

Design and development of second-generation titanium oxide photocatalysts to better our environment—approaches in realizing the use of visible light

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ABSTRACT. The design and development of second-generation titanium oxide photocatalysts which absorb UV-visible light and work as efficient photocatalysts under irradiation of light in the UV-visible light regions were successfully carried out by applying advanced metal ion-implantation techniques. Titanium oxide catalysts were implanted with various transition-metal ions by a high-voltage acceleration technique, then calcined in O₂ at around 723–823 K to produce photocatalysts capable of absorbing visible light, the extent of such red shift depending on the kind and amount of metal ion implanted. The transition-metal ion-implanted titanium oxide photocatalysts, specifically using V, Mn, or Cr ions, were successful in carrying out various photocatalytic reactions such as the decomposition of NO_x and the reaction involving the decomposition of H₂O at 295 K, significantly under irradiation with visible light longer than 450 nm. In outdoor field reactivity tests, these V or Cr ion-implanted titanium oxide photocatalysts showed four to three times higher photocatalytic reactivity for those photocatalytic reactions under solar beam irradiation, as compared with the original unimplanted titanium oxide photocatalyst. The advantages and possibilities of utilizing such second-generation titanium oxide photocatalysts are the only way to address environmental pollution on a large and global scale.

1. INTRODUCTION

Environmental pollution and destruction on a global scale have drawn attention to the vital need for totally new, safe and clean chemical technologies and processes, the most important challenge facing chemical scientists for the 21st century. Strong contenders as environmentally harmonious catalysts are titanium oxide photocatalysts which can operate at room temperature in a clean and safe manner while applications of such photocatalytic systems are urgently desired for the purification of polluted water, the decomposition of offensive atmospheric odors as well as toxins, the fixation of CO₂ and the decomposition of NO_x and chlorofluorocarbons on a global scale [1–8]. Furthermore, transparent titanium oxide thin film photocatalysts prepared on glass, tile and various architectural materials have been actively investigated as promising antibacterial, self-cleaning and deodorization systems [6, 7].

However, unlike photosynthesis in green plants, the titanium oxide photocatalyst in itself does not allow the use of visible light and can make use of only 3–4% of solar beams that reach the earth. Therefore, to address such enormous tasks, photocatalytic systems which are able to operate effectively and efficiently not only under UV but also under the most environmentally ideal energy source, sunlight, must be established.

To this end, it is vital to design and develop unique titanium oxide photocatalysts which can absorb and operate with high efficiency under solar and/or visible light irradiation [9–16].

This chapter deals with the design and development of such unique second-generation titanium oxide photocatalysts which absorb UV-visible light and operate effectively under visible and/or solar beam irradiation by applying an advanced metal ion-implantation method.

2. EXPERIMENTAL SECTION

The main characteristics of the various titanium oxide catalysts used in this chapter have been summarized in Table 1. Titanium oxide thin film photocatalysts were prepared using an ionized cluster beam (ICB) method [13–16]. Using ICB, the titanium metal was heated to 2200 K in a crucible and Ti vapor was introduced into the high vacuum chamber to produce Ti clusters. These clusters then reacted with O₂ in the chamber and stoichiometric titanium oxide clusters were formed. The ionized titanium oxide clusters formed by electron beam irradiation were accelerated by a high electric field and bombarded onto the glass substrate to form titanium oxide thin films.

The metal ion-implantation of the catalysts was carried out using an ion-implanter consisting of a metal ion source, mass analyzer, high voltage ion accelera-

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Table 1. Characteristics of the titanium oxides used in the present study.

| Catalyst | Anatase, % | BET surface area, m ² /g | Particle size, nm | Purity as TiO ₂ , % | Bandgap energy, eV |
|----------|------------|-------------------------------------|-------------------|--------------------------------|--------------------|
| F-2 | 72.3 | 27.1 | 23.4 | 99.97 | 3.25 |
| F-4 | 87.5 | 54.2 | 15.0 | 99.97 | 3.251 |
| F-6 | 81.0 | 102 | 9.30 | 99.99 | 3.262 |
| P-25 | 70.9 | 50.2 | 18.6 | 99.54 | 3.250 |
| S-1 | 86.1 | 30.6 | 30.2 | 99.90 | 3.252 |

