

Use of visible light. Second-generation titanium oxide photocatalysts prepared by the application of an advanced metal ion-implantation method*

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Abstract: Titanium oxide catalysts were implanted with various transition-metal ions by a high-voltage acceleration technique, then calcined in O₂ at around 723 K to produce photocatalysts capable of absorbing visible light, the extent of the red shift depending on the amount and kind of metal ions implanted. Such metal ion-implanted titanium oxide photocatalysts, specifically using Cr or V ions, were successful in carrying out various photocatalytic reactions such as the decomposition of NO into N₂, O₂, and N₂O at 293 K, significantly under irradiation with visible light longer than 450 nm. In outdoor field tests, these Cr and V ion-implanted titanium oxide photocatalysts showed three to four times higher photocatalytic reactivity for the decomposition of NO under solar beam irradiation, as compared with the original unimplanted titanium oxide photocatalyst.

INTRODUCTION

As an “environmentally harmonious catalyst”, TiO₂ photocatalysts have been some of the most actively investigated catalysts for applications in systems that can effectively address environmental pollution [1,2]. However, unlike the photosynthesis in plants, TiO₂ in itself can make use of only 3–4% of the solar beams that reach the earth, necessitating the use of an ultraviolet light source. Clean and safe photocatalytic systems that could be applied to treat very low and dilute concentrations of toxic reactants in water and the atmosphere on a very large and global scale would only be possible with the development of photocatalysts capable of operating under visible light irradiation [3,4].

Investigations into the chemical doping of metal ions into TiO₂ to explore the possibility of visible light absorption had already been intensively carried out in the past. However, in such systems, it was found that the metal ions doped existed only as impurities that enhanced the recombination of the photo-formed electrons and holes and, therefore, did not allow reactions to proceed with any noticeable effect either with ultraviolet or visible light.

Our present research concerns an advanced high-voltage metal ion-implantation method which works to dramatically modify the electronic properties of the TiO₂ by bombarding them with high-energy metal ions, thus enabling the design of unique TiO₂ photocatalysts capable of absorbing visible light and operating as efficient photocatalysts not only under ultraviolet, but also visible light irradiation [3–7].

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EXPERIMENTAL

The TiO₂ catalysts were supplied by the Catalysis Society of Japan as standard reference TiO₂ (JRC-TIO-4: surface area; 50 m²/g, bandgap; 3.25 eV, purity > 99.5%). Metal ion-implantation of the TiO₂ photocatalysts was carried out using an ion-implanter consisting of a metal ion source, mass analyzer, high-voltage ion accelerator (150–200 keV), and a high-vacuum pump. The metal ions were found to be injected into the deep bulk of the catalyst when high acceleration energy was applied to the metal ions, exhibiting a distribution maximum at around 1000–3000 and zero distribution at the surface, the distribution depending on the acceleration energy and the kind of catalyst used. The metal ion-implanted TiO₂ were calcined in O₂ at around 725–750 K for 5 h, degassed at 725 K for 2 h, heated in O₂ at the same temperature for 2 h, and finally outgassed at 473 K to 10⁻⁶ Torr prior to UV-VIS diffuse reflectance, secondary-ion mass spectrometry (SIMS), X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), electron spin resonance (ESR), and electron spectroscopy for chemical analysis (ESCA) measurements as well as investigations on the photocatalytic reactions of the metal ion-implanted and original unimplanted TiO₂. UV irradiation of the photocatalysts in the presence of NO was carried out using a high-pressure Hg lamp (Toshiba SHL-100UV), $\lambda > 450$ nm with visible light and $\lambda < 380$ nm, respectively, with UV light at 275 K. The reaction products were analyzed by gas chromatography. 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 spectrometer (X-band) using 100 kHz field modulation and 10–20 Gauss standard modulation. 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. SIMS analysis of the metal ions implanted was carried out using a Shimadzu/Kratos SIMS1030.

