

PHOTOCATALYTIC PROPERTIES OF Cr DOPED TiO₂-SiO₂ NANOSTRUCTURE THIN FILM

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Cr doped TiO₂-SiO₂ nanostructure thin film on glass substrates was prepared by a sol-gel dip coating method. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV-vis spectrophotometer were used to characterize the structural, chemical and optical properties of the thin film. The XRD showed that thin films contain only anatase phase. FE-SEM images illustrated that anatase average crystallite size in the pure TiO₂ and Cr doped TiO₂-SiO₂ thin films are 15 nm and 10 nm, respectively. XPS spectra confirmed the presence of Cr³⁺ in the thin film. UV-vis absorption spectra indicated that absorption edge in Cr doped TiO₂-SiO₂ thin film shifted to the visible light region. The photocatalytic results pointed that Cr doping in TiO₂-SiO₂ improved decoloring rate of methyl orange in comparison to pure TiO₂ thin film.

INTRODUCTION

The photocatalytic application using semiconductor metal oxides has received a lot of attention to solve the environmental problems in the recent decades. TiO₂ has turned out to be the semiconductor metal oxide with the highest photoreactivity, being non-toxic, stable in aqueous solution and relatively inexpensive [1]. However, most applications so far are limited to UV-light irradiation because the light absorption edge of pure titania is less than 380 nm [2-3]. For efficient photoreactive activity, it is necessary to extend the photoresponse of TiO₂ from the ultraviolet to the visible region by modification of its optical properties. Extensive studies have been conducted to convert the TiO₂ absorption from the ultraviolet to the visible light region by ion doping with transition metals [4]. The most popular dopants for modification of the optical properties of TiO₂ are transition metals such as Cr, Fe, Ni, V, Mn, and Cu [5]. In the literature, many researchers have been indicted that Cr doping increased the photoreactive efficiency of TiO₂. The main purpose is to change the absorption edges of the TiO₂ to a visible light range [6-8]. In addition, Machida et al [9] indicated that the addition of silica on titania improved the photoreactivity of TiO₂ thin film. We have previously studied the photoinduced superhydrophilicity of Cr doped TiO₂-SiO₂ thin film [10]. In the present study, the photocatalytic properties of Cr doped TiO₂-SiO₂ thin film were investigated.

EXPERIMENTAL

The procedure for the preparation of Cr doped TiO₂-SiO₂ thin film is as described in detail in our earlier published work [10]. The mole ratio of TiO₂:SiO₂ was 4:1, and the content of Cr was 0.04 mol%. The thin films were obtained by a dip coating method and withdrawn at a speed of 5 mm/s. The gel films were air dried for 15 h, and then heat-treated at 500°C for 1 h in air (heating rate; 10°C/min).

The crystal structure and surface characteristics of the thin films were evaluated with a Bruker X-ray diffractometer (D8ADVANCE, Germany, Ni-filter, Cu K α radiation $\lambda = 1.5406 \text{ \AA}$) and Field Emission Scanning Electron Microscopy (FE-SEM; JEOL), respectively. Surface properties of the film samples were analyzed by using X-ray photoelectron spectroscopy (XPS, JEOL) using Mg K α source (1253.6 eV). UV-Vis absorption spectra for films were obtained using a UV-vis spectrophotometer (Perkin-Elmer).

The photocatalytic activities of films under irradiation were evaluated by the decoloring rate of methyl orange (C₁₄H₁₄N₃SO₃Na). Methyl orange was also used as a model organic compound to measure the photoreactivity in other studies [11].

One sample of film (surface area 6 cm²) was horizontally placed at the bottom of the testing cell containing 25 ml (2 \times 10⁻⁵ M) methyl orange solution. The solution was irradiated with Xe lamp (power 300 W,

wavelength 300-500 nm). The distance between the sample and irradiation source was 8 cm. After irradiation time, the light absorbance of methyl orange solution was measured using a UV-vis spectrophotometer at 464 nm, which is the maximum absorption of methyl orange [12]. Then, the decoloring rate of methyl orange, was used to quantify the photocatalytic activities of thin films, and calculated using following equation: [13]

$$\eta = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

where A_0 is the light absorbance of methyl orange before the irradiation (absorption equilibrium in the dark place for 30 min) and A is the light absorbance of methyl orange after the irradiation.

RESULTS AND DISCUSSION

The XRD measurements (the XRD figure is not shown here) showed that both TiO_2 and Cr doped $\text{TiO}_2\text{-SiO}_2$ thin films contain only anatase phase [14].

Figure 1 shows FE-SEM images of thin films. According to FE-SEM images, it can be seen that anatase average crystallite size in the pure TiO_2 is 15 nm, whereas in the Cr doped $\text{TiO}_2\text{-SiO}_2$, it is 10 nm. This phenomena can be related to addition of additives to titania. These additives had a suppressive effect on the crystal growth of TiO_2 , since the additives bared the contact between TiO_2 particles and inhibited crystallite growth during the heat treatment [15].

