CHEMISTRY LETTERS, pp. 653-656, 1994.

Photocatalytic Activities for Carbon Dioxide Reduction of TiO_2 Microcrystals Prepared in SiO_2 Matrices Using a Sol-Gel Method

Hiroshi INOUE, Takehiko MATSUYAMA, Bi-Jin LIU, Takao SAKATA,†
Hirotaro MORI,† and Hiroshi YONEYAMA*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka 2-1, Suita, Osaka 565
† Research Center for Ultra-high Voltage Electron Microscopy, Osaka University, Yamada-oka 2-1, Suita, Osaka 565

The size of TiO_2 microcrystals embedded in SiO_2 matrices, which were prepared using a mixed sol of TiO_2 and SiO_2 in ethanol, decreased with a decrease of the mole ratio of TiO_2 to SiO_2 in the sol. The prepared TiO_2 microcrystals showed activities for photoreduction of CO_2 to formate, methane and ethylene, and the quantum efficiencies for the production of these were increased with decreasing the size of the TiO_2 microcrystals.

Titanium Dioxide is an effective photocatalyst for reducing carbon dioxide to multielectron reduction products such as formaldehyde, methanol and methane.$^{1-7)}$ However, the quantum efficiencies for their productions reported so far are very low. To enhance the quantum efficiencies, some breakthrough seems required. Recent studies on photocatalytic activities of TiO_2 microcrystals$^{8-10)}$ and Fe_2O_3 microcrystals$^{11,12)}$ for several kinds of reactions suggested that the use of semiconductor microcrystals may be useful as a means for enhancing the photocatalytic activities. Approaches toward this direction have been reported by Anpo et al., who prepared TiO_2 microcrystals on vycor glass surfaces by using hydrolysis reactions of hydroxyl groups of this support with $TiCl_4$ and discovered that the prepared TiO_2 microcrystals showed high activities for photoreduction of CO_2 in the presence of water vapor.$^{13)}$ They obtained methane, methanol and CO as the reduction products of CO_2, depending on the reaction conditions, though the quantum efficiency for their production was not determined. We have studied the preparation and properties of TiO_2 microcrystals embedded in SiO_2 matrices, and found from the viewpoint of the quantum efficiency that the prepared TiO_2 microcrystals showed high activities for photoreduction of CO_2. It has been found that the technique which we have employed allows the preparation of TiO_2 microcrystals of the different sizes by adjusting the composition of TiO_2 and SiO_2 in sols, and in this regard, versatile applicabilities as photocatalysts can be anticipated.

TiO_2 microcrystals prepared in SiO_2 matrices, which are denoted as Q-TiO_2/SiO_2 in this paper, were prepared in the following way; Aqueous ethanol solution (8%(v/v) of water) containing 1 M(=mol dm^{-3}) HCl was added to ethanol solution containing $Si(OEt)_4$ and $Ti(OEt)_4$ of various mole ratios at an equal volume, resulting in sols consisting of TiO_2 and SiO_2. The total concentration of $Ti(OEt)_4$ and $Si(OEt)_4$

was 0.55 M after the mixing. After stirring for 3 h, 1.6 cm^3 of the sol was casted on quartz glass plates (7.6 cm×2.6 cm). By being dried in a desiccator, transparent gel films of Q-TiO_2/SiO_2 were produced. This transparent films were stripped off from the quartz plate and dried in vacuo at 120 °C for 2 h to give transparent flake films. The photoreduction experiments of carbon dioxide were carried out using a quartz cell of 0.8 cm diameter and 5 cm height. Q-TiO_2/SiO_2 flakes prepared with different Ti/Si mole ratios were added to 4 cm^3 of 1 M 2-propanol aqueous solution in such a way as to give 50 mmol of TiO_2. After bubbling CO_2 for 30 min, the pH of the solution was 3.2. Lights from a 500 W high pressure mercury arc lamp were passed through a UV-29 filter to cut off wavelengths shorter than 270 nm and illuminated from the bottom of the cell. During the illumination, the solution was not stirred to prevent destruction of the flakes, which might cause light scattering. The obtained products were determined by gas chromatography and liquid chromatography. The quantum efficiency was determined at 280 nm using ferrioxalate actinometry, as previously reported.[14]

