Preparation of Visible-Light-Responsive Titanium Oxide Photocatalysts by Plasma Treatment

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The reduction of titanium dioxide (TiO_2) by the hydrogen plasma treatment creates a new absorption band in the visible light region and is expected to create photocatalytic activity in this region. Anatase TiO_2 powder, which has photocatalytic activity in the ultraviolet (UV) region, was treated using microwave and radio-frequency (RF) plasmas. The TiO_2 was reduced thus having an oxygen deficiency. The RF-plasma-treated TiO_2 absorbed visible light between 400 and 600 nm and showed a high activity in this region, as measured by the oxidative removal of nitric oxide from the gas phase. The plasma-treated TiO_2, which can be easily produced on a large scale, is expected to have a higher efficiency in utilizing solar energy than the raw material.

Titanium dioxide (TiO_2) shows photocatalytic activity in the ultraviolet (UV) region, because the optical band gaps are 3.0 eV for rutile and 3.2 eV for anatase.[1] Under ambient environmental conditions, TiO_2 produces active oxygen species such as hydroxyl radicals on its surface upon illumination with UV light. Such applications of TiO_2 include air and water purification, deodorization, and antibacterial and self-cleaning coatings.[2–5] If the photocatalytically active region is expanded to the visible light region, sunlight can be used more efficiently.

Many attempts have been made to make TiO_2 photocatalysts responsive to visible light. The doping of transition metals into TiO_2 extended the absorption band to the visible region, but the efficiency was often reduced by the formation of recombination centers.[6] Recently, a visible-light-active TiO_2 photocatalyst was prepared by transition metal ion implantation, in which transition metal ions were added in a well-controlled manner.[7] Spectral sensitization by the adsorbed or chemically bound dyes has also been used to enhance light use. Although the application of metal complex dyes in electrochemical solar cells seems to be successful,[8] the life of organic compounds is generally shorter than that of inorganic compounds.

On the other hand, the thermal reduction of TiO_2 powder increases its absorption in the visible light region.[9] Thus the photocatalytic activity can be expected to occur for the reduced TiO_2 powder under illumination by visible light. However, the absorption in the visible light region of TiO_2 has not been linked to the photocatalytic activity.

McTaggart reported the reduction of TiO_2 by microwave plasma.[10] We tried to prepare reduced TiO_2 by different methods, and obtained visible-light-responsive products with excellent optical and photocatalytic properties. In this article, we report the preparation and properties of these products when used as photocatalyst.

Anatase-type TiO_2 powder (ST-01, ca. 300 m^2 g^{-1}, Ishihara Sangyo Kaisha, Tokyo) was treated in a microwave discharge (2450 MHz, 400 W)[11] and in an inductive-type RF discharge (13.56 MHz, 400 W)[12] in a 130-Pa H_2 atmosphere for 10 min at 400 °C. A film-type TiO_2 was also prepared by chemical vapor deposition (CVD)[13] and was similarly treated for the Hall-effect measurement. The absorption spectra of these powder oxides were measured with a Shimadzu 2500PC spectrophotometer equipped with an integrating sphere.

Removal of NO_x by these samples was tested as described elsewhere.[14,15] Purified air containing 1.0 ppmv NO was continuously fed at 1.5 l min^{-1} into a Pyrex glass vessel that contained 0.2 g of an oxide sample. The vessel was illuminated by a JASCO SM-5 monochromatic light source with a 300-W xenon lamp (bandwidth: 20 nm). Though the light intensity was not corrected, spectral irradiance was measured with a CDI Optical Spectrograph Card. The removal percentage was calculated from the decrease in the NO_x concentration measured with a Monitor Labs 8840 chemiluminescent NO_x analyzer.

The color of the powder changed from white to grayish blue after microwave treatment and to beige after RF treatment. Figure 1 shows the UV and visible absorption spectra of the starting material and products. The absorbance of the raw TiO_2 sharply decreased to zero at 400 nm, while the RF-treated TiO_2 showed an extended absorption in the visible region up to 600 nm. The microwave-treated TiO_2 showed a stronger absorption in the visible region with a trough at around 400 nm.

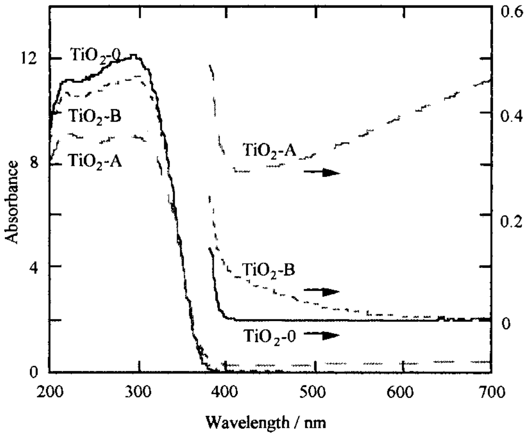

Figure 1. UV and visible absorption spectra of different TiO_2 powder samples using an integrating sphere. TiO_2-0: Starting material. TiO_2-A: Microwave-plasma-treated TiO_2. TiO_2-B: RF-plasma treated TiO_2.