Figure 2 shows the XPS scan spectra for Cr doped $\text{TiO}_2\text{-SiO}_2$ thin film. The Ti 2p and Si 2p spectra indicated the chemical states of Ti and In to be Ti^{+4} and Si^{+4} , respectively. According to XPS spectra, the binding energy of Cr 2p_{3/2} was near 576.7 eV which indicating the presence of Cr^{3+} in the thin film [10].

Figure 3 shows the UV-vis absorption spectra of thin films. It is obvious that the doped Cr^{3+} can significantly improve the absorption of $\text{TiO}_2\text{-SiO}_2$ in the visible light region. This extended absorbance indicates the possible enhancement in the photocatalytic activity of TiO_2 illuminate by visible light.

The photo-catalytic activities of films were characterized by the degradation of methyl orange. The methyl orange degradation rate after 3 h irradiation in the presence of thin films is shown in the Figure 4.

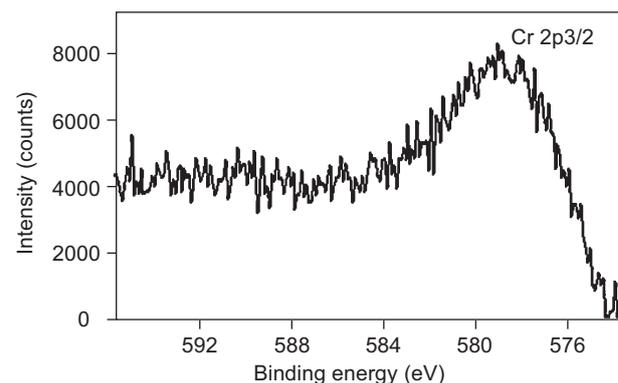
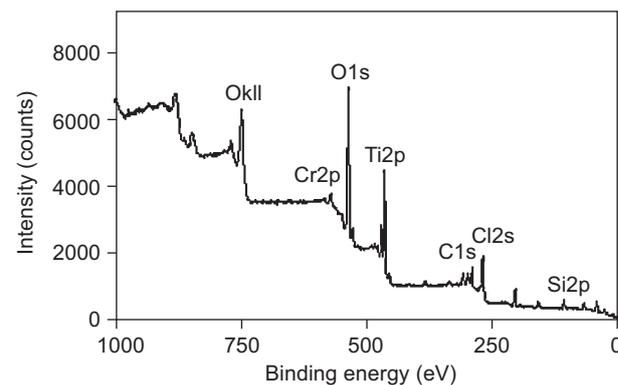
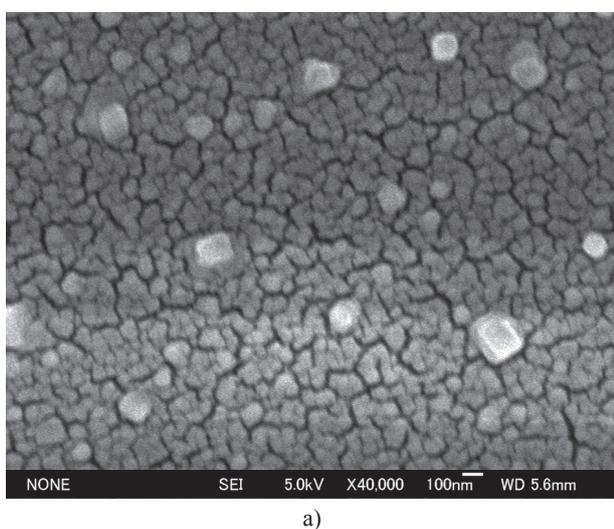
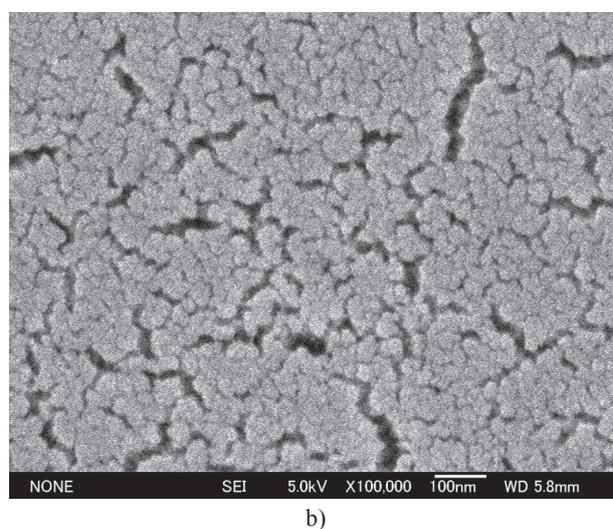


Figure 2. XPS spectra of Cr doped $\text{TiO}_2\text{-SiO}_2$ thin film [10].



a)



b)

Figure 1. FE-SEM image of TiO_2 (a) and Cr doped $\text{TiO}_2\text{-SiO}_2$ thin film (b).

