

New Preparation Method of Visible Light Responsive Titanium Dioxide Photocatalytic Films

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Abstract

We report a new and simple preparation method of the visible light responsive Titanium dioxide (TiO₂) photocatalytic films using sol-gel method and ultraviolet light (UV) irradiation. Proposed films were prepared on fused silica plates using titanium tetra-isopropoxide, urea, 2-methoxyethanol, water and UV irradiation. The 650°C-annealed films were carbon-containing anatase type TiO₂, not carbon-doped ones. The prepared films absorbed visible light with wavelengths longer than 400 nm. Also, organic dyes were effectively photodegraded by visible light irradiation in the presence of these films.

Keywords

Titanium Dioxide Films; Sol-Gel Method; UV Irradiation; Visible Light Responsive Photocatalyst

1. Introduction

Titanium dioxide (TiO₂) has been widely studied for many applications, such as paints, cloth fibers, cosmetics and microelectronics, optical cells, solar energy conversion, photocatalyst for environmental purification and production of hydrogen gas, and so on. This is because TiO₂ is a cheap material and shows nontoxicity, high activities and chemical stability. In particular, various anatase type TiO₂ powders and films have been fabricated for development of photocatalytic activities such as strong organic degradation and superhydrophilicity [1]-[6]. However, photocatalytic reactions by TiO₂ only proceed under ultraviolet (UV) irradiation, but do not proceed

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under visible light irradiation. That is because the anatase type pure TiO₂ only absorbs UV light with wavelength shorter than 380 nm, based on its wide band gap (3.0 - 3.2 eV). However, UV light accounts for only about several % of solar energy. In addition, UV light responsive photocatalysts had been limited for use in the room because there are not a lot of UV lights in the room.

Recently, many attempts to develop the effective photocatalysts for the visible light region have been done [7]-[11]. That is, a lot of visible light responsive TiO₂ photocatalysts, whose photocatalytic reaction can proceed under visible light, have been developed by doping something elements to the TiO₂ crystal lattice or reduction of TiO₂. The shift of the optical response of TiO₂ from UV to the visible spectral range will have a profound positive effect on the efficient use of solar energy in photocatalytic reactions and the use in the room. The doping of TiO₂ is currently attracting considerable interest as a promising route to extend the optical absorption of this material to visible spectral region. One promising approach to synthesizing visible light active photocatalysts is the substitution of Ti by transition metals, such as V, Cr, Ni, or Fe, and so on [12]-[15]. However, most of these metal-doped TiO₂ do not show long-term stability or do not have sufficient activities for wide range of applications. Another promising approach is the doping of nonmetal atoms, such as N, S, or C [16]-[21]. The nonmetal atoms doping have been reported to be more effective for the band gap narrowing of TiO₂ than transition metal doping [19] [20]. That is because their impurity levels are near the valence band edge of TiO₂. Therefore, they do not act as charge carriers and their roles as recombination centers are minimized compared to the metal doping [13] [19] [20]. As a famous example of nonmetal doping, Asahi and co-workers proposed that substitutional-type N doping was effective for the band gap narrowing of TiO₂ due to the mixing of N 2p with O 2p states in the valence band [16]. As for the investigation of TiO₂ modified with C, it has been reported some types of TiO₂ such as substitutional C-doped TiO₂, interstitial carbonate-doped TiO₂ and highly condensed coke-like carbon containing TiO₂ and so on [21]-[34]. It is reported that the TiO₂ modified with C induce the visible light absorption by band gap narrowing or a role as photosensitizer like organic dyes. In these ways, the design of the electronic structure or the chemical modification of metal oxides was very effective for controlling their optical properties. However, an expensive apparatus was used or there were some safety hazard in these proposed methods.

