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Photocatalytic decomposition of formic acid under visible light irradiation over V-ion-implanted TiO_2 thin film photocatalysts prepared on quartz substrate by ionized cluster beam (ICB) deposition method

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Unique visible-light-responsive TiO_2 photocatalysts ($\lambda > 450$ nm) were successfully developed by implantation of V ions into the TiO_2 thin films prepared on a quartz substrate by an ionized cluster beam (ICB) deposition method. After V ions implantation into TiO_2 thin film, the photocatalytic activity of the thin films for the decomposition of formic acid into CO_2 and H_2O was found to proceed efficiently under visible light irradiation longer than 450 nm. The TiO_2 thin film photocatalysts were characterized by XRD, UV-vis, XPS, FE-SEM and AFM.

KEY WORDS: TiO_2 thin films; ionized cluster beam deposition method; V ions implantation; visible-light-responsive TiO_2 photocatalysts; decomposition of formic acid.

1. Introduction

TiO_2, an environmentally friendly photocatalyst, has been applied to lots of environmental issues, such as wastewater treatment, photodegradation of toxic organic compounds, and production of clean hydrogen from water due to its high efficiency, non-toxicity, thermal stability and low cost [1–4]. However, its large bandgap ($E_g = 3.2$ eV) requires the utilization of near-UV light (shorter than 380 nm) to activate TiO_2, an attractive photocatalyst. Therefore, TiO_2 photocatalysts can utilize only 3% of the solar light which reaches on the earth. Furthermore, if powdered TiO_2 photocatalysts are used in aqueous solution systems, it is very difficult and costly to separate TiO_2 fine powders from the suspension systems by a filtration process after the photocatalytic reactions. Since thin films prepared on substrates can be easily separated from the aqueous solution systems after photocatalytic reactions such as the purification of polluted aqueous systems, the utilization of TiO_2 thin film photocatalysts would be a better solution with a lower cost [5]. Generally, TiO_2 thin films have been prepared by the sol–gel method [6], a wet preparation processes, followed by high-temperature calcination post-treatment which necessitates the desired mechanical strengths or stabilities when supported on various substrates [5,7,8]. The high temperature calcination causes potential damages to some porous supports [9,10]. From these various reasons, it is of great significance to prepare and develop unique TiO_2 thin film photocatalysts which can work efficiently even under visible light irradiation while having a high mechanical and physical stability [11,12].

In the present paper, a new and unique type of TiO_2 thin film photocatalyst, which is responsive to visible light, has been developed on a quartz substrate by a combination of the ionized cluster beam (ICB) deposition method as a dry preparation process and an advanced metal-ion-implantation method which can modify the electronic properties of TiO_2, and used for the photocatalytic complete oxidation (degradation) of formic acid in aqueous solution under visible light irradiation. The prepared TiO_2 thin films were characterized by XRD, UV-vis, XPS, FE-SEM and AFM. The photocatalytic reactivity for the complete oxidation of formic acid dissolved in aqueous solution was carried out under visible light irradiation ($\lambda > 450$ nm).

2. Experimental

The TiO_2 thin films were prepared on a quartz substrate by an ICB deposition method as reported elsewhere [13–15]. Ti metal in a crucible was heated upto about 2000 °C to generate Ti vapor, which was introduced into a high vacuum chamber and a low pressure O_2 atmosphere (10^{-4} Torr) to produce small TiO_2 clusters. These stoichiometric TiO_2 small clusters were ionized by electron beam irradiation, and then these ionized