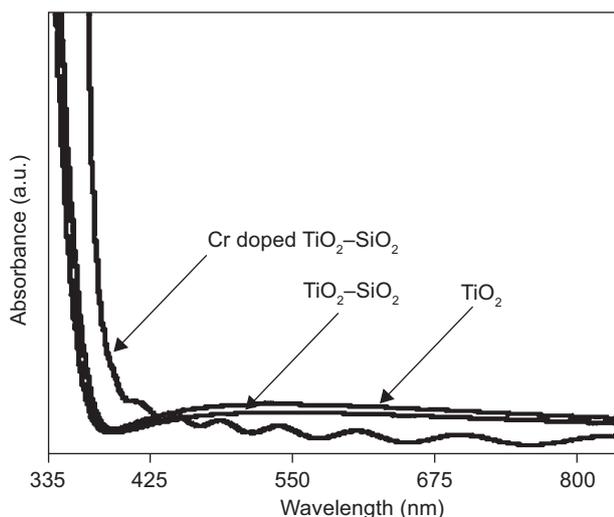


Figure 3. Absorption spectra of films on glass substrates.

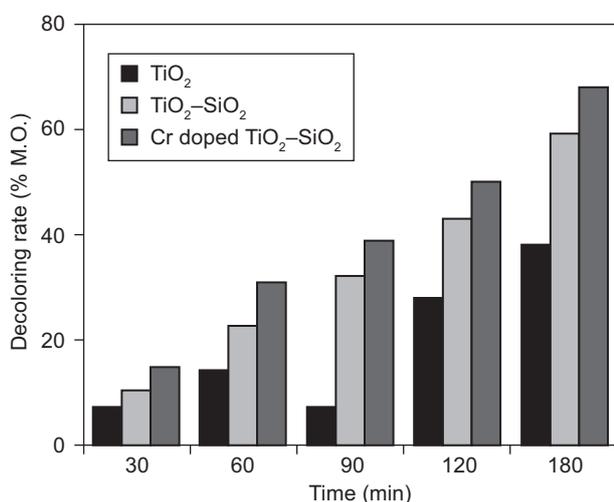


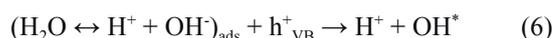
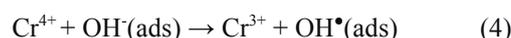
Figure 4. Methyl orange decoloring rate.

According to the photocatalytic results, doping TiO₂-SiO₂ thin film with Cr ions improves the photocatalytic decomposition of methyl orange. This phenomenon is described in the following:

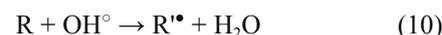
TiO₂ is a semiconductor with band gap energy of 3.2 eV. When titanium oxide is irradiated with UV light ($\lambda < 380$ nm), the electrons and holes are produced in conduction and valence band, respectively. These photo electron-hole pairs have an oxidizing potential which is enough to oxidize most pollutants present in aqueous systems. The photogenerated electrons react with molecular oxygen (O₂) to produce superoxide radical anions (O₂⁻), and photogenerated holes react with water to produce hydroxyl radicals. These highly reactive species are able to decompose a variety of organic compounds [16-17]. However, the photocatalytic activity of TiO₂ thin depends on several parameter such as surface hydroxyl group density, recombination rate of electron-hole

pairs, crystalline structure and etc. it is well accepted that hydroxyl groups have a significant effect on the photoreactivity of TiO₂. Hydroxyl groups are important factors in the TiO₂ because not only they can reduce the recombination of electron-hole pairs but also they have a strong photo-oxidation capability which can improve the photocatalytic activity of the films [18]. Methyl orange is attacked by hydroxyl radicals and generates inorganic radicals or some other intermediates. Eventually methyl orange and intermediate compounds are oxidized into CO₂, SO₄²⁻, and NO₃⁻. As we have previously shown, Lewis acidity is present in the structure of TiO₂-SiO₂ thin film which is due to the appearance of excessive positive charges [10]. Therefore, hydroxyl groups are adsorbed on to the thin film surfaces. Therefore TiO₂ shows higher photoreactivity with the presence of SiO₂ than in pure TiO₂. Since both photocatalytic oxidation of organic pollutants and photoinduced superhydrophilicity are initiated by electron-hole pairs, recombination of photo-generated electron-hole pairs can decrease the photoreactive efficiency of TiO₂ [5]. The high recombination rate of photo-generated electron-hole pairs can be limited by introducing charge traps for electrons and/or holes, thus prolonging the recombination time. The beneficial effect of Cr³⁺ can be described by considering the efficient separation of photogenerated electrons and holes. Cr³⁺ can act as trap for photogenerated holes [19].

