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Photocatalytic of TiO_2-SiO_2 Thin Films Co-Doped with Fe^{3+} and Thio-Urea in the Degradation of Formaldehyde by Indoor and Outdoor Visible Lights

Charuwan Kaewtip, Kamolporn Accanit, Nat-a-nong Chaowai, Kanokpun Areerat,
Pasuree Reanjaruan, Virote Boonumnauyvitaya
Chemical Engineering Department, King Mongkut's University of Technology Thonburi, Bangkok, Thailand
Email: virote.boo@kmutt.ac.th

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ABSTRACT

In this work the photocatalytic activity of TiO_2-SiO_2 thin films co-doped with Fe^{3+} and thio-urea in the degradation of the gaseous formaldehyde was investigaged by indoor and outdoor visible lights. The films were synthesized by Peroxo Titanic Acid (PTA) method. The physicochemical properties of prepared samples were characterized using SEM and UV-vis absorption spectroscopy. It was found that the average film thickness of all coated samples was about 394 ± 5 nm. The band gap energy of un-doped and co-doped photocatalysts was 3.08 and 2.88 eV, respectively. The photocatalytic experimental results showed that the co-doped TiO_2-SiO_2 thin film yield higher photocatalytic efficiency. Under the outdoor light (sunlight in the shade condition) irradiation, with the initial concentrations of formaldehyde of 1000, 3000 and 5000 ppmV, the efficiencies of formaldehyde degradation were 94.7%, 89.5% and 85.1%, respectively. Under the indoor light (the fluorescent lamp) irradiation, with the same formaldehyde initial concentrations, the photocatalytic activities were 87.4%, 85.3% and 81.5%, respectively.

Keywords: Perxo Titanic Acid; Titanium Dioxide; Sunlight in the Shade; Formaldehyde

1. Introduction

Formaldehyde is a toxic volatile organic compound (VOCs), which causes cancer and is harmful to health when uptake into human bodies. Therefore, purification of ambient air form this toxic gas is essential for improving indoor air quality and human being's health [1]. Titanium dioxide (TiO_2) is a promising tool for environmental purification due to its specific optical and electronic properties, low cost, chemical stability and non-toxicity [2-4]. However, the need of an ultraviolet (UV) excitation which accounts for only a small fraction of the total solar energy (~5%) hinders its utility for limited applications [5].

Many attempts have been made to enhance the utilization of solar energy by doping the base photocatalyst with co-dopants elements such as C and N [6], Fe^{3+} and C [7], and Fe^{3+} and N [8,9]. *Ohno et al.* reported that the effect of adsorbing Fe^{3+} on the N- or S- doped TiO_2 and found that the photocatalytic efficiency under visible light region was about twice as high as without Fe^{3+} doping [10]. One element can extend the response of TiO_2 to visible light, the other can act as electron and hole traps. Then TiO_2 can respond to visible light and present a high catalytic activity [11].

In our previous work [12], TiO_2-SiO_2 thin films with co- dopants of Fe^{3+} and N,S yielded high efficiency in formaldehyde degradation. However, the study was limited in small lab scale using fluorescent lamp as the light source. The objective of this work is to confirm the practical use of these films by studying the efficiency of formaldehyde degradation using co-doped TiO_2-SiO_2 thin films in a large cubic glass chamber under the outdoor light compared with the indoor fluorescent light.

2. Experimental

2.1. Catalysts Preparation

All reagents were of analytical grade and used without further purification. The co-doped TiO_2-SiO_2 thin films were prepared using the peroxo titanic acid (PTA) approach combined with the sol–gel method. The procedures for co-doped PTA sol (solution A) preparing were as follows: First, 4.3 g of Titanyl sulfate ($TiOSO_4$) was added to 150 cm^3 deionized water. While under vigorous stirring, 26 cm^3 of NH_4OH (3 mol/dm^3) was added to the solution. Next, the white precipitates were filtered and sufficiently washed four to six times with distilled water to remove residues of $NH4^+$ and SO_4^{2-} ions, then dispersed homogeneously in 112.5 ml of distilled water. The resulting sol was peptized in 25 cm^3 of hydrogen peroxide (30%), and then stirred for 15 min. The obtained orange transparent sol was kept under reflux at 100°C. Before adding the co-dopants, the PTA sol was kept at room temperature for 24 h. Dopants added into the TiO_2 based on the mass of TiO_2 1.64 g in PTA sol. Finally, CSN_2H_4 of 0.125 wt.% and $Fe(NO_3)_3$ of 1.0 wt.% were added into the PTA sol.