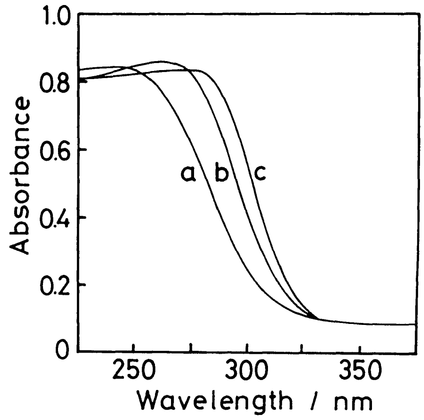

Fig. 1. Absorption spectra of Q-TiO_2/SiO_2 flakes with the Ti/Si ratio of (a)0.027, (b)0.048 and (c)0.10.

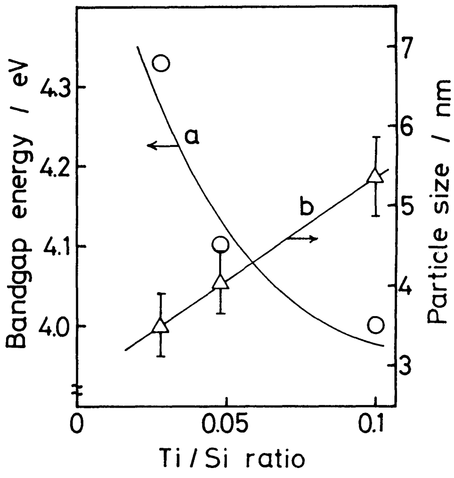

Fig. 2. Bandgap energy (a) and particle size (b) as a function of the Ti/Si ratio.

Figure 1 shows absorption spectra of the Q-TiO_2/SiO_2 flakes prepared with different mole ratios of $Ti(OEt)_4$ and $Si(OEt)_4$. Since SiO_2 is transparent in a wavelength range of Fig. 1, these spectra are attributable to those of the TiO_2 microcrystals. As seen in Fig. 1, absorption spectra were blue-shifted with decrease of the Ti/Si ratio. If the bandgap of TiO_2 is obtained by applying $(\varepsilon h\nu)^2$ vs. $(h\nu - E_g)$ to the spectra in their onset region,[12] results shown by curve a of Fig. 2 were obtained, where ε, $h\nu$, and E_g are the absorption coefficient, photon energy and bandgap energy, respectively. It is evident that the bandgap of TiO_2 microcrystals in the Q-TiO_2/SiO_2 flakes can be varied by controlling the Ti/Si ratio.

Figure 3 shows a transmission electron micrograph (TEM) and a scanning electron micrograph (SEM) of the Q-TiO_2/SiO_2 flakes prepared with the Ti/Si ratio of 0.048. Black spots in the TEM picture shows TiO_2 microcrystals, which were identified to be rutile from electron diffraction analysis. As shown in Fig. 3(a), TiO_2 microcrystals are present dispersedly in the SiO_2 matrices, and as Fig. 3(b) shows, there are a lot of pores in the Q-TiO_2/SiO_2 flakes. The mean particle size and the standard deviation of TiO_2 microcrystals in the flakes, which were obtained by counting the particles for several micrographs, are shown by curve b of Fig. 2 as a function of the Ti/Si ratio. The mean particle size decreases with decrease of the Ti/Si ratio, the results being in conformity with the results of the bandgap