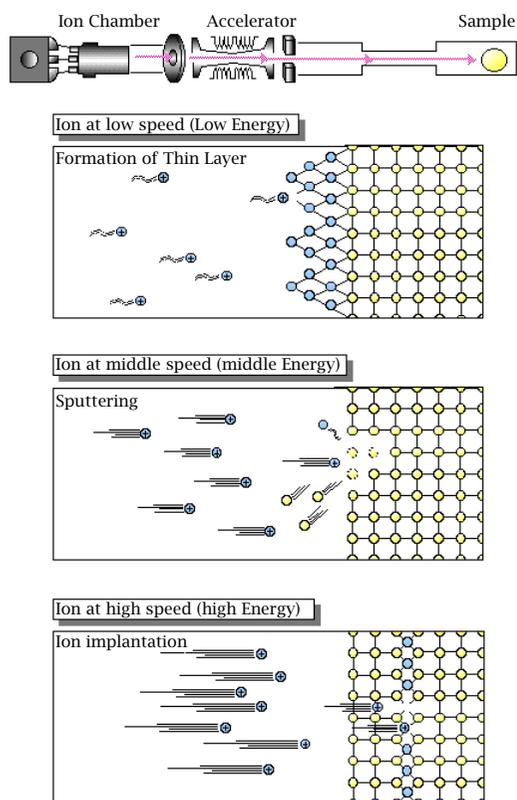


Figure 1. Schematic diagram of an advanced metal ion-implantation method. High energy implantation (bottom) was used in the present studies.

tor (50–200 keV), and a high vacuum pump (Figure 1) [2–5, 10–12]. The metal ions were expected to be injected into the deep bulk of the catalyst when high acceleration energy was applied to the metal ions. In fact, as expected, SIMS analyses using a Shimadzu/Kratos SIMS1030 clearly showed that the metal ions implanted into the titanium oxide catalyst exist in a highly dispersed state and are injected into the deep bulk of the catalyst, exhibiting a distribution maximum at around 1000–3000 Å from the surface and zero distribution at the surface [10–12]. Although such distribution depends on the acceleration energy and the kind of catalyst, one of the most significant advantages in using the

metal ion implantation method is to modify the bulk electronic properties of a catalyst.

The metal ion-implanted titanium oxide catalysts were calcined in O₂ at around 723–823 K for 5 h. Prior to various spectroscopic measurements such as UV-VIS diffuse reflectance, SIMS, XRD, EXAFS, ESR and ESCA as well as investigations on the photocatalytic reactions, both the metal ion-implanted and unimplanted original pure titanium oxide photocatalysts were heated in O₂ at 753 K and then degassed in cells at 753 K for 2 h, heated in O₂ at the same temperature for 2 h, and finally outgassed at 473 K to 10⁻⁶ Torr [12–15].

Light irradiation of the photocatalysts in the presence of reactant molecules such as NO_x and a mixture of CH₃C≡CH and H₂O was carried out using a high-pressure Hg lamp (Toshiba SHL-100UV) through water and color filters, i.e., λ > 450 nm for visible light irradiation and λ < 380 nm for UV irradiation, respectively, at 275–295 K. The reaction products were analyzed by GC and GC-MASS. The UV-VIS diffuse reflectance spectra were measured using a Shimadzu UV-2200A spectrophotometer at 295 K. The ESR spectra were recorded at 77 K with a Bruker ESP300E and a JEOL RE-2X spectrometer (X-band). The binding energies and the element composition of the catalysts were measured using a Shimadzu ECSA-3200 electron spectrometer. The XAFS (XANES and FT-EXAFS) spectra were measured at the BL-7C facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba.