RESULTS AND DISCUSSION

The absorption spectrum of the original unimplanted pure TiO₂ photocatalyst does not overlap with the solar beam spectrum (A), indicating that the catalyst does not work under visible light and absorbs only the UV light from the solar beams (3–4%), as shown in Fig. 1a. However, the absorption spectra of the Cr ion-implanted TiO₂ photocatalysts are found to shift smoothly toward visible light regions, the extent of the red shift depending on the amount of Cr ions implanted as well as on the kind of metal ions implanted, while the absorption maximum and minimum values remain consistently constant, allowing

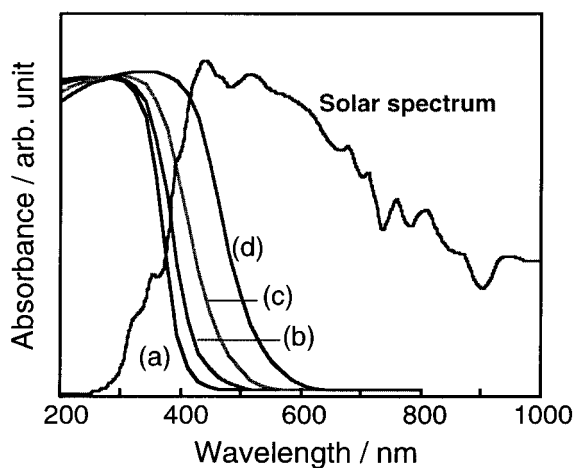


Fig. 1 Solar spectrum and the diffuse reflectance UV-VIS absorption spectra of TiO₂ (a) and Cr ion-implanted TiO₂ photocatalysts (b–d).

the Cr ion-implanted TiO₂ photocatalysts to use solar beams more effectively and efficiently from 3–4% (line a) up to 25–30% (line d), as can be seen in Fig. 1b–d [3–10].

It should be emphasized that the absorption spectra of the Cr ion-implanted catalysts without calcination in O₂ showed no difference in reactivity with that of the original unimplanted TiO₂. Significantly, calcination in O₂ in combination with the ion-implantation was found to be instrumental in the shift of the absorption spectrum toward visible light regions. Calcination of the metal ion-implanted TiO₂ at around 725–875 K was found to show the largest shift and such a shift toward visible light regions could be observed not only with Cr ions but also with other metal ions such as V, Fe, Ni, Rh, Mn, and Nb, albeit with differing levels of effectiveness. However, Ar, Mg, or Ti ion-implanted TiO₂ exhibited no shift, showing that shifts in the absorption bands are not caused by a modification in the local structure of the photocatalyst due to the high energy implantation process itself, but to the interaction of the metal ions with the TiO₂ catalyst.

The most effective amount which yielded the most remarkable and smooth shift in the absorption band was found to be in the range of 1×10^{16} to 5×10^{17} ions per g of TiO₂ catalyst, although these numbers vary depending on the kind of metal ions implanted. It was also found that the energy voltage of the accelerated ion implantation should be at least 30 keV, and most ideally at a high voltage level of between 100 to 200 keV. Such high-energy voltage not only disperses the metal ions more uniformly and in a more highly dispersed state, but also prevents the destructive modification of the crystalline structure of the catalyst by the implanted metal ions. Moreover, XRD and XAFS measurements of the metal ion-implanted TiO₂ have shown that, even after calcination in O₂ at around 723 K, all of the catalysts were able to retain their original anatase TiO₂ structure as well as their local surface structures.

Figure 2 shows the absorption spectra of the TiO₂ photocatalysts doped with Cr ions that were prepared by conventional chemical processes such as impregnation or sol-gel methods. The Cr ion-doped TiO₂ exhibited no shift in the absorption band, however, a new absorption shoulder could be observed at around 430 nm due to the appearance of the Cr ions (and/or oxide species) as impurities, its intensity increasing with the amount of Cr ions chemically doped, while the photocatalytic reactivities was negligibly low under irradiation with UV light of around 350 nm. It is clear that the absorp-