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TiO_2 clusters were accelerated by a high electric field and bombarded onto a quartz substrate to form TiO_2 thin film on it (TiO_2/Quartz photocatalyst). The TiO_2 thin film thickness of TiO_2/Quartz photocatalyst was easily monitored by a quartz thicknessmeter and controlled to be of 300 nm in thickness, which was calibrated by consideration of the absorption coefficient of the TiO_2 thin films. Since the TiO_2 thin films were prepared in a high vacuum chamber as a dry process, the contamination with some impurities can be completely prevented. These advantages are very useful to improve the photocatalytic reactivity of the TiO_2 thin films by changing the thickness etc. Implantation of V^+ ions into the transparent TiO_2 thin films was carried out by using a conventional 200 keV ion implanter. The acceleration energy and the amount of V ions were chosen to be 150 keV and 3×10^{16} ions/cm^2, respectively, based on the previous results [11,12]. After the V ion implantation, the V ion implanted TiO_2/Quartz photocatalyst (size $10\times10\times1$ mm) was calcined in O_2 at 450 °C for 3 h. Prior to the photocatalytic reaction of formic acid, the catalysts were calcined at 500 and 700 °C for 5 h (with a heating rate of 3 °C/min). The photocatalytic reaction of formic acid was carried out in a sealed Pyrex reaction tube (cutoff wavelength of Pyrex glass; ca. 300 nm) with an aqueous solution of formic acid (1.63×10^{-2} mmol/l, 10 ml) using a 500 W Xenon Lamp (SAN-EI XEF-501S) with a cutoff color filter (cutoff wavelength of Toshiba glass, Y-45; 450 nm) at 25 °C. The reaction products were analyzed by gas chromatography (Shimadzu GC-14A, Porapak Q 4 m, TCD detector). X-ray diffraction patterns of the films were recorded on a Rigaku RAD-γA X-ray diffractometer using Cu Kα radiation. UV-vis transmittance spectra were recorded on a Shimadzu UV 2200A spectrophotometer at room temperature. The surface topographies of the films were examined with an atomic force microscope (AFM; NanoScope III) in the tapping mode to minimize damage of the surface structures and to reduce the scratch noises using a single-crystal silicon probe. Surface chemical analysis of the films was performed by X-ray photoelectron spectroscopy (XPS; AXIS His; Kratos Analytical) using Mg Kα X-ray source ($h\upsilon = 1253.6$ eV) and an analyzer pass energy of 40 eV. The microstructures of the films were also observed with a field-emission scanning electron microscope (FE-SEM; JEOL JSM-6700F).

3. Results and discussion

The crystallographic structures of the TiO_2 thin film prepared by an ICB deposition method and V ion implanted TiO_2 thin films calcined at different temperatures were investigated by XRD patterns, as shown in figure 1. All the XRD peaks of the TiO_2 thin films can be attributed to rutile phase. V ion implanted TiO_2 thin film calcined at 700 °C for 5 h displays very sharp XRD peaks and the peak intensities of this sample were higher than that of the sample calcined at 500 °C for 5 h. According to Bragg's Law, the lattice parameters of the TiO_2 thin film calcined at 500 °C for 5 h are $a = 4.5880$ Å and $c = 2.9697$ Å, respectively. However, only slight changes of the lattice parameters in terms of V-ion-implanted TiO_2 thin films calcined at 500 °C for 5 h ($a = 4.5913$ Å and $c = 2.9622$ Å) and calcined at 700 °C for 5 h ($a = 4.5978$ and $c = 2.9560$ Å) were seen. Considering that the radii of V^{4+} ion (0.72 Å) being quite close to that of Ti^{4+} ion (0.74 Å) in an octahedral coordination, V^{4+} ions are believed to enter and replace Ti^{4+} sites in the lattice of TiO_2, resulting in the observed slight changes in the lattice parameters of TiO_2 crystal [16]. XPS analyses of the V ion implanted TiO_2 thin films did not show any significant peaks attributed to VOx species (data not shown here). This result is the clear evidence that the implanted V ions exist in the deep bulk inside of TiO_2 lattice with a high dispersion state.

