. Because the amount of doped nitrogen was low, the XPS peak of N 1s at 397 eV will not be observed for the yellowish-white and yellow powders. We tried to determine the doped-nitrogen amount for samples prepared with the urea/$Ti(OH)_4$ ratio from 1.5 to 2.5, which the peak of N 1s could be observed, by the comparison of the peak areas of N 1s and O 1s [12]. However, it was difficult to obtain the nitrogen-doped amount with certainty because a little difference in the determined range for binding energy and in the correction of background signal resulted in large difference in the peak areas.

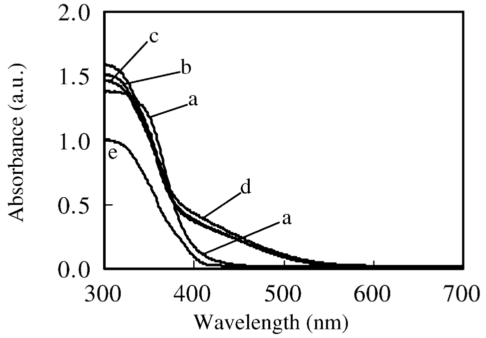

Fig. 1. Light absorption spectra of TiO_2 powder prepared without urea (curve a) and with the weight ratios of urea/$Ti(OH)_4$ of 0.5 (curve b), 1.5 (curve c) and 2.5 (curve d). The absorption of P25 sample (curve e) is also shown as a reference.

According to the latest paper [13], carbon doping also causes visible-light response. However, C 1s peak assigned as Ti–C bond was not observed for our samples. Therefore, we considered that visible-light responses described below were originated from doped-nitrogen.

The specific surface areas of the prepared N-doped samples using 1 g of $Ti(OH)_4$ were $92 \pm 2\ m^2\ g^{-1}$ and higher by about 15% compared to the TiO_2 powder ($80\ m^2\ g^{-1}$) prepared by heating of $Ti(OH)_4$ at 400 °C for 1 h and was almost equal in spite of changing the urea weight ratio of $Ti(OH)_4$ from 0.5 to 2.5. The specific surface areas of the N-doped TiO_2 powder prepared by the heating of TiO_2 with urea were $80 \pm 2\ m^2\ g^{-1}$ and almost equal in spite of changing the urea/TiO_2 weight ratios.

It is desired to develop a visible-light response without a decrease in the original ultraviolet light response of TiO_2 by N-doping. Both the UV- and visible-light responses were measured. Fig. 3 shows the oxidation profiles of the KI solution with TiO_2 powders prepared by heating the $Ti(OH)_4$ with various amounts of urea. This figure contains two photo-responses: one for the visible light ($\lambda > 410$ nm) and the other

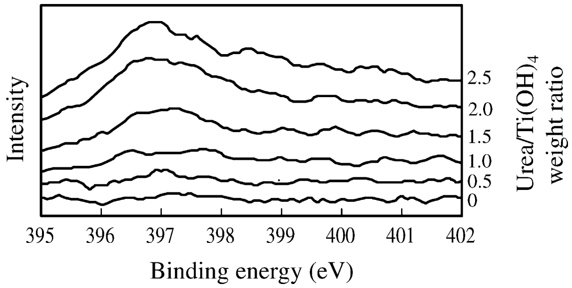

Fig. 2. N 1s XPS spectra of N-doped TiO_2 powders prepared with various urea/$Ti(OH)_4$ ratios using 2 g of $Ti(OH)_4$ and sputtered with argon (2 × 30 s) for removal of the decomposition products of urea.

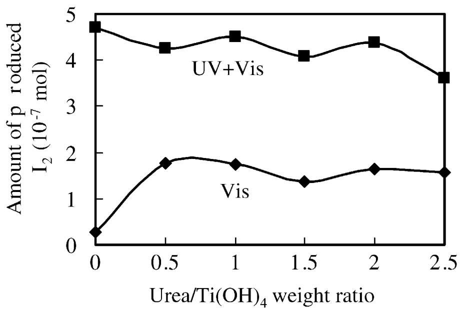

Fig. 3. Dependence of photocatalytic activity of TiO_2 powders for the oxidation of a 0.1 mol dm^{-3} KI aqueous solution on the weight ratio of urea/Ti(OH)$_4$ during heating for preparing the TiO_2 samples using 1 g of Ti(OH)$_4$.

for the visible- and UV-light contained in the FL lamp irradiation. The difference in the two responses corresponds to the UV response. The TiO_2 sample prepared without urea and P25 were inactive under visible-light but active under UV-light and their photocatalytic activities for I^- oxidation were identical. All the samples prepared with urea show a visible-light response while their UV-light responses decreased. It is suggested that the doped nitrogen responds to visible light and acts as a recombination center for the photo-generated carriers. The visible- and also UV-light responses of the prepared TiO_2 samples were almost the same in spite of changing the weight ratio of urea to Ti(OH)$_4$ from 0.5 to 2.