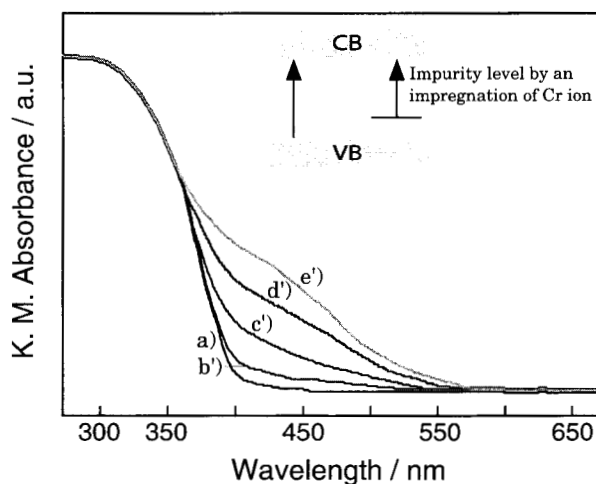


Fig. 2 The UV-VIS absorption spectra of TiO₂ (a) and Cr ion-doped TiO₂ (b'–d') photocatalysts prepared by an impregnation method. The amount of doped Cr ions (wt%); (a) 0, (b') 0.01, (c') 0.1, (d') 0.5, (e') 1. (0.1 wt% equals to 4.9 $\mu\text{mol/g-TiO}_2$)

tion spectra of TiO_2 physically implanted with Cr ions are completely different from those of TiO_2 chemically doped with Cr ions, indicating that the method of doping causes the electronic properties of the photocatalyst to be modified in completely different ways, as can be seen in Figs. 1 and 2.

Thus, these results confirm that only TiO_2 implanted with transition-metal ions such as Cr and V are able to absorb visible light and, as can be seen in Fig. 3, exhibit photocatalytic reactivity under visible light irradiation. Moreover, the photocatalytic reactivity of the metal ion-implanted TiO_2 under bandgap irradiation ($\lambda < 380 \text{ nm}$) is the same as that of the original unimplanted TiO_2 , thus showing that the photocatalytic reactivity under bandgap irradiation could be sustained even when the electronic state of the catalyst had been dramatically modified.

Visible light irradiation ($\lambda > 450 \text{ nm}$) of the metal ion-implanted TiO_2 was successful in initiating various significant photocatalytic reactions such as the decomposition of NO into N_2 , O_2 , and N_2O , the isomerization of cis-2-butene into 1-butene and trans-2-butene, the hydrogenolysis of unsaturated hydrocarbons such as $\text{CH}_3\text{C}\equiv\text{CH}$ with H_2O , and the oxidative degradation of alcohol dissolved in water. Figure 3 shows the reaction time profiles of the photocatalytic decomposition of NO into N_2 , O_2 , and N_2O on the Cr ion-implanted TiO_2 as well as the original unimplanted TiO_2 under visible light irradiation ($\lambda > 450 \text{ nm}$) at 295 K. The Cr ion-implanted TiO_2 leads to the direct decomposition of NO into N_2 , O_2 , and N_2O with a good linearity against the irradiation time. Under the same conditions, however, these photocatalytic reactions do not proceed on the original unimplanted TiO_2 nor on TiO_2 chemically doped with Cr ions, as can be seen by their absorption spectra in Fig. 2. Furthermore, when metal ions were chemically doped into TiO_2 , the reaction efficiency of the catalyst decreased dramatically even under UV light irradiation ($\lambda < 380 \text{ nm}$). However, for the photocatalytic decomposition of NO, the Cr and V ion-implanted TiO_2 retained the same photocatalytic efficiency as the original unimplanted TiO_2 even under bandgap irradiation ($\lambda < 380 \text{ nm}$). The action spectrum was in good agreement with the absorption spectrum (solid line d), indicating that only the Cr and V ion-implanted TiO_2 is effective for the photocatalytic decomposition of NO under visible light irradiation, as shown in Fig. 1d.