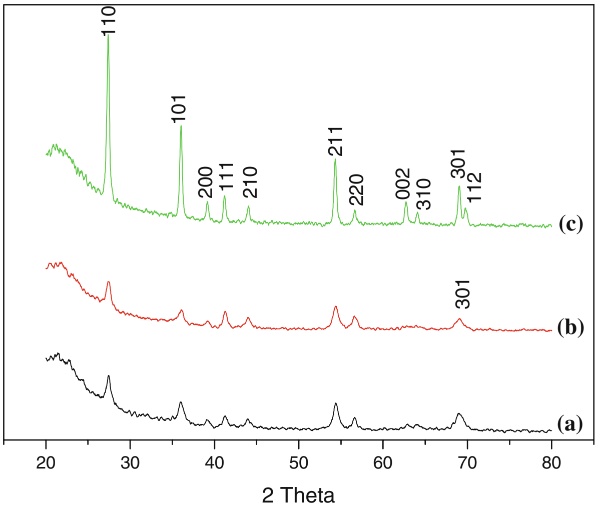

Figure 1. XRD patterns of (a) TiO_2 thin film calcined at 500 °C for 5 h and V-ion-implanted TiO_2 thin films calcined at (b) 500 °C and (c) 700 °C for 5 h.

Figure 2 shows the UV-vis transmittance spectra of TiO_2 thin film and V ion implanted TiO_2 thin film calcined at 500 °C for 5 h. These films exhibit high transparency and clear specific interference fringes in the visible light regions [12]. Thus, it is clearly indicated that the highly transparent and uniform TiO_2 thin films have been successfully prepared on a quartz substrate by the ICB deposition method and the implanted V ions have improved the electronic properties of the TiO_2 thin films, resulting in the shift of the absorption edge towards visible light regions [11,12]. The V ion implanted TiO_2 thin films actually showed transparent pale yellow color, its extent depending on the thickness, meaning the efficient absorption of visible light. The photocatalytic complete oxidation of formic acid dissolved in an aqueous solution was performed under visible light irradia-

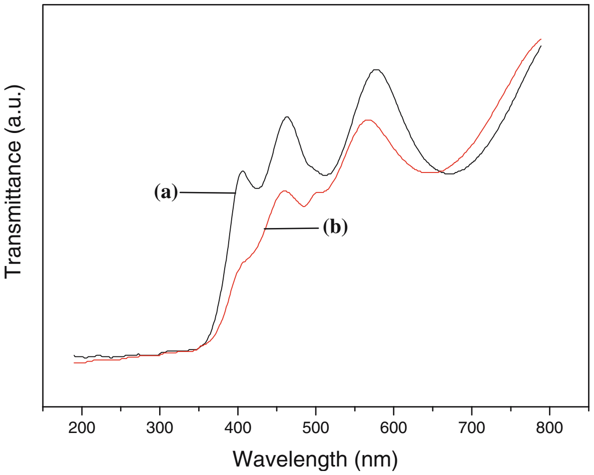

Figure 2. The UV-vis transmittance spectra of (a) TiO_2 thin film calcined at 500 °C for 5 h and (b) V-ion-implanted TiO_2 thin film calcined at 500 °C for 5 h.

tion ($\lambda > 450$ nm) using the prepared TiO_2 thin films, and their reaction profiles are shown in figure 3. The original TiO_2 thin film almost did not show any photocatalytic reactivity under visible light irradiation even after a prolonged irradiation of 20 h. However the photocatalytic complete oxidation was observed to proceed on the V ion implanted TiO_2 thin films under visible light irradiation. The photocatalytic reactivity of the V ion implanted TiO_2 thin films was found to be remarkably enhanced and improved as compared to that of the original TiO_2 thin film. This indicates that the TiO_2 electronic properties had been successfully modified by the implantation of V ions by the substitution of the lattice Ti^{4+} ion with V^{4+} ion, shifting its absorption band towards visible light regions, and exhibiting the photocatalytic reactivity even under visible light irradiation, as reported in the previous papers [11,12]. However, if the V ions were doped into TiO_2 by chemical methods such as the sol–gel and impregnation, the doped V ions formed small V-oxide islands in the bulk TiO_2 which act as the electron–hole recombination centers, and resulting in a dramatic decrease in the photocatalytic reactivity under band gap irradiation, as it is well known. Thus, the modification by the ion-implantation is not the case, and this physical doping causes a completely different modification of the electronic properties of TiO_2 photocatalyst from the chemical doping.