On the other hand, the sol-gel method is one of the suitable and simple techniques for preparation of metal oxide films. In addition, it is also suited to design the network formation of metal oxide precursors, resulting in materials with special optical and catalytic properties. Furthermore, UV irradiation of metal oxide gel films is effective for the decomposition of organic compounds in the films or improvement of crystallinity of the films, and so on [35]-[38]. In this paper, we report a safety and simple preparation method of the visible light responsive TiO₂ photocatalytic films by sol-gel and UV irradiation method.

2. Materials and Methods

2.1. Preparation of TiO₂ Precursor Sol Solutions

All chemicals used in this study were of analytical grade and were used without further purification. The preparation methods of TiO₂ precursor sol solutions (a)-(d) were as follows: The 0.25 mol/dm³ titanium-*tetra*-isopropoxide (Ti(O-*i*-Pr)₄) was dissolved in 2-methoxyethanol under dry argon gas. Then urea was added to the solution and it was refluxed at 130°C for 3 hours. After cooling the solution to room temperature, UV light (250 W ultra-high pressure mercury lamp, 100 mW/cm² at 365 nm) was irradiated to the sol solution for 4 hours in the air at room temperature. After that, a small amounts of distilled water was added to it and it was stirred for one night. The preparation conditions of sol solutions were shown in **Table 1**.

2.2. Preparation of TiO₂ Films

Fused silica plates (25 × 25 × 1 mm) were used as support substrates. The fused silica plate was dipped into the TiO₂ precursor sol solution. The dipped plate was withdrawn from the solution at the rate of 0.5 mm/s. The dip-coated films were dried at room temperature for 30 s and then dried at 100°C for 30 min. After drying, the films were heated at the rate of 10°C/min and annealed at 650°C for 1 hour in the air.

2.3. Characterization

The crystal structures of the films were identified by thin film X-ray diffraction (XRD: MPX, Mac Science)

Table 1. Preparation conditions of TiO₂ precursor sol solutions and films.

TiO ₂ films	Sol	Ti(O- <i>i</i> -Pr) ₄ (mol/dm ³)	Urea (mol/dm ³)	H ₂ O (mol/dm ³)	UV irradiation
(A)	(a)	0.25	0.5	0.5	Irradiated
(B)	(b)	0.25	0	0.5	Irradiated
(C)	(c)	0.25	0.5	0.5	Non
(D)	(d)	0.25	0	0.5	Non

measurements using CuK α radiation. The acceleration voltage and current were 40 kV and 30 mA, respectively. The UV-visible (UV-vis) absorption spectra of the films were taken on a Hitachi U-4100. Elemental analysis of C, H, and N in the dried and annealed gels was carried out in an elemental analyzer Thermo Finnigan Flash EA 1112. The dried gels were prepared by vacuum drying of the sols at room temperature and the annealed gels were prepared by sintering of the dried gels at 650°C for 1 hour. X-ray photoelectron spectroscopy measurements of the films were carried out using a Sigmaprobe spectrometer (XPS: Thermo Electron) with MgK α X-ray ($h\nu = 1254$ eV) radiation to investigate the surface properties. The shift of the binding energy due to relative surface changing was corrected using the C1s level at 284.5 eV as an internal standard. Ar⁺ etching was applied to clean the surface of samples and to measure the depth profiles. The estimated etch rate of the ion gun was expected to be about 0.05 nm/s for the TiO₂ thin films [39]. ¹H-NMR spectra of the TiO₂ precursor dried gels were recorded on a Varian INOVA300 spectrometer in CDCl₃.

2.4. Photocatalytic Evaluation of TiO₂ Films

The photocatalytic activities of prepared TiO₂ films were evaluated by examining photodecomposition of methylene blue (MB). The substrates coated with TiO₂ films were placed in a 1.0×10^{-2} mmol/dm³ aqueous solution containing MB for 18 hours under dark. Then the solutions were irradiated with visible light (wavelength: 410 - 520 nm). Used lamp was 250 W ultra-high pressure mercury lamp (UHPML: multilight UIV-270, Ushio) and two pieces of glass filters were used for selection of wavelength (No. 3-73 and 7-59, Corning). The concentration change of MB by visible light irradiation was evaluated by monitoring 665 nm absorbance using the UV-vis light spectrometer U-4100 at hourly intervals.