3. RESULTS AND DISCUSSION

The metal ion-implantation method was applied to modify the electronic properties of titanium oxide photocatalysts by bombarding them with high energy metal ions, and it was discovered that metal ion-implantation with various transition metal ions such as V, Cr, Mn, Fe and Ni accelerated by high voltage enables a large shift in the absorption band of the titanium oxide catalysts toward visible light regions, with differing levels of effectiveness. However, Ar, Mg, or Ti ion-implanted titanium oxides exhibited no shift, showing that such a shift is not caused by the high energy implantation process itself, but to the interaction of the transition metal ions with the titanium oxide catalyst. As can be seen in Figure 2-(b-d), the absorption band of the Cr

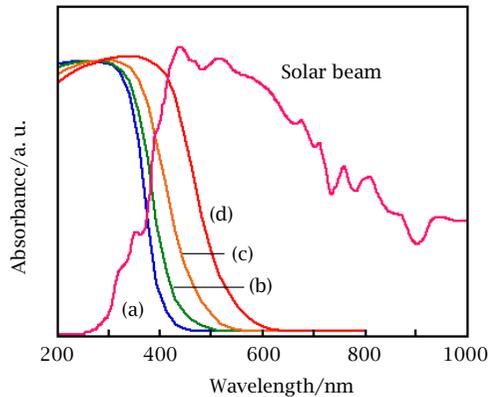


Figure 2. *Uv-Vis absorption spectra (diffuse reflectance) of the original unimplanted pure TiO₂ (a) and the Cr ion-implanted TiO₂ (b-d), and the solar spectrum which reaches the earth. (amounts of Cr ion-implanted in 10⁻⁷ mol/g, b: 2.2, c: 6.6, d: 13.0)*

ion-implanted titanium oxide shifts smoothly to visible light regions, the extent of the red shift depending on the amount and type of metal ions implanted, with the absorption maximum and minimum values always remaining constant. The order of the effectiveness in the red shift was found to be V > Cr > Mn > Fe > Ni ions. Such a shift allows the metal ion-implanted titanium oxide to use solar beams more effectively and efficiently, at up to 20–30% [4, 12].

Furthermore, as shown in Figure 3, such red shifts in the absorption band of the metal ion-implanted titanium oxide photocatalysts can be observed for any kind of titanium oxide except amorphous types, the extent of the shift changing from sample to sample.

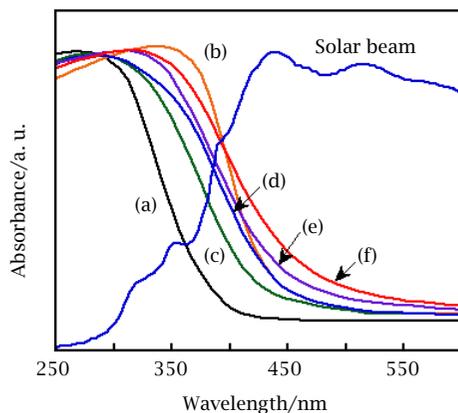


Figure 3. *Shifts in the absorption spectra of various types of TiO₂ photocatalysts (shown in Table 1) implanted with the same amounts of V ions. a: original unimplanted pure p-25, b: V/F-6, c: V/F-4, d: V/P-25, e: V/F-2, f: F/S-1. (amount of V ion-implanted was 6.6 × 10⁻⁷ mol/g (3.4 × 10⁻³ wt%))*

It was also found that such shifts in the absorption band can be observed only after calcination of the metal ion-implanted titanium oxide samples in O₂ at around 723–823 K. Therefore, calcination in O₂ in combination with metal ion-implantation was found to be instrumental in the shift of the absorption spectrum toward visible light regions. These results clearly show that shifts in the absorption band of the titanium oxides by metal ion-implantation are a general phenomenon and not a special feature of a certain kind of titanium oxide catalyst.

Figure 4 shows the absorption bands of the titanium oxide photocatalysts impregnated or chemically doped with Cr ions in large amounts as compared with those for Cr ion-implanted samples. The Cr ion-doped catalysts show no shift in the absorption band, however, a new absorption shoulder appears at around 420 nm due to the formation of the impurity energy level within the bandgap, its intensity increasing with the amount of Cr ions chemically doped. Such results indicate that the method of doping causes the electronic properties of the titanium oxides to be modified in completely different ways, thus confirming that only metal ion-implanted titanium oxide catalysts show shifts in the absorption band toward visible light regions.