The XAFS (XANES and FT-EXAFS) spectra of the TiO_2 photocatalysts physically implanted with Cr ions and chemically doped with Cr ions were measured. The analyses of the XAFS spectra of

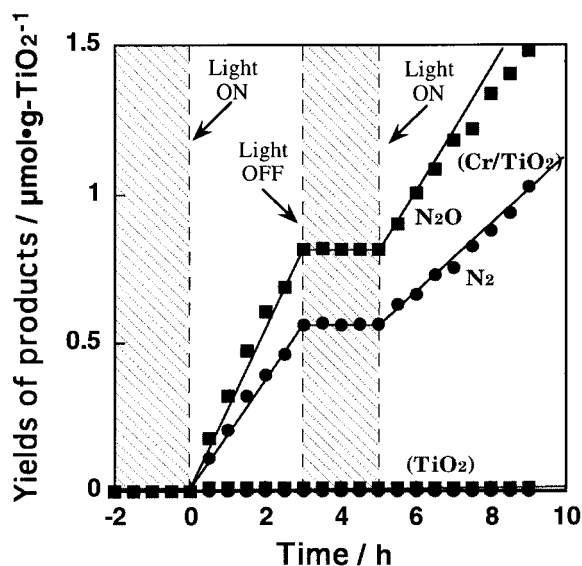


Fig. 3 The reaction time profiles of photocatalytic decomposition of NO into N_2 , O_2 , and N_2O on TiO_2 and Cr ion-implanted TiO_2 photocatalysts at 273 K.

the TiO₂ chemically doped with Cr ions by conventional doping or sol-gel methods showed that the Cr ions are present mainly as aggregated Cr-oxides having octahedral coordination similar to Cr₂O₃. While in the TiO₂ physically implanted with Cr ions, the metal ions were found to be present in a highly dispersed and isolated state, having octahedral coordination, suggesting that the Cr ions are incorporated in the lattice in place of the Ti ions. These results were in good agreement with the results obtained by ESR investigations where the reticular V⁴⁺ signal can be observed in TiO₂ physically implanted with V ions, indicating that the implanted metal ions, in fact, are present at the lattice positions in place of the Ti ions, while such reticular metal ions could not be observed with the TiO₂ catalysts chemically doped with V ions by conventional methods [10].

It was further found that the smooth shifts in the absorption bands shown in Fig. 1b–d, caused by the combination of metal ion-implantation and calcination, could be observed not only with semiconducting materials such as TiO₂ and ZnO but also with titanium oxides highly dispersed atomically in or on silica matrices having tetrahedral coordination as well as on transparent TiO₂ thin-film photocatalysts (thickness: about 1000–10000). These results clearly indicate that the modification of the electronic state of TiO₂ is closely associated with the strong and long-distance interaction which arises between TiO₂ and the metal ions implanted, and not by the formation of impurity energy levels between the valence band and the conduction band of the semiconducting catalysts which is often observed in the chemical doping of metal ions into catalysts, resulting in the absorption spectra shown in Fig. 2b–e.

We have conducted various outdoor field tests to evaluate the actual reactivity of the newly developed TiO₂ photocatalysts under natural solar beam irradiation. The Cr and V ion-implanted TiO₂ exhibited three and four times higher photocatalytic reactivity, respectively, for the decomposition of the NO_x in the air under solar light irradiation of 38.5 mW/cm² as compared with the original unimplanted TiO₂. It can therefore be seen that this advanced metal ion-implantation method works to dramatically modify the bulk electronic properties of TiO₂ without any detrimental changes in the chemical reactivities or properties of the top and/or near surfaces of the catalysts. It is, however, yet unclear whether the electronic properties of the 4d orbital of the Ti⁴⁺ ions and/or the 2p orbital of the O²⁻ ions of TiO₂ have been modified.

SUMMARY

TiO₂ photocatalysts were incorporated with transition-metal ions, specifically Cr or V ions, using a high-energy ion-implantation technique, then calcined in O₂ at around 723–753 K, yielding new and unique photocatalysts that allow the efficient absorption of visible light and thus enables the modified TiO₂ to initiate reactions effectively even under visible or solar light irradiation. The strong and long-distance interaction between TiO₂ and the highly uniform and dispersed metal ions implanted were found to play a significant role in the modification of the bandgap energy of the catalysts. These dramatically modified TiO₂ worked effectively to initiate reactions for the decomposition and elimination of toxic compounds in the environment, the most urgent and desirable aim in catalytic research today. The advantages and possibilities in utilizing solar energy as an abundant and safe energy source are unlimited, and such photocatalytic systems will be the only way to address environmental pollution on a large and global scale.

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