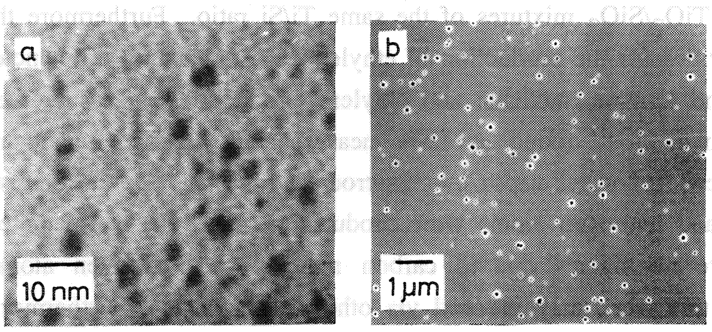

Fig. 3. (a) TEM and (b) SEM images of Q-TiO_2/SiO_2 flakes (Ti/Si ratio= 0.048).

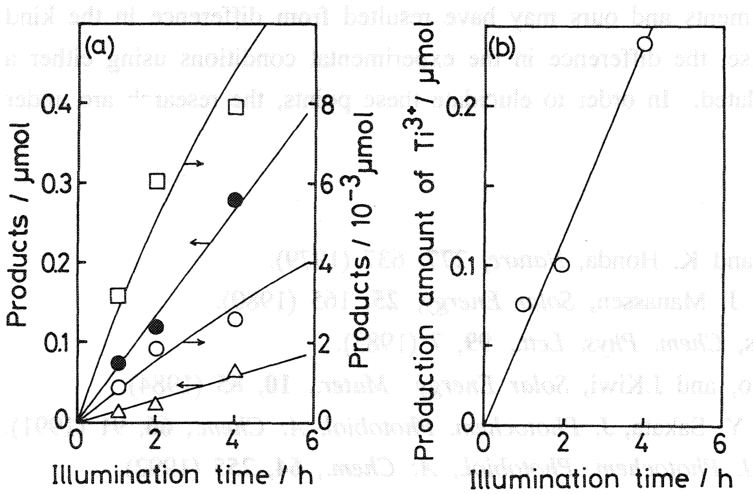

Fig. 4. (a) Time course of the production of (△)formate, (○)methane, (□) ethylene and (●)acetone and (b) time course of Ti^{3+} production. Ti/Si ratio is 0.10.

Table 1. Quantum efficiency at 280 nm for reduction products obtained in the photoreduction of CO_2 in the presence of 1 M 2-propanol on the Q-TiO_2/SiO_2 and bulk TiO_2/SiO_2 photocatalysts having various Ti/Si ratios

Sample	Ti/Si ratio	Quantum efficiency / %		
		$HCOO^-$	CH_4	C_2H_4
Q-TiO_2/SiO_2	0.10	9.0	0.50	0.15
	0.048	12.7	1.5	1.8
	0.027	14.2	3.4	2.3
bulk TiO_2/SiO_2[a)]	0.10	5.0	0.019	0
	0.048	4.2	0.061	0
	0.027	2.4	0.030	0

a) Mixture of TiO_2 powders (Japan Aerosil, P-25) and SiO_2 powders (Japan Aerosil, 200CF).

variation given by curve a of this figure. The SiO_2 matrices provide a good support for preventing aggregation of Q-TiO_2 particles.

The prepared Q-TiO_2/SiO_2 flakes worked effectively as photocatalysts for the photoreduction of CO_2 in 2-propanol. Figure 4(a) shows the time course of the production of reduction and oxidation products. Formate was produced as a major product of the CO_2 reduction with methane and ethylene as minor products. If either CO_2 or the Q-TiO_2/SiO_2 photocatalyst was absent, none of these products were obtained. It is recognized from the observed photocatalytic activities of the TiO_2/SiO_2 flakes that the TiO_2 microcrystals were not completely covered with SiO_2.

