

Self-Cleaning Properties of Vanadium Doped TiO₂ Sol-Gel Derived Thin Films

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ABSTRACT

In this study, vanadium doped TiO₂ thin films were deposited on glass substrates using a sol-gel dip-coating process. X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectrophotometer were used to characterize the structural, chemical and the optical properties of the thin films. The photo-catalytic activities of films were investigated by methylene blue degradation. Water contact angle on the film surfaces was measured by a water contact angle analyzer. The results indicated that vanadium doping had a significant effect on the self-cleaning properties of TiO₂ thin films.

Keywords: TiO₂; Sol-Gel; Vanadium Doping; Self-Cleaning Property

1. Introduction

Self-cleaning applications using TiO₂ thin films have become a subject of an increasing interest especially in recent years. The self-cleaning property has been known to be a combined effect between super-hydrophilicity and photo-catalysis [1-3]. The photo-catalytic property helps decompose the organic compounds that come into contact with the surface and thus prevents them from building up. The super-hydrophilic property of the TiO₂ film on the surface allows water to spread completely across the surface rather than remain as droplets, thus making the surface easy to wash [4,5]. Therefore, the photo-catalytic and hydrophilic properties of the TiO₂ coated surface allow the water to more easily wash away deposited particles. Because of the light absorption edge of pure Titania, which is less than 380 nm, most applications are so far limited to UV-light irradiation [6,7]. For efficient photo-reactive activity, it is necessary to extend the photo-response of TiO₂ from the ultraviolet to the visible region by modification of its optical properties. Further studies have been carried out for modification of the optical properties of TiO₂ absorption from the ultraviolet to the visible light region, by ion doping with transitional metals such as: Cr, Fe, Ni, V, Mn, and Cu [8-10]. In the present study, V doped TiO₂ thin films were pre-

pared by the sol-gel dip coating method on the glass substrates. Then, photo-catalytic, super-hydrophilic and self-cleaning properties of films were investigated.

2. Materials and Methods

The TiO₂ sol was prepared by dissolving tetra butyl orthotitanate (1 mole, TBOT, 97%) in ethanol (20 mole, 99%) and acetyl acetone (0.2 mole, 99.99%). Then acetic acid (1.5 mole, 99.7%), ethanol (20 mole, 99%) and de-ionized water (3 mol) were mixed separately and added to the first mixture. The final solution was stirred for two hours [11,12]. At this stage, a solution of ammonium metavanadate (NH₄VO₃) with certain concentration was prepared [10]. The content of V was 0.06 atomic percent. Before coating, the glass substrates (2 × 7 × 1 mm) were ultrasonically cleaned in boiled acetone and ethanol. 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 550°C for 2 h in air atmosphere [11-13]. The crystal structure, thickness and surface characteristics of the thin films were evaluated with a Bruker X-ray diffract-meter (Ni-filter, Cu K_α radiation λ = 1.5406 Å) and Field Emission Scanning Electron Microscopy (FE-SEM), respectively and UV-Vis transmittance spectra for films were obtained using a UV-Vis spectrophotometer.

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The photo induced super-hydrophilicity of the films was measured by the contact angle of water droplet on the film surfaces with an experimental error of ± 1 . A droplet was injected on to the surface using a 5 μL micro-injector. It should be mentioned that UV light was irradiated to the surfaces by a Hg Lamp (16 W/cm^2) [14].

The photo-catalytic activities of thin films under UV-irradiation were evaluated by the decoloring rate of methylene blue ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$). For this purpose, one sample of thin film (surface area 14 cm^2) was horizontally placed at the bottom of the testing cell containing specific amount of methylene blue solution (10 ppm). The solution was irradiated with Hg lamp. After the irradiation time, the light absorbance of methylene blue solution was measured using a UV-Vis spectrophotometer at the absorption rate (200 - 900 nm). The decoloring rate of methylene blue was used to evaluate the photo-catalytic activities of the films, with the following equation [15].

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

where A_0 is the light absorbance of methylene Blue before the irradiation (absorbance equilibrium in dark place for 30 min) and A is the light absorbance of methylene blue after the irradiation [15].