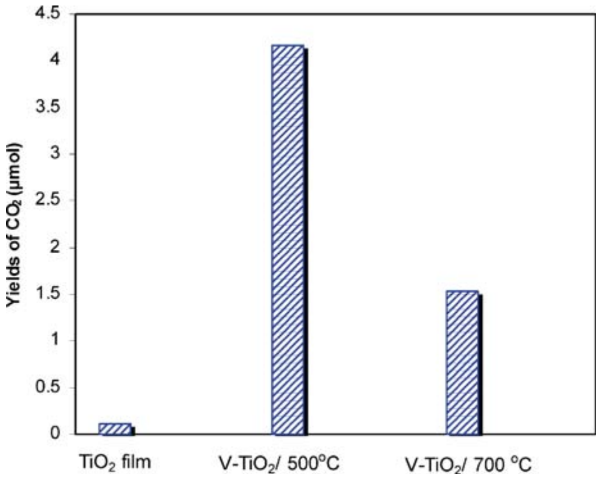

Figure 3. Photocatalytic degradation of formic acid diluted in water over TiO_2 thin film and V-ion-implanted TiO_2 thin films calcined at different temperatures under visible light irradiation ($\lambda > 450$ nm) after 20 h reaction.

In order to clarify the differences of the V ion implanted TiO_2 thin films under different calcination temperatures in terms of surface parameters, FE-SEM and AFM measurements were performed, and their images are shown in figure 4. Compared with the morphology of V ion implanted TiO_2 thin film calcined at 700 °C for 5 h, the surface of the V ion implanted TiO_2 thin film calcined at 500 °C is more uniform. The relevant surface properties such as particle diameter and roughness are reported in table 1. It can be seen from table 1 that the V ion implanted TiO_2 thin film calcined at 500 °C for 5 h exhibit the lowest roughness, indicating that the surface of the V ion implanted TiO_2 thin film is more regular than that of V ion implanted TiO2 thin film calcined at 700 °C for 5 h. When the calcination temperature was 700 °C, the particle size of the V ion implanted TiO_2 thin film increased. The V ion implanted TiO_2 thin film calcined at 700 °C for 5 h exhibits a morphology of mixed small and elongated hexagonal dipyramid, in which the particle size is not uniform. The AFM image of the V ion implanted TiO_2 thin film was in a good accordance with the FE-SEM image. The roughness of the V ion implanted TiO_2 thin film calcined at 700 °C for 5 h was 10.5 (given by AFM software), larger than that of TiO_2 thin film calcined at 500 °C for 5 h. Although the photocatalytic reactivity of the TiO_2 thin film increased remarkably by the implantation of V ions, the calcination temperature is also believed to be an important factor to modify and improve the photocatalytic reactivity of TiO_2 thin films.

In conclusion, TiO_2 thin film photocatalysts, which are environmentally friendly, have been successfully prepared on a quartz substrate by a combination of an ICB deposition method and a metal-ion-implantation method. The V ion implanted TiO_2 thin films was found to work as an efficient photocatalyst under visible light irradiation ($\lambda > 450$ nm) for the complete oxidation of formic acid diluted in water. The origin of an enhancement of photocatalytic reactivity of the V ion implanted TiO_2 thin film was attributed to the modification of the electronic properties of TiO_2 thin film photocatalyst by the efficient substitution of the lattice Ti ions with V ions by ion-implantation, a physical doping method, which allows the doping of V ions with a high dispersion state.