3. Results and Discussion

3.1. Characterization of the TiO₂ Films

Figure 1 shows the XRD patterns of TiO₂ films (A)-(D) prepared using the sol solutions (a)-(d). For each sample, all peaks were indexed to the anatase phase of TiO₂ (JCPDS file No. 21-1272). The average crystallite sizes were calculated using (101) diffraction peaks according to the Scherrer equation. The crystallite sizes of all films were almost the same, ca 18 nm.

Figure 2(a) shows UV-vis absorption spectra of TiO₂ films (A)-(D). A strong absorption assigned to the band-band transition can be observed in the ultraviolet region for all samples. In addition, all TiO₂ films absorbed not only UV light, but also visible light with wavelength longer than 400 nm. In particular, the absorbance of the TiO₂ film (A) prepared using the sol solution (a) was higher than that of the films (B)-(D). Assuming the materials to be an indirect semiconductor, the band gap energies of films were estimated from the intercept of the tangents to the plots of $(\alpha h\nu)^{1/2}$ versus photon energy $h\nu$ as shown in **Figure 2(b)** [21]. The optical band gap energies of all films estimated from the plots of **Figure 2(b)** were around 3.2 eV. It is known that the band gap energy of anatase type TiO₂ is 3.2 eV. Accordingly, it was expected that the visible light absorptions in these films were not due to band gap narrowing.

The CHN elemental analysis of 650°C-annealed TiO₂ powder samples was carried out in order to examine the reasons of visible light absorption as shown in **Table 2**. The found values of elemental analysis were C: 0.12% - 0.23%, H: 0.00% and N: 0.00% in all samples. The visible light absorption of TiO₂ will be due to carbon species including in the films.

The XPS measurements were carried out to determine the chemical state of elements around the surface of films in details. **Figure 3** shows N1s spectra of films (A)-(D). Broad energy bands were observed in the range

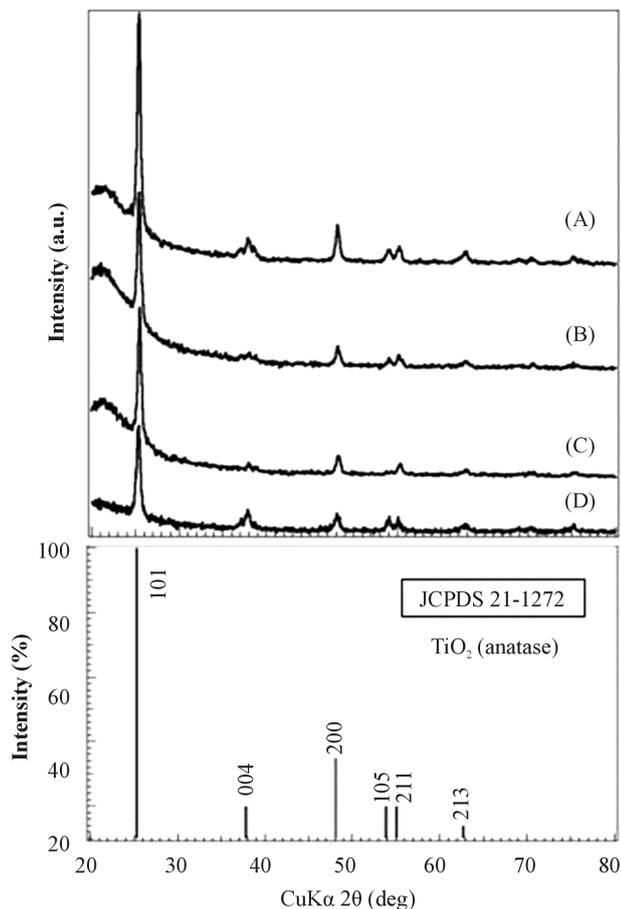


Figure 1. XRD patterns of sol-gel derived TiO₂ films. (A) TiO₂ film which was made from the sol solution (a); (B) TiO₂ film which was made from the sol solution (b); (C) TiO₂ film which was made from the sol solution (c); (D) TiO₂ film which was made from the sol solution (d).