3. Results

3.1. FE SEM Analysis

The average thickness of the films was measured according to a FE-SEM cross section method. A FE-SEM cross section image of a TiO₂-V thin film is shown in the **Figure 1**. The results indicated that the film thicknesses were approximately 266 and 313 nm for pure TiO₂ and V doped TiO₂ film, respectively.

3.2. XRD Measurements

The XRD figure is not shown here. However, the pattern illustrated that both TiO₂ and V doped TiO₂ thin films contain only an anatase phase.

3.3. FTIR Spectra

Figure 2 shows the UV-Vis absorption spectrum of thin films. It can be seen that the absorption edge for V doped TiO₂ films shows a red shift compared with that of the pure TiO₂. The shift is consistent with the incorporation of V^{5+} into the titania matrix. This indicates that the band gap energy in V doped TiO₂ is lower than that of undoped TiO₂.

3.4. UV-Vis Spectra

Figure 3 shows the UV-Vis absorption spectrum of thin

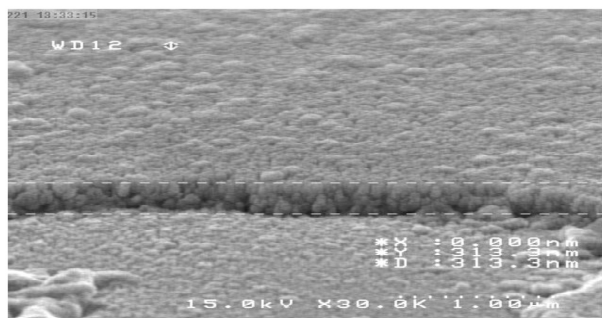


Figure 1. FE-SEM cross section image of V doped TiO₂ thin film.

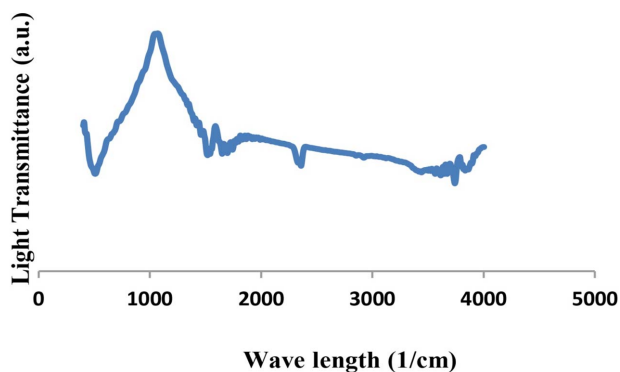


Figure 2. FTIR spectra of V doped TiO₂ thin film.

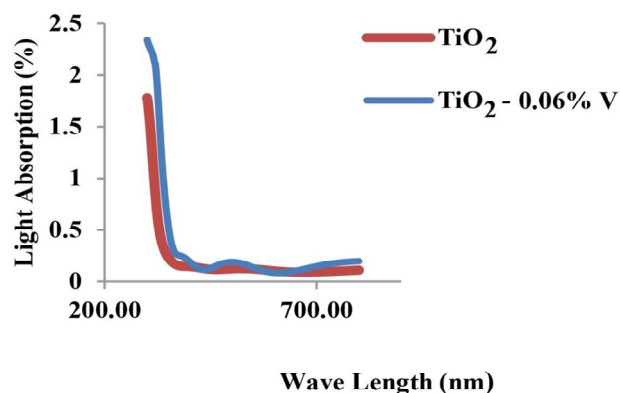


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3.5. Water Contact Angle

Figure 4 presents the results of water contact angle measurements on the thin film surfaces under irradiation. As shown in the **Figure 4**, TiO₂-V thin film turned super-hydrophilicity after 120 min irradiation. Meanwhile,

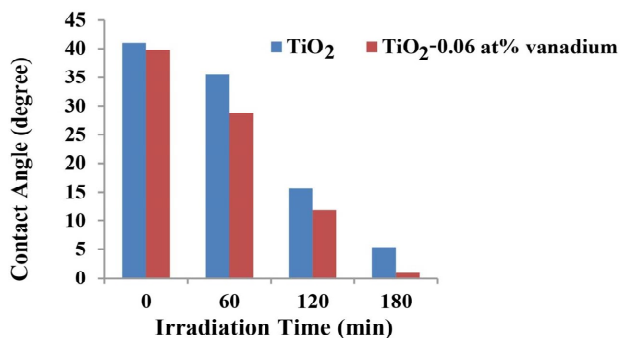


Figure 4. Water Contact Angle on the thin film surfaces under UV irradiation.

the pure TiO₂ obtained super-hydrophilic after 180 min irradiation. This difference in the appearance of superhydrophilicity will be further discussed.