Then the trapped holes can migrate to the surface to produce hydroxyl radicals from adsorbed hydroxyl ions [19-21]:



Oxidation of the organic reactant (R) via successive attacks by OH[•] radicals:



Direct oxidation by reaction with holes:



Therefore, the increase in the hydroxyl content on the surface of Cr³⁺ doped TiO₂-SiO₂ is beneficial to the enhancement of photocatalytic activity. As a result, the introduction of Cr³⁺ ions in TiO₂-SiO₂ thin film is responsible for reducing the photo-generated hole-electron recombination rate. Thus, photocatalytic activity of TiO₂-SiO₂ thin film increased with Cr³⁺ doping.

CONCLUSIONS

In this research, Cr doped TiO₂-SiO₂ thin film was prepared by the sol-gel dip coating method. XRD measurements indicated the presence of anatase phase in the thin films. The SEM images and UV absorption spectra illustrated that the addition of Cr and SiO₂ decreased the crystalline size of anatase phase and shifted the absorption edge of TiO₂ to the visible region, respectively. XPS spectra confirmed the presence of Cr³⁺ in the thin film. Photocatalytic measurements pointed that Cr dopant increased the decoloring rate of methyl orange in TiO₂-SiO₂ in comparison to pure TiO₂ thin film. This efficiency can be related to (i) by decreasing in the crystallite size; an increase in the amount of surface active area, and a charge transfer in TiO₂ films is promoted (ii) by enhancing electron-hole pair separation and inhibiting their recombination, the Cr dopant enhances charge pair separation efficiency in doped TiO₂ film (iii) by increasing the hydroxyl group density, adsorption of water molecules increases on the TiO₂ surface.

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References

1. Ma Y., Fu J.W., Tao X., Li X., Chen J.F.: *Appl. Surf. Sci.* 257, 5046 (2011).
2. You L., Li T.Q., Ge F.Q.: *Appl. Surf. Sci.* 257, 5544 (2006).
3. Arana J., Cabo C.G, Dona-Rodriguez J.M., Gonzalez-Diaz O., Herrera-Melian J.A., Perez-Pena J.: *Appl. Surf. Sci.* 239, 60 (2004).
4. Luca D., Mardare D., Iacomi F., Teodorescu C.M.: *Appl. Surf. Sci.* 252, 6122 (2006).
5. Dholam R., Patel N., Adami M., Miotello A.: *Int. J. Hydrogen Energy* 34, 5337 (2009).
6. Takaoka G.H., Nose T., Kawashita M.: *Vacuum* 83, 679 (2009).
7. Mardare D., Iacomi F., Cornei N., Girtan M., Luca D.: *Thin Solid Films* 518, 4586 (2010).
8. Anpo M., Kishiguchi S., Takeuchi M., Yamashita H., Ikeue K., Morin B., Davidson A.: *M. Che. Res. Chem. Intermed.* 27, 459 (2001).
9. Machida M., Norimoto K., Watanabe T., Hashimoto K., Fujishima A.: *J. Mater.Sci.* 34, 2569 (1999).
10. Eshaghi A., Eshaghi A.: *Appl. Surf. Sci.* 258, 2464 (2011).
11. Chen L., Tian J., Qiu H., Yin Y., Wang X., Dai J., Wu P., Wang A., Chu L.: *Ceram. Inter.* 35, 3275 (2009).
12. Tian H., Ma J., Li K., Li J.: *Ceram. Inter.* 35, 1289 (2009).
13. Eshaghi A., Mozaffarinia R., Pakshir M., Eshaghi A.: *Ceram. Int.* 37, 327 (2010).
14. Eshaghi A., Pakshir M., Mozaffarinia R.: *Appl. Surf. Sci.* 256, 7062 (2010).
15. Yu J., Zhao X., Yu J., Zhong G.: *J. Mater. Sci. Lett.* 20, 1745 (2001).
16. Parida K.M., Sahu N.: *J. Molecular Catalysis A Chemical.* 287, 151 (2008).
17. Meng F., Sun Z.: *Appl. Surf. Sci.* 255, 6715 (2009).
18. Guan K., Yin Y.: *Mater. Chem. Phys.* 92, 10 (2005).
19. Meng F., Xiao L., Sun Z.: *J. Alloy. Compd.* 485, 848 (2009).
20. Choi W., Termin A., Hoffman M.R.: *J. Phys. Chem. B.* 98, 13669 (1994).
21. Zhu J., Deng Z., Chen F., Zhang J., Chen H., Anpo M., Huang J., Zhang L.: *Appl. Catal. B: Environ.* 62, 329 (2006).