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Photocatalytic activity of metal-doped titanium oxide films prepared by sol-gel process

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Abstract. Visible-light photocatalytic activity of metal-doped TiO$_2$ films prepared by dip-coating method was investigated. Cu, Fe, and Al atoms were doped in the TiO$_2$ films and they exist as their oxide in the nearly stoichiometric TiO$_2$ matrices. It is found that the Cu doping is effective for visible-light photocatalysis of the TiO$_2$ films, while Fe- and Al-doped films hardly shows visible-light photocatalytic activity. The optical absorption spectra for the non-doped and metal-doped TiO$_2$ films show that effective band gap narrowing is observed in the Fe- and Cu-doped TiO$_2$ films. Recombination of the photogenerated electron/hole pairs takes place quickly in the Fe-doped TiO$_2$ film, while the charge separation of the photogenerated electron/hole pairs takes place effectively in the Cu-doped TiO$_2$ film. Al doping into the TiO$_2$ film has hardly effect on photocatalysis of TiO$_2$ films.

1. Introduction
Titanium dioxide (TiO$_2$) is well known as chemically stable and harmless material, and has been applied widely in various fields [1-5]. For example, it is used for surface coating, photoelectrodes, high-k dielectrics, paints, cosmetics, and so on. In recent years, it has been received a great deal of attention especially as a photocatalytic material [5-7]. TiO$_2$ which shows specific photocatalytic properties, such as photo-induced decomposition of organic compounds and photo-induced hydrophilicity [5, 8, 9], is expected to apply in the environmental fields. Various utilizations such as antibacterial, antipollution and deodorization have been attained [6]. Because of these unique photocatalytic properties, application of the TiO$_2$ will spread increasingly from now on. However, ultraviolet-light (UV-light) irradiation is necessary to fulfill its photocatalytic functions, so the TiO$_2$ photocatalyst is holding many problems on limitation of application range, effective use of light, and so on. In order to improve the photocatalytic efficiency and to expand the application fields, development of the photocatalyst responding to visible-light (VIS-light) is demanded.

Development of visible light photocatalytic materials has been intensively investigating, for example, noble metal oxides with narrow band gap, doping of transition metals or non-metallic elements into the TiO$_2$ [10-18]. In case of the transition metal doping into the TiO$_2$, it has been reported that ion-implantation is effective, but chemical doping is ineffective [19].

This paper describes the VIS-light photocatalytic activity of the metal-doped TiO$_2$ films prepared by sol-gel method. In this study, Cu, Fe, and Al were selected as dopants with coordination number of 2 or 3. It is found that Cu-doping is effective for VIS-light photocatalysis, while Fe- and Al-doped TiO$_2$ films hardly show VIS-light photocatalytic activity.
2. Experimental

Metal-doped TiO$_2$ films were prepared by dip-coating using sol solution mixed tetraisopropoxymethyl, ethanol, hydrochloric acid, water, and metallic salt. The procedure of preparation of the sol solution was as follows: the mixture of tetraisopropoxymethyl (TIPT) and ethanol (C$_2$H$_5$OH) was stirred for 2 hours, and metallic salt was dissolved in the mixture of C$_2$H$_5$OH, deionized water (H$_2$O), and hydrochloric acid (HCl) and also stirred for 2 hours, after then both solutions were mixed and stirred for more 2 hours. The ratio of each reagent was TIPT:C$_2$H$_5$OH:H$_2$O:HCl=1:5:5:0.4, and 2 mol. % of metallic salt against TIPT was added in case of deposition for the metal-doped TiO$_2$ films. The metallic salts used in this study were all anhydrous; CuCl$_2$, FeCl$_3$, and AlCl$_3$. The flow of preparation of the sol solution is shown in figure 1. Dip-coating and pre-annealing at 120 ºC for 10 min were repeated three times and then post-annealed at 500 ºC for 30 min. After post-annealing, film thickness was about 300 nm. All heat treatments were carried out under nitrogen ambient. Characterizations of the deposited films were carried out by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and optical absorption spectroscopy, respectively.

Photocatalytic activity of the metal-doped TiO$_2$ films was evaluated by measuring the decomposition of stearic acid using Fourier-transform infrared spectroscopy (FT-IR). The film surface was covered by dip-coated stearic acid using the solution which the stearic acid powder (0.475 g) was solved in the hexane solvent (100 ml). The withdrawal speed was 10 mm/sec. After the stearic acid coated on the backside surface was wiped off, substrates were dried for 10 min in a dark space. Iterative measurements of infrared spectra were carried out after 1 hour VIS- or UV-light irradiation. These procedures were carried out under room temperature. The fluorescent light with UV-cut filter (<420 nm) and black-light were used for VIS- and UV-light sources, respectively.

3. Results and Discussion

3.1. Structural evaluation of the films

The film composition was analyzed by XPS. The XPS spectra of Ti 2p and O 1s electrons of Cu-doped TiO$_2$ film are shown in figures 2 (a) and (b). The binding energy of Ti 2p at 459.1 eV shifting from 454 eV of metallic Ti is the signal of Ti in TiO$_2$ [20], and that of O 1s at 531 eV is assigned to metallic oxide [20].