Figure 2 shows the dependence of the NO removal by different TiO_2 samples on the illumination wavelength. The removal percentages were high for each sample in the UV region, but those for the raw and microwave-treated TiO_2 rapidly decreased with increasing wavelength. In contrast, the RF-treated TiO_2 showed an extended activity up to 600 nm without losing its UV activity.

Based on X-ray photoelectron spectroscopy, the O:Ti

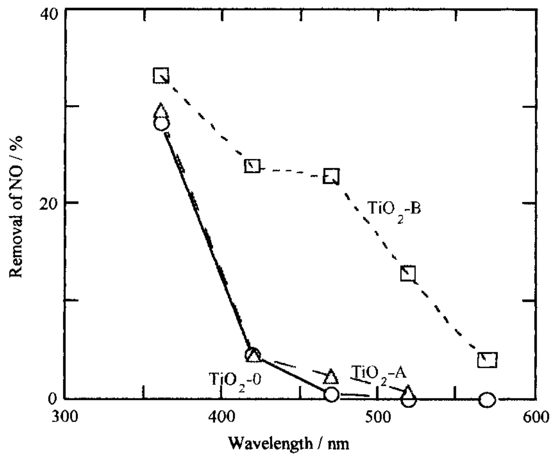

Figure 2. Dependence of NO removal percentage by TiO_2 on illumination wavelength. TiO_2-0, TiO_2-A and TiO_2-B are as in Figure 1.

atomic ratios of the raw, microwave- and RF-plasma-treated samples were 2.0, 1.6 and 1.7, respectively. Thus oxygen-deficient oxides were prepared by treatment with microwave and RF discharge. Before and after the treatment, the binding energies of the Ti 2p and O 1s electrons in the TiO_2 did not change.

Why did only the RF-treated sample show photocatalytic activity with visible light? For any photocatalytic reactions to proceed under visible light, the TiO_2 has to absorb light. In partly reduced TiO_2, oxygen vacancies (V_O) are formed in the oxygen ion lattice that is ionized to form free electrons:

$$O^{2-}(\text{in } TiO_2) \longrightarrow (V_O) + 1/2\, O_2(g) + 2\, e^- \qquad (1)$$

Breckenridge and Hosler[9] reported that Ti^{4+} ions in the lattice react with the electrons due to their electron affinity:

$$e^- + Ti^{4+} \longrightarrow Ti^{3+} \qquad (2)$$

Also, Cronemeyer[16] reported that the oxygen vacancies could trap the excess electrons:

$$V_O + e^- \longrightarrow V_O^- \qquad (3)$$

Electrons associated with either Ti^{4+} ions or V_O will have a much lower mobility than in the conduction band. Therefore, additional energy levels, intermediate between the normal valence and conduction bands, are created in lightly reduced anatase-type TiO_2.[9,16] As the XPS and electron spin resonance (ESR)[17] studies did not indicate the presence of Ti^{3+}, we tentatively suggest that the visible light absorption is due to a new energy state based on the oxygen vacancies. The new state is expected to be 2.0 eV above the valence band, corresponding to visible light of ca. 600 nm.[16]

Based on Hall-effect measurements of the TiO_2 films prepared by CVD, we observed that the films changed from insulator to semiconductor after treatment with the RF plasma and to a metal-like oxide after treatment with microwave plasma. In addition, the microwave treatment changed the crystal structure of TiO_2 to some extent due to local heating under our experimental conditions. The microwave-treated TiO_2 showed small peaks attributed to rutile in its X-ray diffraction pattern, and the specific surface area as measured by N_2-BET method decreased to 93 $m^2\, g^{-1}$. However, the RF-treated TiO_2 showed none of these changes, indicating that it was considerably reduced and maintained the anatase structure. Thus, in spite of the plasma treatment, the RF-treated TiO_2 maintained most of the physical properties of the raw TiO_2 that are photocatalytically active, and obtained additional activity during the illumination by visible light.

For the RF-plasma-treated TiO_2, the apparent quantum efficiency (ϕ_{app}) for NO oxidation at 360, 470, and 570 nm were 0.25, 0.034, and 0.006, respectively, indicating an exponential decrease with increasing wavelength. The ϕ_{app} for the raw TiO_2 was almost zero at 450 nm. The photon flux from the sun at 470 nm is 6.3 times greater than that at 360 nm (at the earth's surface with a zenith angle of 40°).[18] By integrating effective photons over the wavelength range, we roughly conclude that the RF-plasma-treated TiO_2 can effectively utilize twice as many photons as the non-treated TiO_2 in sunlight.

Another question about the oxygen deficient TiO_2 may be its stability against reoxidation. Our repeated tests of removing NO and washing with water gave constant results at least for 10 cycles if a small loss in catalyst recovery was taken into account. Exposure of the RF-plasma-treated TiO_2 to outdoor air and direct sunlight for a month resulted in a reduction of the visible light absorption by 30%, and the activity for NO oxidation decreased accordingly. However, further exposure did not change the visible absorption and activity even after 4 months. We assume that some of the defects produced by the RF-plasma treatment are curable, while most of them (probably those in the subsurface layers) are stable against oxidation. The RF-plasma-treated TiO_2 lost most of its color and visible-light activity after heating in air at 400 °C for 2 h. The visible-light-responsive TiO_2 reported here will greatly enhance the efficiency not only in the treatment of environmental pollutants but also in solar energy conversion, without using any additives.

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