With unimplanted or chemically doped titanium oxide photocatalysts, the photocatalytic reaction does not proceed under visible light irradiation ($\lambda > 450$ nm). However, we have found that visible light irradiation of metal ion-implanted titanium oxide photocatalysts can initiate various significant photocatalytic reactions. As shown in Figure 5, visible light irradiation ($\lambda > 450$ nm) of the Cr ion-implanted titanium oxide in the presence

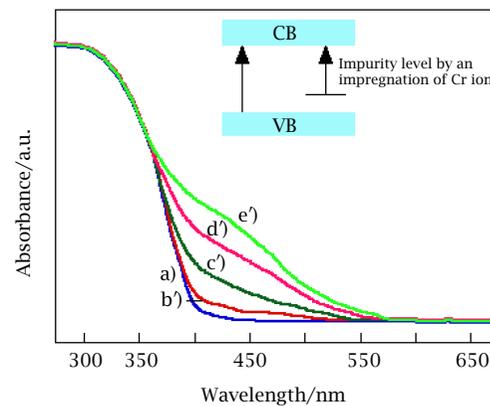


Figure 4. *Uv-Vis absorption spectra of (diffuse reflectance) of the original undoped pure TiO₂ (a) and TiO₂ chemically doped with Cr ions (b'-e'). (Cr ions chemically doped in 10⁻⁷ mol/g, a: undoped original pure TiO₂ (P-25), b': 16, c': 200, d': 1000, e': 2000) These TiO₂ photocatalysts chemically doped with Cr ions did not exhibit any photocatalytic reactivity.*

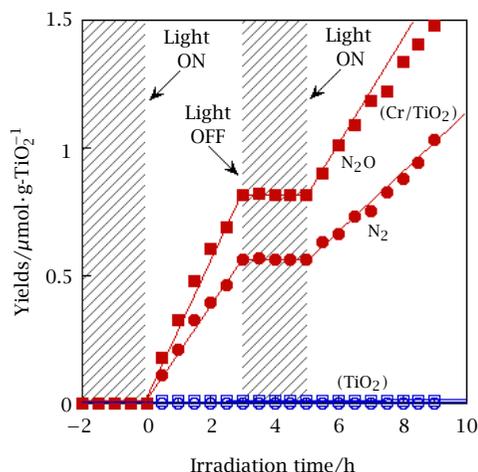


Figure 5. Reaction time profiles of the photocatalytic decomposition of NO on the Cr ion-implanted TiO_2 photocatalyst under visible light ($\lambda > 450 \text{ nm}$) irradiation at 295 K. Unimplanted original pure TiO_2 photocatalyst did not show any photocatalytic reactivity under the same reaction conditions.

of NO at 275 K leads to the decomposition of NO into N_2 , O_2 , and N_2O with a good linearity against the irradiation time. Under the same conditions of visible light irradiation, the unimplanted original pure titanium oxide photocatalyst did not exhibit any photocatalytic reactivity. The action spectrum for the reaction on the metal ion-implanted titanium oxide was in good agreement with the absorption spectrum of the photocatalyst shown in Figure 2, indicating that only metal ion-implanted titanium oxide photocatalysts were effective for the photocatalytic decomposition reaction of NO. Thus, metal ion-implanted titanium oxide photocatalysts were found to enable the absorption of visible light up to a wavelength of 400–600 nm and were also able to operate effectively as photocatalysts, hence their name, “second-generation titanium oxide photocatalysts” [4, 11, 15].

It is important to emphasize that the photocatalytic reactivity of the metal ion-implanted titanium oxides under UV light ($\lambda < 380 \text{ nm}$) retained the same photocatalytic efficiency as the unimplanted original pure titanium oxides under the same UV light irradiation conditions. When metal ions were chemically doped into the titanium oxide photocatalyst, the photocatalytic efficiency decreased dramatically under UV irradiation due to the effective recombination of the photo-formed electrons and holes through the impurity energy levels formed by the doped metal ions within the bandgap of the photocatalyst (in the case of Figure 4) [17]. These results clearly suggest that metal ions physically implanted do not work as electron and hole recombination centers but only work to modify the electronic property