Figures 3 (a), (b), and (c) show the XPS spectra of Cu 2p, Fe 2p, and Al 2p of each metal-doped TiO$_2$ film, respectively. These results reveal that every metal element exists as its oxide in the nearly stoichiometric TiO$_2$ matrices and its content is estimated about 2 at. % by calculation using sensitivity factor of each metal element.

The crystalline structure of the films was evaluated by XRD. The X-ray diffraction patterns for the non-doped, Cu-doped, Fe-doped, and Al-doped TiO$_2$ films after annealing at 500 ºC are shown in figure 4. All the films show the diffraction peak of anatase (101) of TiO$_2$. It is found that the crystallization of the TiO$_2$ is hardly affected by metal doping though the peak intensities of the metal-
doped films are slightly weaker than that of the non-doped film.

![Figure 2 XPS spectra of Ti 2p and O 1s electrons of Cu-doped TiO\textsubscript{2} film: (a) Ti 2p and (b) O 1s.](image)

![Figure 3 XPS spectra of metal-doped TiO\textsubscript{2} film: (a) Cu, (b) Fe, and (c) Al.](image)

![Figure 4 XRD patterns of non-doped and metal-doped TiO\textsubscript{2} films.](image)
3.2. Photo-induced decomposition of stearic acid

The photo-induced decomposition reaction was evaluated by measuring degradation of stearic acid using FT-IR. Figure 5 shows the photo-induced degradation of stearic acid as a function of VIS-light irradiation time. Vertical axis expresses the absorption intensity normalized to that before irradiation. For the Cu-doped TiO₂ film, VIS-light photocatalytic degradation is obviously observed, while Fe- or Al-doped film hardly shows photocatalytic activity. Figure 6 shows the optical absorption spectra for the non-doped and metal-doped TiO₂ films. Because the absorption edge shift toward longer wavelength compared with that of the non-doped TiO₂ film is observed for the Cu- and Fe-doped films, effective band gap narrowing occurs in these films. It is considered that Cu and Fe atoms doped in the TiO₂ films substitute for Ti sites and exist as their oxides and these oxides form impurity levels in the band gap of TiO₂ films. The XPS measurements show that Al atoms also substitute for Ti sites and form aluminum oxides, however, it is not clear whether these oxides form impurity levels in the band gap of TiO₂.

![Figure 5](image1.png)

**Figure 5** Normalized absorbance of stearic acid as a function of VIS-light irradiation time.

![Figure 6](image2.png)

**Figure 6** Absorption spectra for non-doped and metal-doped TiO₂ films.

The photocatalytic decomposition of stearic acid was also measured in case of UV-light irradiation and the results are shown in figure 7. For the non-doped and Al-doped TiO₂ films, almost of stearic acid are decomposed for 1 hour irradiation, while the photocatalytic activity is degraded in the initial stage of irradiation in the Fe- and Cu-doped TiO₂ films. It is noticed that the degradation in the Fe-doped film is observed larger than that in the Cu-doped film. It has been reported that the photocatalytic reactions are triggered by the photogeneration of electron-hole pairs [21]. Therefore, the degradation of activity is considered to be caused by recombination of photogenerated electron/hole

![Figure 7](image3.png)

**Figure 7** Normalized absorbance of stearic acid as a function of UV-light irradiation time.
pairs through the impurity levels, and therefore the recombination takes place easily in the Fe-doped TiO$_2$ film.

The impurity levels formed by doped metal oxides act as not only absorption centers of VIS-light but also recombination centers of electron/hole pairs. In the Cu-doped TiO$_2$ films, it is considered that the charge separation of the photogenerated electron/hole pairs takes place effectively because of low recombination rate of the photogenerated electron/hole pairs. As a result, obvious VIS-light response of photocatalysis is observed in the Cu-doped TiO$_2$ films.

4. Conclusion
Photocatalytic activity of the Cu-, Fe-, and Al-doped TiO$_2$ films prepared by the sol-gel dip-coating method was investigated. Metal element exists as its oxide in the nearly stoichiometric TiO$_2$ matrices, and the crystallinity of TiO$_2$ is hardly affected by metal doping. The absorption edge of the Cu- and Fe-doped TiO$_2$ films shifts to longer wavelength compared with that of non-doped TiO$_2$ film, that is, these films become to be able to absorb the VIS-light. The photocatalytic activity by VIS-light irradiation is observed in the Cu-doped TiO$_2$ film while it hardly observed in the Fe- and Al-doped TiO$_2$ films. On the other hand, the photocatalytic activity by UV-light irradiation reduces in the Cu- and Fe-doped TiO$_2$ films. In these films, the impurity levels formed by doped metal oxides act as not only absorption centres of VIS-light but also recombination centres of electron/hole pairs. It is found that the recombination of the photogenerated electron/hole pairs takes place quickly in the Fe-doped TiO$_2$ films, while the charge separation of the photogenerated electron/hole pairs takes place effectively in the Cu-doped TiO$_2$ films.

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