Table 2. The CHN elemental analysis of TiO₂ annealed at 650 °C.

Sol solution	650 °C-annealed TiO ₂		
	C (%)	H (%)	N (%)
(a)	0.23	0.00	0.00
(b)	0.20	0.00	0.00
(c)	0.16	0.00	0.00
(d)	0.12	0.00	0.00

from 404 to 396 eV before surface etching (etching time 0 s). However, these bands disappeared after surface etching for 20 s (ca. 1 nm etching from the surface). From the results, broad N1s bands around 400 eV can be assigned to adventitious nitrogen species on the surface. Accordingly, it was clear that nitrogen is not included in the films. The results of N1s spectra agreed with those of the elemental analysis. **Figure 4** shows C1s spectra of films (A)-(D). Broad energy bands were observed in the range from 290 to 282 eV before surface etching (etching time 0 s). The peaks around 289, 286 and 284.5 eV for all films before surface etching can be assigned to adventitious carbon species, C = O of CO₃²⁺, C-O and C-C, respectively [21] [25]. After surface etching for 20 s, adventitious carbon species on the surface disappeared and new peaks appeared around 283.5 eV. Accord-

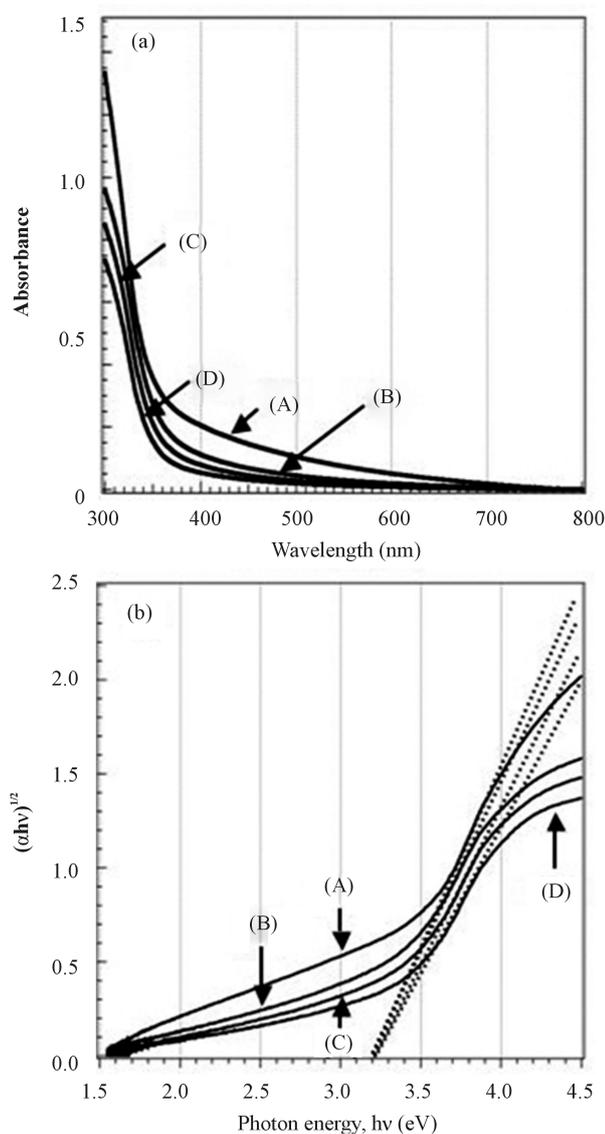


Figure 2. UV-vis absorption spectra (a) and plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) (b) of sol-gel derived TiO_2 films. (A) TiO_2 film which was made from the sol solution (a); (B) TiO_2 film which was made from the sol solution (b); (C) TiO_2 film which was made from the sol solution (c); (D) TiO_2 film which was made from the sol solution (d).