Furthermore, the color of the flakes gradually changed into purple during the course of the photoreduction experiments of CO_2. An ESR measurement of the purple-colored Q-TiO_2/SiO_2 flakes at 77 K gave a spectrum of g= 1.96,[15)] evidencing the photo-formation of Ti^{3+} species. Figure 4(b) shows the time course of the Ti^{3+} production determined from the ESR measurements using 1,1'-diphenyl-2-picrylhydrazyl as a standard reference compound.

The chemical stoichiometry of the reduction and oxidation products was satisfied. Table 1 shows the quantum efficiency for the reduction products of CO_2 at 280 nm obtained for three different Ti/Si ratios. As seen in this table, the Q-TiO_2/SiO_2 flakes showed higher quantum efficiencies for the formate and methane production than bulk TiO_2/SiO_2 mixtures of the same Ti/Si ratio. Furthermore the bulk TiO_2/SiO_2 mixture did not show activities for the production of ethylene. The quantum efficiencies obtained at the Q–TiO_2/SiO_2 flakes for the formate, methane and ethylene productions were increased with a decrease of the Ti/Si ratio. Anpo et al.[13)] found by ESR measurements that when methane production occurred from CO_2 in the presence of water vapor over microcrystalline TiO_2 photocatalysts anchored on vycor glass, carbon radicals and hydrogen atoms were produced as reaction intermediates. In our ESR spectra, however, there were no signals due to carbon radicals and hydrogen atoms, suggesting that hydrocarbons produced in this work may proceed via other mechanisms. Furthermore, Anpo et al.[13)] obtained methane, methanol and CO as the photoreduction products of CO_2, while methanol and CO were not obtained but formate was obtained in the present study. The difference in the kind of products between their experiments and ours may have resulted from difference in the kind of hole scavengers used. As another cause, the difference in the experimental conditions using either a gas phase or a liquid phase may be postulated. In order to elucidate these points, the research are under way.

References

1) T. Inoue, A. Fujishima, S. Konishi, and K. Honda, *Nature,* **277**, 637 (1979).
2) B. Aurian–Blajeni, M. Halmann, and J. Manassen, *Solar Energy,* **25**, 165 (1980).
3) K. Chandrasekaran and J. K. Thomas, *Chem. Phys. Lett.,* **99**, 7 (1983).
4) M. Halmann, V. Katzir, E. Borgarello, and J.Kiwi, *Solar Energy Mater.,* **10**, 85 (1984).
5) K. Ogura, M. Kawano, J. Yano, and Y. Sakata, *J. Photochem. Photobiol. A: Chem.*, **66**, 91 (1991).
6) K. Hirano, K. Inoue, and T. Yatsu, *J. Photochem. Photobiol., A: Chem.*, **64**, 255 (1992).
7) O. Ishitani, C. Inoue, Y. Suzuki, and T. Ibusuki, *J. Photochem. Photobiol., A: Chem.*, **72**, 269 (1993).
8) M. Anpo, T. Shima, S. Kodama, and Y. Kubokawa, *J. Phys. Chem.,* **91**, 4305 (1987).
9) H. Yoneyama, S. Haga, and S. Yamanaka, *J. Phys. Chem.,* **93**, 4833 (1989).
10) S. Al–Thabaiti and R. R. Kuntz, *Langmuir*, **6**, 782 (1990).
11) H. Miyoshi and H. Yoneyama, *J. Chem. Soc., Faraday Trans. 1*, **85**, 1873 (1989).
12) H. Miyoshi, S. Nippa, H. Uchida, H. Mori, and H. Yoneyama, *Bull. Chem. Soc. Jpn.*, **63**, 3380 (1990).
13) M. Anpo and K. Chiba, *J. Mol. Catal.,* **74**, 207 (1992).
14) H. Inoue, T. Torimoto, T. Sakata, H. Mori, and H. Yoneyama, *Chem. Lett.,* **1990**, 1483.
15) A. Ookubo, E. Kanezaki, and K. Ooi, *Langmuir*, **6**, 206 (1990).

(Received January 5, 1994)