Photocatalytic decomposition of NO under visible light irradiation on the Cr-ion-implanted TiO_2 thin film photocatalyst

Masato Takeuchi [a], Hiromi Yamashita [a], Masaya Matsuoka [a], Masakazu Anpo [a,*], Takashi Hirao [b], Nobuhisa Itoh [c]
and Nobuya Iwamoto [d]

[a] *Department of Applied Chemistry, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan*
[b] *Department of Electronic Engineering, Osaka University, Yamadaoka 1-1, Suita, Osaka 565-0871, Japan*
[c] *Human Environment Systems Development Center, Matsushita Electric Industrial Co., Ltd., Seika-cho, Souraku, Kyoto 619-0237, Japan*
[d] *Ion Engineering Research Institute Corporation, Tsuda, Hirakata, Osaka 573-0128, Japan*

Received 3 April 2000; accepted 26 April 2000

Transparent TiO_2 thin film photocatalysts were prepared on transparent porous Vycor glass (PVG) by the ionized cluster beam (ICB) method. In order to improve the photocatalytic performance of these thin films under visible light irradiation, transition metal ions such as Cr and V were implanted into the deep bulk inside of the films using an advanced metal-ion-implantation technique. The UV-vis absorption spectra of these metal-ion-implanted TiO_2 thin films were found to shift smoothly toward visible light regions, its extent depending on the amount and kinds of metal ions implanted. Using these metal-ion-implanted TiO_2 thin films as photocatalysts, the photocatalytic decomposition of NO_x into N_2 and O_2 was successfully carried out under visible light ($\lambda > 450$ nm) irradiation at 275 K.

Keywords: TiO_2 thin film photocatalyst, ionized cluster beam deposition method, ion implantation, visible light, decomposition reaction of NO

1. Introduction

In recent years, titanium dioxide photocatalysts have attracted much attention as an environmentally harmonious and clean catalyst [1–4]. Especially, transparent TiO_2 thin film photocatalysts prepared on glass, tile and various architectural materials have been actively investigated as promising antibacterial, self-cleaning and deodorization systems [5,6]. However, the TiO_2 photocatalyst in itself does not allow the absorption of visible light and only makes use of the 3–5% of the solar beams that reach the earth, necessitating the use of an ultraviolet light source such as a high-pressure Hg lamp or a black lamp. In order to make more efficient use of solar beams as a light and energy source, it is necessary to develop a new and unique type of TiO_2 photocatalysts which are able to work under visible and/or solar light irradiation. Recently, we have reported that by applying an advanced metal-ion-implantation method, unique TiO_2-powdered semiconductors which are able to absorb visible light and operate under visible light irradiation were successfully developed [7–9]. In the present paper, we deal with the preparation of TiO_2 thin film photocatalysts by the ionized cluster beam (ICB) method, a dry preparation process, and the modification of their electronic properties by an advanced metal-ion-implantation method in order to achieve the absorption of visible light for the decomposition of NO at 275 K.

2. Experimental

TiO_2 thin films were prepared by an ionized cluster beam (ICB) method [10,11]. The metal titanium in the crucible as the ion source was heated up to about 2000 K and then titanium vapor was introduced into a high-vacuum chamber producing TiO_2 clusters on a support in the O_2 atmosphere. The ionized TiO_2 clusters were accelerated by the high electric field (acceleration voltage 500 V) and bombarded onto the support substrate (PVG). In the presence of a low pressure of O_2 at around 10^{-4} Torr, TiO_2 thin films were prepared on the support without any calcination at high temperature. The film thickness was monitored by a quartz thicknessmeter and controlled to retain a 300 nm thickness, which was calibrated by consideration of the absorption coefficient of the TiO_2 thin films. The Cr ions accelerated by an acceleration energy of as high as 150 keV were implanted into the TiO_2 thin films using a metal ion implanter (the amounts of implanted Cr ions 3×10^{16} and 6×10^{16} ions/cm^2) [7–9]. After the metal ion implantation, the Cr-ion-implanted TiO_2 thin film photocatalysts were calcined in O_2 at 725 K. The catalyst (size 10 mm × 10 mm × 1 mm) was then put on the flat bottom of a quartz reaction cell (30 ml) and then connected to a conventional vacuum system (10^{-6} Torr range). Prior to photoreactions and spectroscopic measurements, the catalysts were degassed at 725 K for 2 h, heated in O_2 at the same temperature for 2 h, and finally outgassed at 475 K to 10^{-6} Torr. Visible light irradiation of the TiO_2 thin film photocatalysts in the presence of NO (12.3 mol) was carried

---

[*] To whom correspondence should be addressed.

out using a 100 W high-pressure Hg lamp (Toshiba SHL-100UVQ-2) through a color and water filter ($\lambda > 450$ nm) at 275 K. The reaction products were analyzed by gas chromatography. The UV-vis absorption spectra (measured by the transmittance method) of the catalysts were measured at 295 K using a Shimadzu UV-2200A spectrophotometer. The depth profiles of the Cr ion contents for the Cr ion-implanted TiO_2 thin films were measured using a Shimadzu/Kratos ESCA3200 at 295 K.