ing to the literatures, it has been reported that there are highly condensed coke-like carbon originated from another C-C species, that is, Ti-alkoxide derived C-C species in the films in the case of sol-gel method using alkoxide precursors [22] [27]. Thus, it was suggested that the new peaks around 283.5 eV were originated from Ti-alkoxide derived C-C species that were different from adventitious carbon species. Furthermore, the peak around 283.5 eV of film (A) was greater than those of films (B)-(D) in the case of surface etching for 20 s. In addition, the peak around 283.5 eV of film (A) after surface etching for 140 s (ca. 7 nm etching from the surface) got larger than that after surface etching for 20 s. From the results of **Figures 2, 4** and **Table 2**, it was found that the visible light absorption got stronger with increasing of the amounts of C species in the sample. These results agreed with an earlier report [20] [27]. On the other hand, new small peaks appeared around 281 eV for all films after etching for 140 s. The peak around 281 eV can be assigned to Ti-C species [21] [24] [25]. It was expected that the oxygen sites of TiO_2 lattice were substituted by carbon atoms and Ti-C structures were formed in the

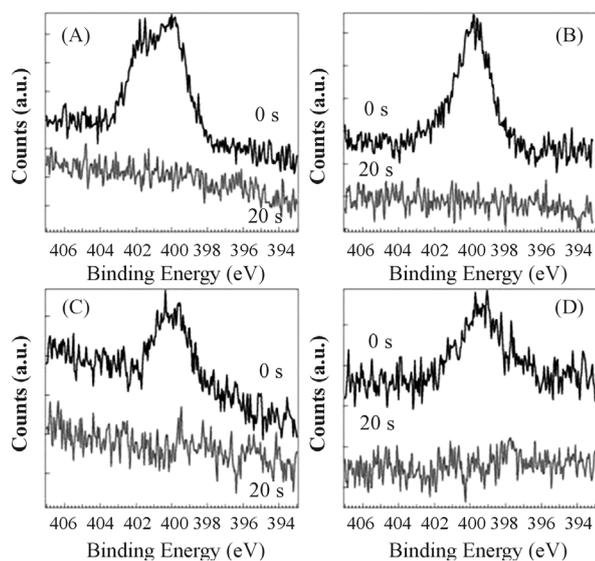


Figure 3. XPS spectra of N1s of sol-gel derived TiO₂ films. The digits, 0 s and 20 s, in figures show etching time. (A) TiO₂ film which was made from the sol solution (a); (B) TiO₂ film which was made from the sol solution (b); (C) TiO₂ film which was made from the sol solution (c); (D) TiO₂ film which was made from the sol solution (d).