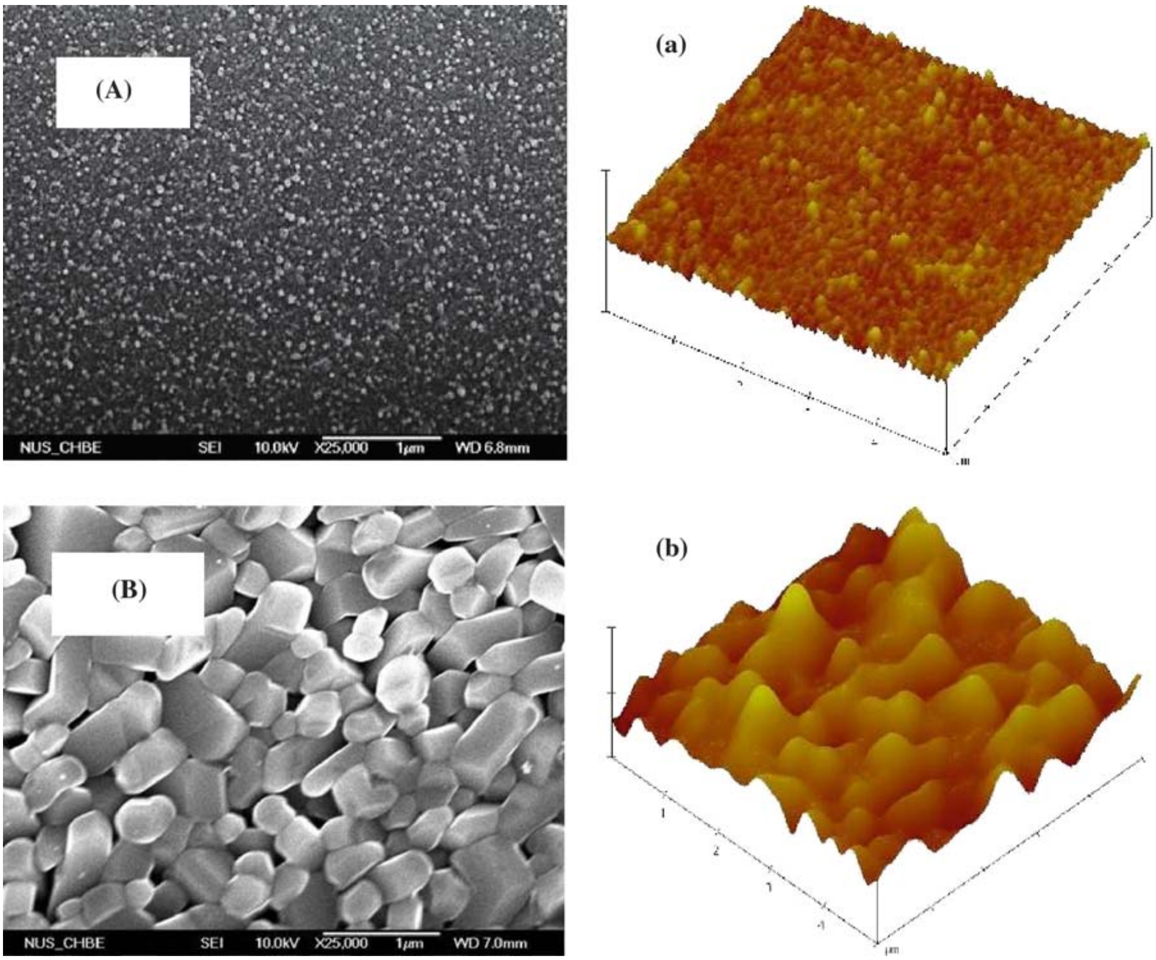

Figure 4. FE-SEM micrographs (A–B) and AFM images (a–b) of V-ion-implanted TiO_2 thin films calcined at 500 °C for 5 h (A, a) and 700 °C for 5 h (B, b).

Table 1
Particle diameter and roughness of V-ion-implanted TiO_2 thin film

	V-ion-implanted TiO_2 film (500 °C 5 h)	V-ion-implanted TiO_2 film (700 °C 5 h)
Min. particle diameter (nm)	15	230
Max. particle diameter (nm)	325	779
Mean particle diameter (nm)	89	493
Roughness rms (nm)	1.6	10.5

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