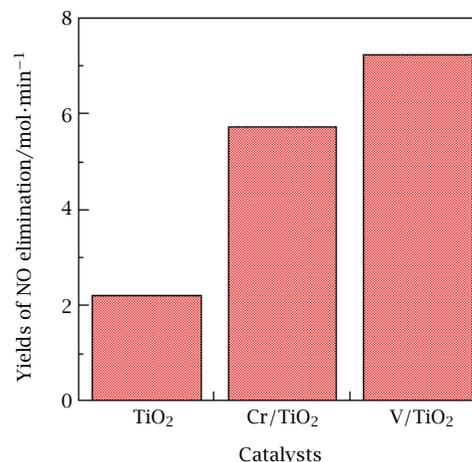


Figure 6. Effect of the Cr and V ion-implantation on the photocatalytic reactivity of TiO_2 under outdoor solar beam irradiation for the photocatalytic decomposition of NO at 295 K. (solar beam: 38.5 mW/cm^2)

of the catalyst [11, 12, 14, 15].

We have conducted various field work experiments to test the photocatalytic reactivity of the newly developed titanium oxide photocatalysts under solar beam irradiation. As can be seen in Figure 6, under outdoor solar light irradiation at ordinary temperatures, the Cr and V ion-implanted titanium oxide photocatalysts showed several times higher photocatalytic reactivity for the photocatalytic decomposition of NO. As Figure 7 shows, it is also found that under solar light irradiation at ordinary temperatures, the V ion-implanted titanium oxide photocatalysts showed several times higher photocatalytic reactivity for the photocatalytic hydrogenation of $\text{CH}_3\text{C}\equiv\text{CH}$ with H_2O than the unimplanted original pure titanium oxide photocatalysts. These results, together with the results shown in Figure 2, clearly show that by using second-generation titanium oxide photocatalysts developed by applying the metal ion-implantation method, we are able to utilize visible and solar light energy more efficiently.

The relationship between the depth profiles of the metal ions of the metal ion-implanted titanium oxide photocatalysts having the same number of metal ions, such as V or Cr ions, and their photocatalytic efficiency under visible light irradiation were investigated. It was found that when the metal ions were implanted in the same amounts into the deep bulk of the catalyst by applying high voltage acceleration energy, the photocatalyst exhibited a high photocatalytic efficiency under visible light irradiation. On the other hand, when a low voltage was applied, the photocatalyst exhibited a low efficiency under the same conditions of visible light irradiation [15, 16].

It was also found that increasing the number (or

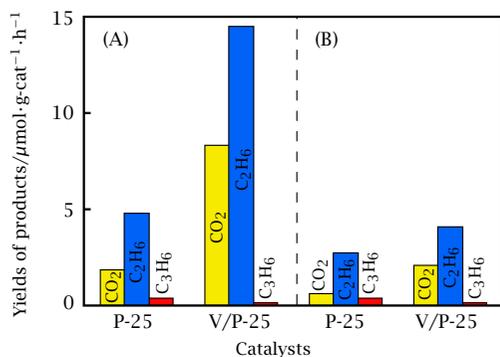


Figure 7. Effect of the Cr and V ion-implantation on the photocatalytic reactivity of TiO₂ under outdoor solar beam irradiation for the photo-catalytic reaction of CH₃CCH with H₂O leading a hydrogenolysis reaction of CH₃CCH with H₂O at 295 K. (A: fine, B: clody weather) (solar beams of fine weather: 12 mW/cm², amount of photocatalyst: 6.0 g)

amounts) of metal ion-implanted into the deep bulk of the titanium oxides caused the photocatalytic efficiency of these photocatalysts to increase under visible light irradiation, passing through a maximum at around 6×10^{16} V/cm² of the catalyst, then decreasing with a further increase in the number of metal ions implanted. Only on samples implanted with an increased number of metal ions could the presence of ions at the near surfaces be observed by ESCA measurements. Thus, these results clearly suggest that there are optimal conditions in the depth and number of metal ions implanted to achieve a high photocatalytic reactivity under visible light irradiation.

The ESR spectra of the V ion-implanted titanium oxide catalysts were measured before and after calcination of the samples in O₂ at around 723–823 K, respectively. Distinct and characteristic reticular V⁴⁺ ions were detected only after calcination at around 723–823 K. It was found that when a shift in the absorption band toward visible light regions was observed, the reticular V⁴⁺ ions could be detected by ESR. No such reticular V ions or shift in the absorption band have ever been observed with titanium oxides chemically doped with V ions [16, 18, 19].