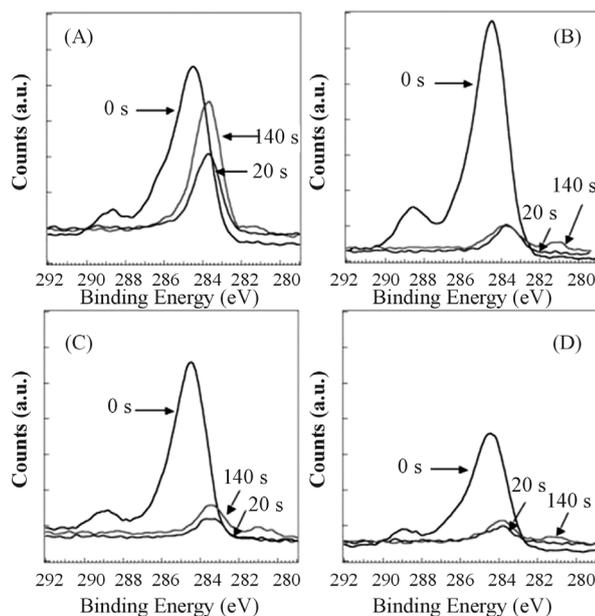


Figure 4. XPS spectra of C1s of sol-gel derived TiO₂ films. The digits, 0 s, 20 s and 140 s, in figures show etching time. (A) TiO₂ film which was made from the sol solution (a); (B) TiO₂ film which was made from the sol solution (b); (C) TiO₂ film which was made from the sol solution (c); (D) TiO₂ film which was made from the sol solution (d).

crystal lattice. However, it might not be effective for the visible light absorption because a quantity of Ti-C species formed in the crystal lattice was very few and the formed Ti-C species were not in the surface. Therefore, it was expected that the visible light absorption of TiO₂ is due to photosensitization by coke-like carbon formed in

the films [20]-[22] [27] [28]. In the literature [21], it has been reported that two possible pathways ascribed to band gap narrowing by carbon doping and to carbon photosensitization are not involved in the photoreaction for single-nonmetal doped TiO₂. The results in this paper accorded with the former report.

3.2. Formation Mechanism of Carbon-Containing TiO₂

Formation mechanism of carbon-containing TiO₂ will be considered as follows: Ti(O-*i*-Pr)₄ was easy to be hydrolyzed by H₂O addition and form precipitations in the solution in the case of using isopropyl alcohol as a reaction solvent. However, Ti(O-*i*-Pr)₄ formed a stable and homogeneous TiO₂ precursor sol without precipitating in the solution after H₂O addition in the case of using 2-methoxyethanol as a reaction solvent. From these phenomena, it was expected that Ti(O-*i*-Pr)₄ caused solvent exchange reaction and/or alcoholysis reaction with 2-methoxyethanol, that is, 2-methoxyethanol attached to the titanium metal center [40]-[43]. As a result, the six-coordinated Ti complexes were formed in the reaction and stabilized for hydrolysis.

Table 3 shows the colors of prepared sol solution and results of the CHN elemental analysis of TiO₂ precursor gels dried in a vacuum oven at room temperature. The sol solution prepared without urea remained transparent after H₂O addition as shown in **Tables 3(b)** and **(d)**. It has shown that these solutions are stabilized for hydrolysis. That will be because Ti(O-*i*-Pr)₄ caused solvent exchange reaction and/or alcoholysis reaction with 2-methoxyethanol as described above. Furthermore, the color of sol solution prepared without urea has changed from clear transparent to yellow transparent after UV irradiation (**Tables 3(b)** and **(d)**). Considering the ligand field theory, the result may be because division width of the *d*-orbitals in titanium became narrow by change of ligand field, that is, ligands of titanium fully exchanged from isopropoxides to 2-methoxyethoxides by UV irradiation [44]-[47]. According to ¹H-NMR spectra, the doublet peak at 1.25 ppm originated from methyl groups of isopropoxides disappeared by irradiating UV light as shown in **Figure 5**. From the result, it was suggested that the ligand substitution reaction occurred by UV irradiation. In addition, carbon contents in the dried gel and the annealed TiO₂ prepared from sol solution (b) with UV irradiation were more than those in the dried gel and the annealed TiO₂ prepared from sol solution (d) without UV irradiation as shown in **Tables 2** and **3**. It may be because eliminated organic ligands (isopropoxides) were decomposed and condensed as cokes in the gels by UV irradiation.