3. Results and discussion

As shown in figure 1, the UV-vis absorption spectra exhibit specific interference fringes, indicating that uniform and transparent TiO_2 thin films are formed by the ICB method. The absorption spectra of the Cr-ion-implanted TiO_2 thin films are found to shift toward visible light regions as the amount of Cr ions implanted was increased, indicating that the TiO_2 thin films have been modified to absorb visible light by Cr ion implantation. On the other hand, Cr ions chemically doped TiO_2 thin films by an impregnation method did not exhibit such a shift in the absorption spectra but instead exhibited a new peak due to the formation of the impurity energy levels within the bandgap of the TiO_2 catalyst [7–9]. Thus, the absorption spectra of the TiO_2 thin films physically implanted with Cr ions are completely different from those of catalysts chemically doped with Cr ions or impregnated with Cr ions. These results indicate that the method of doping causes the electronic properties of the TiO_2 catalysts to be modified in completely different ways.

Visible light ($\lambda > 450$ nm) irradiation of the Cr-ion-implanted TiO_2 thin film photocatalyst in the presence of NO was found to lead to the evolution of N_2 and O_2 as well as N_2O into the gas phase at 275 K, while this NO decomposition reaction did not take place, neither on the unimplanted original TiO_2 thin film photocatalyst nor on the TiO_2 thin films chemically doped with Cr ions. Figure 2 shows the reaction time profiles of the photoinduced decomposition of NO into N_2 and O_2 on the Cr-ion-implanted TiO_2 thin films under visible light irradiation ($\lambda > 450$ nm). The reaction proceeds with a good linearity against the irradiation time, suggesting that the reaction proceeds photocatalytically. These results clearly indicate that Cr ions implanted into the TiO_2 thin films do not work as electron–hole recombination centers but only work to modify the electronic properties of the catalyst, enabling the absorption of visible light and operation under visible light irradiation.

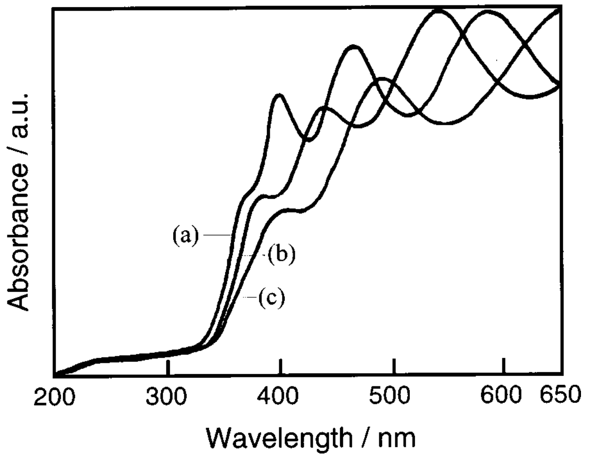

Figure 1. The UV-vis absorption spectra of TiO_2 thin film prepared on PVG (a) and Cr-ion-implanted TiO_2 thin film (b,c) photocatalysts. The amount of implanted Cr ions: (a) 0, (b) 3×10^{16} and (c) 6×10^{16} Cr ions/cm^2.

Figure 3 shows the depth profiles of the Cr ions implanted into the TiO_2 thin film obtained from the analysis of the relative intensities of the Cr $2p_{1/2}$ (576.5 eV) and Ti 2s (564.5 eV) measured by the XPS of the thin film as a function of the depth from the surface of the sample. It is

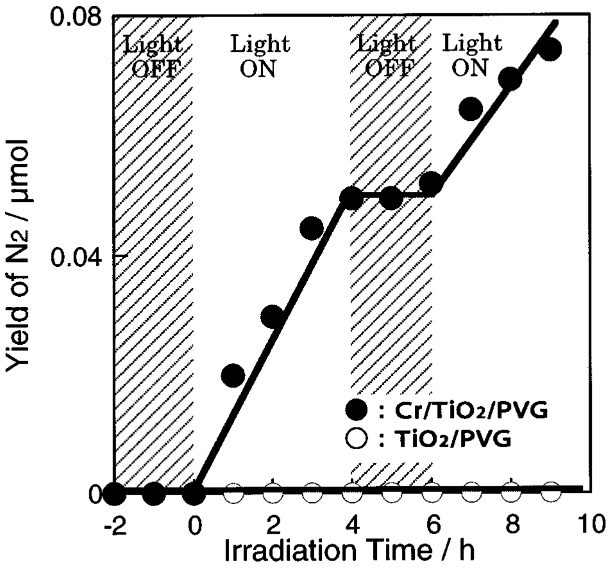

Figure 2. The time profile of the evolution of N_2 for the photocatalytic decomposition of NO on the Cr-ion-implanted TiO_2 thin film photocatalyst under visible light ($\lambda > 450$ nm) irradiation.