Figure 8 shows the XANES and FT-EXAFS spectra of the titanium oxide catalysts physically implanted with Cr ions (b and B) and also chemically doped with Cr ions (a and A), respectively. Analyses of these XANES and FT-EXAFS spectra show that in the titanium oxide catalysts chemically doped with Cr ions by an impregnation or sol-gel method, the ions are present as aggregated Cr-oxides having octahedral coordination similar to Cr₂O₃ and tetrahedral coordination similar to CrO₃, respectively. On the other hand, in the catalysts physically implanted with Cr ions, the ions are present in a highly dispersed and isolated state in octahedral coordination,

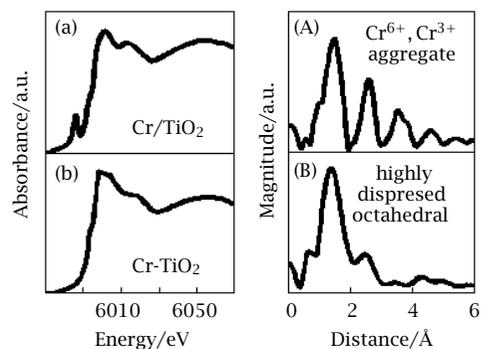
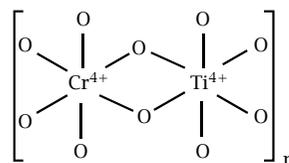


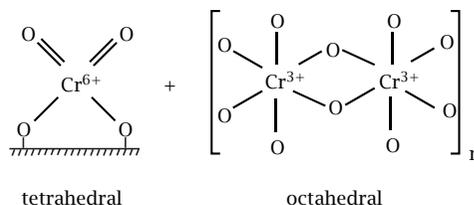
Figure 8. XANES (left) and FT-EXAFS spectra (right) of Cr ion chemically doped TiO₂ (a) and (A) and Cr ion-implanted TiO₂ catalysts (b) and (B), respectively.



Scheme 1. Molecular structure of titanium oxide photocatalyst modified by metal ion-implantation. Metal ions are located at the lattice position in substitution of Ti⁴⁺.

clearly suggesting that the Cr ions are incorporated in the lattice positions of the catalyst in place of the Ti ions.

Our results clearly show that modification of the electronic state of titanium oxide by metal ion-implantation is closely associated with the strong and long distance interaction which arises between the titanium oxide and the metal ions implanted, as shown in Scheme 1, and not by the formation of impurity energy levels within the bandgap of the titanium oxides resulting from the formation of impurity oxide clusters which are often observed in the chemical doping of metal ions, as shown in Figures 4 and Scheme 2.



Scheme 2. Molecular structure of titanium oxide photocatalyst chemically doped with Cr ions. Clusters of Cr oxides are formed in TiO₂.

4. CONCLUSIONS

The advanced metal ion-implantation method has been successfully applied to modify the electronic properties of the titanium oxide photocatalysts, enabling the absorption of visible light even longer than 550 nm and initiating the photocatalytic reactions effectively not only under UV but also visible light irradiation. The results obtained in the photocatalytic reactions and various spectroscopic measurements of the photocatalysts indicate that the implanted metal ions are highly dispersed within the deep bulk of the catalysts and work to modify the electronic nature of the photocatalysts without any changes in the chemical properties of the surfaces. These modifications were found to be closely associated with an improvement in the reactivity and sensitivity of the photocatalyst, thus enabling the titanium oxides to absorb and operate effectively not only under UV but also under visible light irradiation. As a result, under outdoor solar light irradiation at ordinary temperatures, metal ion-implanted titanium oxide photocatalysts showed several times higher photocatalytic efficiency than the unimplanted original pure titanium oxide photocatalyst.

Thus, the advanced metal ion-implantation method has opened the way to many innovative possibilities, and the design and development of such unique titanium oxide photocatalysts can also be considered an important breakthrough in the utilization of solar light energy which will advance research in sustainable green chemistry for a better environment [4, 5, 15, 16, 20].

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