3.6. Photo Catalytic Activity

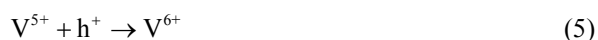
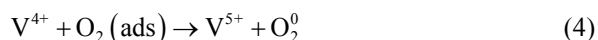
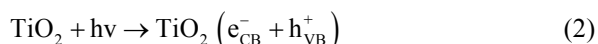
The photo-catalytic activities of films were characterized by the degradation of methylene blue. The methylene blue degradation rate after irradiation in the presence of thin films is shown in the **Figure 5**.

4. Discussion

According to the photocatalytic results, doping TiO₂ thin film with 0.06 at % V ions decrease the photocatalytic decomposition of methylene blue.

Since both photocatalytic oxidation of organic pollutants and photo induced superhydrophilicity are initiated by electron-hole pairs, the recombination of photo-generated electron-hole pairs can decrease the photoreactive efficiency of TiO₂-V [16,17].

The high rate of recombination of photo-generated electron-hole pairs, which in turn prolongs the recombination time can be limited by introducing charge traps for electrons and/or holes. The beneficial effect of V⁵⁺ in photohydrophilicity can be described by considering the efficient separation of photo-generated electrons and holes. V⁵⁺ can act as a trap for photo-generated holes [10]. In order to produce hydroxyl radicals from absorbed hydroxyl ions the trapped holes can migrate to the surface [10]:



hydroxyl groups have a significant effect on the photo-reactivity of TiO₂. Hydroxyl groups are important factors

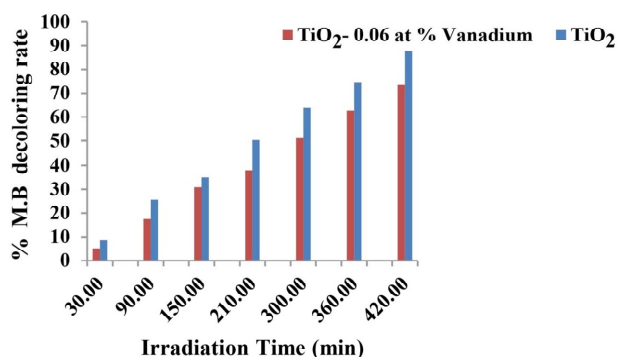


Figure 5. The Methylene Blue degradation rate under UV irradiation in the presence of thin films.

in the TiO₂ because they can reduce the recombination of electron-hole pairs. Therefore, the increase in the hydroxyl content on the surface of V⁵⁺ doped TiO₂ is beneficial to the enhancement of superhydrophilicity property. On the other side, the introduction of V⁵⁺ ions in TiO₂ thin film may responsible for reducing the photo-generated hole-electron recombination rate. Thus, in comparison with pure TiO₂, photocatalytic activity of thin film decreased with 0.06 at % V doping. Thus, the V doped TiO₂ thin film shows higher hydrophilicity and a slight decrease in photo-catalytic effect than pure TiO₂. It is then concluded that 0.06 atomic % Vanadium doped TiO₂ thin film can have a noticeable effect on self-cleaning property.

5. Conclusion

In this research, V doped TiO₂ thin film was immobilized on the glass substrates using the dip coating process. Water contact angle measurements and photo-catalytic methylene blue degradation indicated that the V doping improved the photo-reactivity of TiO₂ film surfaces. Although TiO₂ sol-gel derived thin film has better photocatalytic activity than V doped TiO₂, the super-hydrophilicity effect can show a great decrease in contact angle for TiO₂-V surfaces. So, this product can be useful in exhibiting a self-cleaning effect for practical purposes such as constructional applications, especially for wherever the superhydrophilicity effect would be a significant parameter.

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