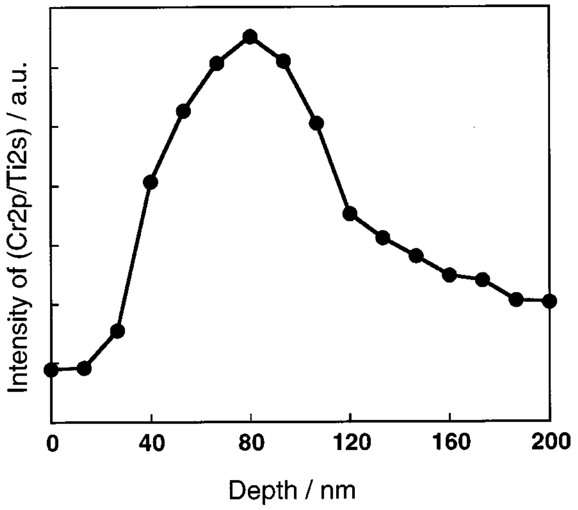

Figure 3. The depth profiles of the Cr ion content for the Cr-ion-implanted TiO_2 thin film photocatalyst, where Cr ions were implanted at the energy of 150 keV.

clear from figure 3 that the Cr ions implanted into the TiO_2 thin film are located in the deep inside of the film and a distribution maximum of the Cr ions is observed at around 70–80 nm from the surface. And, Cr ions are not present on the surface nor the near surface. Thus, the XPS measurements of the Cr-ion-implanted TiO_2 thin film clearly show that the Cr ions are not present at the surface but distribute within the deep bulk inside of the TiO_2 thin film photocatalyst. It was found that the TiO_2 thin films which were implanted with Cr ions by acceleration energies such as 70 and 250 keV did not show such remarkable shift in the absorption spectra toward visible light regions. These results clearly suggest that the appropriate depth profile of the metal ions implanted causes an electronic modification of the TiO_2 thin film photocatalysts due to the interaction between the implanted Cr ions and TiO_2.

In conclusion, we have successfully prepared TiO_2 thin film photocatalysts which can absorb visible light and work efficiently as photocatalysts for the decomposition of NO into N_2 and O_2 at 275 K even under visible light irradiation by means of a combination of the ICB method and an advanced metal-ion-implantation technique. The development of such environmentally harmonious photocatalysts as these Cr-ion-implanted TiO_2 thin film photocatalysts which can operate under visible light to eliminate toxic compounds such as NO in the atmosphere, can be considered a breakthrough in the utilization of solar energy to address urgent environmental concerns.

References

[1] M. Anpo, Catal. Surv. Jpn. 1 (1997) 169.
[2] M. Anpo, Y. Ichihashi, M. Takeuchi and H. Yamashita, Res. Chem. Intermed. 24 (1998) 151.
[3] M. Anpo, in: *Green Chemistry*, eds. P. Tundo and P. Anastas (Oxford University Press, 2000) p. 1.
[4] M. Anpo, M. Takeuchi, S. Kishiguchi and H. Yamashita, in: *Proc. Trombay Symp. Radiation and Photochemistry* (2000) p. 460.
[5] A. Heller, Acc. Chem. Res. 28 (1995) 503.
[6] N. Negishi, T. Iyoda, K. Hashimoto and A. Fujishima, Chem. Lett. 841 (1995).
[7] M. Anpo, Y. Ichihashi, M. Takeuchi and H. Yamashita, *Science and Technology in Catalysis 1998*, Vol. 305 (Kodansha/Elsevier, Tokyo/Amsterdam, 1999) p. 121.
[8] M. Anpo, M. Takeuchi, S. Kishiguchi and H. Yamashita, Surf. Sci. Jpn. 20 (1999) 60.
[9] M. Anpo, M. Takeuchi, H. Yamashita, T. Hirao, N. Itoh and N. Iwamoto, in: *Proc. 4th Int. Conf. Ecomaterial*, Vol. 333 (1999).
[10] K. Fukushima, I. Yamada and T. Takagi, J. Appl. Phys. 58 (1985) 4146.
[11] M. Takeuchi, H. Yamashita, M. Matsuoka, M. Anpo, T. Hirao, N. Itoh and N. Iwamoto, Catal. Lett. 66 (2000) 185.