On the other hand, the rate of hydrolysis and gelation for the sol solutions prepared using urea (**Tables 3(a)** and **(c)**) was faster than that for the sol solutions prepared without urea (**Tables 3(b)** and **(d)**). In addition, the dried gels prepared with urea have included nitrogen as shown in **Tables 3(a)** and **(c)**. According to the literatures [48]-[50], it has been reported that urea coordinates to titanium through weak C=O → Ti coordination bonding with remaining the carbonyl groups. Therefore, it was expected that the sites coordinated by urea are

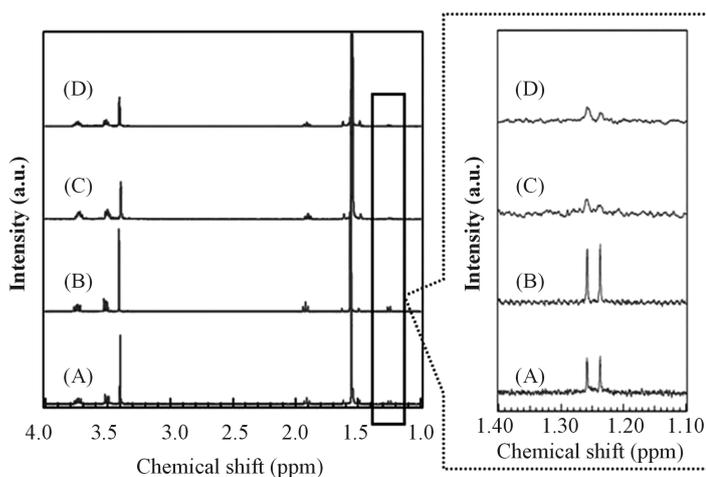


Figure 5. ¹H-NMR spectra of the TiO₂ precursor dried gels prepared without urea. (A) Dried gel before UV irradiation and without H₂O addition; (B) Dried gel prepared without UV irradiation and with H₂O addition; (C) Dried gel prepared after UV irradiation and without H₂O addition; (D) Dried gel prepared after UV irradiation and with H₂O addition.

easy to be hydrolyzed by H₂O. Furthermore, nitrogen and carbon contents in the dried gels increased by UV irradiation (Tables 3(a) and (c)). According to ¹H-NMR spectra, the ratio of integral value of peak assigned to NH₂ groups in urea and that of OCH₃ groups in 2-methoxyethoxides became larger by UV irradiation. From the results, in the case of the samples prepared using urea, it was suggested that ligands of titanium changed from 2-methoxyethoxides to urea by UV irradiation. After that, the released organic ligands were decomposed and condensed by UV irradiation, coke-like carbon would have been formed in the gels. About nitrogen, it was expected that urea eliminated by hydrolysis was decomposed after annealing and nitrogen species released completely from the gels. In this way, it was suggested that TiO₂ became able to absorb the visible light because the carbon contents in the TiO₂ improved by urea addition and UV irradiation.

3.3. Photocatalytic Evaluation of TiO₂ Films

In order to evaluate the photocatalytic activities of the prepared TiO₂ films toward visible light irradiation, the absorbance change of MB at 665 nm was monitored as a function of visible light irradiation time. Figure 6 shows plots of ln(C/C₀) vs irradiation time *t*, where C₀ and C are the concentrations of MB at *t* = 0 and *t* = *t*, respectively. Concentrations of MB were calculated from the absorbance. MB aqueous solutions immersing TiO₂

Table 3. The colors of TiO₂ precursor sol solution and the CHN elemental analysis of TiO₂ precursor gels dried in a vacuum oven at room temperature.

Sol solution	Sol color	Dried gel		
		C (%)	H (%)	N (%)
(a)	Milky yellow (gelation)	18.4	4.9	21.5
(b)	Yellow transparent	14.4	3.5	0.0
(c)	Milky white (gelation)	18.0	4.8	17.0
(d)	Clear transparent	13.5	3.4	0.0