Fig. 4 shows the oxidation profile of KI solution for the N-doped TiO_2 powders prepared by the heat treatment of the TiO_2 powder (1 g) with urea. The samples obtained with urea/TiO_2 at 0.5 and 1.0 showed only a UV response. The samples obtained with urea/TiO_2 above 1.5 showed a visible response. From the comparison of the photocatalytic activities shown in Figs. 3 and 4, it can be concluded that the N-doped TiO_2 powders having almost the same activity were obtained by the heating of Ti(OH)$_4$ and TiO_2 with urea.

Fig. 5 shows the I^- oxidation by N-doped TiO_2 prepared by heating Ti(OH)$_4$ with urea as a function of the cutoff wavelength of the optical cutoff filters. The visible-light response to 550 nm was observed.

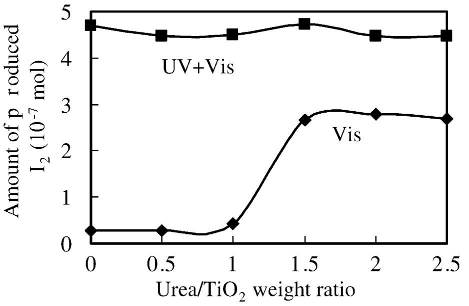

Fig. 4. Dependence of photocatalytic activity of TiO_2 powders for the oxidation of a 0.1 mol dm^{-3} KI aqueous solution on the weight ratio of urea/TiO_2 during heating for preparing the TiO_2 samples using 1 g of TiO_2.

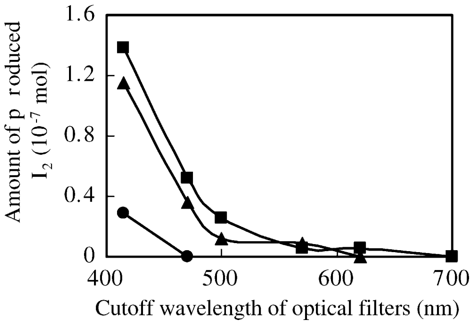

Fig. 5. Visible-light response, measured by the oxidation of KI aqueous solution using optical cutoff filters, of samples prepared by heating Ti(OH)$_4$ with urea. The weight ratios of urea/Ti(OH)$_4$ are 0 (●), 1.5 (▲) and 2.5 (■).

4. Conclusion

We prepared N-doped TiO_2 powders that respond to visible light by the heating of Ti(OH)$_4$ with urea showing similar photocatalytic activity to that prepared by heating of TiO_2 with urea.

Acknowledgements

This work was partially supported by a Grant-in-Aid of Scientific Research on Priority Area (417) from Ministry of Education, Culture, Sports, Science and Technology of Japan. The authors would like to thank Prof. Kazuhito Hashimoto (The University of Tokyo) for the measurement of the absorption spectra.

References

[1] A.K. Ghosh, H.P. Maruska, J. Electrochem. Soc. 124 (1977) 116.
[2] W. Choi, A. Termin, M.R. Hoffman, J. Phys. Chem. 98 (1994) 13669.
[3] R. Asahi, T. Ohkawa, K. Aoki, Y. Taga, Science 293 (2001) 269.
[4] T. Lindgren, J.M. Mwabora, E. Avendaňo, J. Jonsson, A. Hoel, C.G. Granqvist, S.E. Lindquist, J. Phys. Chem. B 107 (2003) 5709.
[5] H. Irie, Y. Watanabe, K. Hashimoto, J. Phys. Chem. B 107 (2003) 5483.
[6] S. Sato, Chem. Phys. Lett. 123 (1986) 126.
[7] Y. Sakatani, K. Okusako, H. Koike, H. Ando, Proceedings of the Symposium on Recent Development of Photocatalysis, Photo-functional Materials Society of Japan, 2001, p. 10 (abstract).
[8] H. Irie, T. Kako, A. Nakajima, T. Watanabe, K. Hashimoto, Proceedings of the 8th Symposium on Recent Development of Photocatalysis, Photo-functional Materials Society of Japan, 2001, p. 26 (abstracts).
[9] K. Aoki, T. Morikawa, R. Asahi, T. Ohwaki, K. Suzuki, Y. Taga, Proceedings of the 88th Meeting of Catalysis Society of Japan Meeting, 2001, p. 4B15 (abstracts).
[10] P.M. Schaber, J. Colson, S. Higgins, E. Dietz, D. Thielen, B. Anspach, J. Brauer, Am. Lab. (1999) 13.
[11] W. Xu, D. Raftery, J. Phys. Chem. B 105 (2001) 4343.
[12] H. Irie, S. Washizuka, N. Yoshino, K. Hashimoto, Chem. Commun. (2003) 1298.
[13] H. Irie, Y. Watanabe, K. Hashimoto, Chem. Lett. 32 (2003) 772.