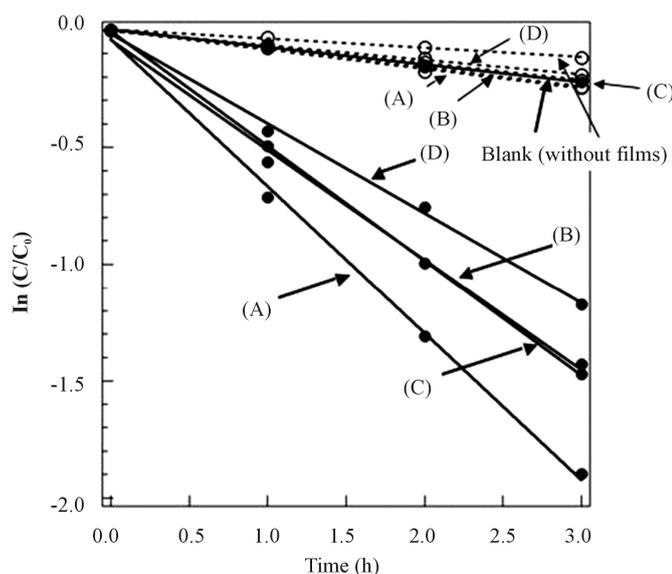


Figure 6. Photocatalytic activities of sol-gel derived TiO₂ films under visible light irradiation (wavelength: 410 - 600 nm). Dotted lines show the concentration changes of methylene blue under dark. (A) TiO₂ film which was made from the sol solution (a); (B) TiO₂ film which was made from the sol solution (b); (C) TiO₂ film which was made from the sol solution (c); (D) TiO₂ film which was made from the sol solution (d).

films (A)-(D) were clearly photo-bleached by visible light irradiation. The photo-bleaching of MB is caused by photo-oxidative decomposition derived from electron holes on valence band of TiO₂ or photo-reduction derived from electrons photo-generated on conduction band of TiO₂. Generally, it is reported that photo-reduction is difficult to occur because the electrons photo-generated and excited from valence band to conduction band are trapped by O₂ in the air [2] [4] [51] [52]. Therefore, photo-oxidative decomposition is easy to be caused by electron holes on valence band of TiO₂ instead. When photo-reduction of MB occurs, a new peak originated from reduction form of MB is observed at 256 nm in the UV-visible absorption spectra. In this experiment, the new peak at 256 nm did not appear together with photo-bleaching of MB. Therefore, the photo-bleaching in this experiment was judged to be due to the photo-oxidative decomposition. The photo-oxidative decomposition of MB in the presence of the TiO₂ films obeyed good first-order kinetics. The apparent rate constant was obtained from the slope of the straight line, which was strongly dependent on the visible light absorbance of films as shown in **Figure 6**. In particular, the decomposition rate of MB in the presence of the film (A) was faster than that of the other films (B)-(D). In this way, the TiO₂ films prepared by these methods showed visible light responsive photocatalytic activities.

On the other hand, upon illumination in the absence of the photocatalytic films, the concentration of MB slightly decreased with increasing of visible light irradiation time. This fact meant that MB itself slightly absorbed visible light in this region and was a little photo-bleached. According to the UV-visible absorption spectral measurement of MB, the phenomena were suggested to be due to the photodecomposition of MB. Moreover, the concentration changes of MB aqueous solutions under dark were measured and shown in dotted lines of this figure. Also under dark, the concentration of MB slightly decreased over time in the solution immersing TiO₂ films (A)-(D) and without films (blank). From the results, MB has been slightly removed from the liquid phase just by their adsorption on TiO₂ films and/or the glass beaker surface. However, their influence can be omitted because the amounts of the photo-absorption of MB itself and the adsorption of MB on the surface are little.

4. Conclusion

Carbon-containing TiO₂ films were prepared using the four types of sol solutions. All films were anatase type TiO₂ and absorbed visible light with wavelength longer than 400 nm effectively. In addition, the photocatalytic activities of the films under visible light (410 - 520 nm) irradiation were confirmed by evaluation of the MB decomposition. The sol-gel method using urea addition and UV irradiation was simple and effective method for the fabrication of visible light responsive TiO₂ photocatalyst.

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