The SiO_2 (solution B) sol was prepared via the condensation reaction of methyltrimethoxysilane (MTMOS). First, 4.3 cm^3 of MTMOS were hydrolyzed with the mixture of 8.22 cm^3 of methanol, 2 cm^3 of H_2O, and 0.5 cm^3 of HCl (0.055M) aqueous solution. After the solutions were vigorously stirred at 50°C for

60 min, the mixture of 8.22 cm^3 of methanol and 3.2 cm^3 of NH_4OH (0.856M), which was stirred at 25°C for 60 min, was added into the hydrolyzed MTMOS solution and stirred for 15 min. Then, solution B was added into solution A under stirring at room temperature for 15 min. The obtained sol was coated on a glass plate (100 x 100 x 3 mm) by spin coating machine, and then kept for drying for 24 h at room temperature before using.

The obtained photocatalysts were characterized by Scanning electron microscopy (SEM) to determine the thickness of coted film on the glass plate. The optical transmission and absorption spectra of the films were measured using UV-vis spectrophotometer (U1900 UV/VIS, Hitachi) with the wave range of 200-1000 nm.

2.2. Photocatalytic Activity of Formaldehyde Degradtion

The experiments were conducted in a cubic 9.1 x 10^4 cm^3 glass chamber where 70 pieces of coated glasses were attached around the inner wall. The schematic and components of glass reactor chamber showed in **Figure 1**. Injection and sampling of formaldehyde gas in the glass chamber were conducted through the septum port by means of a syringe. The initial concentrations of formaldehyde gas of 1000, 3000 and 5000 ppmV were used. The glass reactor chambers were covered with black fabric for shutting out light around 50-60 min until adsorption equilibrium conditions have been reached. Then the black fabric was removed to start the photocatalytic reaction. The chambers were placed indoor for fluorescent light and outdoor for sunlight (in the shade) exposures. The concentration of formaldehyde before and after photocatalytic reactions were measured by a gas chromatography (Shimadzu: GC2014) equipped with DB-WAX column.

3. Result and Discussion

3.1. Characterization of the Photocatalysts

Cross sectional SEM image as shown in **Figure 2** shows a complete coverage of the substrate surface by the photocatalysts film with the average film thickness 394 ± 5 nm.

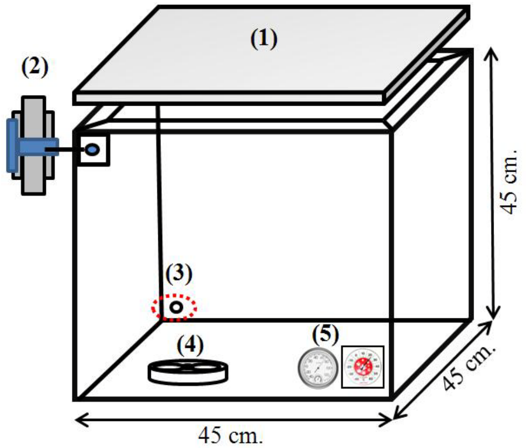

Figure 1. The schematic and components of glass reactor chamber (1) lid, (2) septum port, (3) fan hole, (4) fan, and (5) hygrometer and thermometer.

The color of a coated film is opalescent -semitransparent due to the TiO_2 powder dispersed in the film. The corresponding UV-Vis spectra for coated film are shown in **Figure 3**. Compared with the un-doped film, the transmittance of the co-doped film was about 80% in the visible wavelength region and lower than those of the un-doped film. The difference in transmittance between the un-doped and the co-doped films was attributed to the adsorption of light by dopant. A significant decrease in the transmittance below 400 nm can be assigned to absorption of light caused by the excitation of electrons from the valence band to the conduction band of TiO_2 [13]

Figure 4 shows the UV-Vis absorption spectra of un-doped

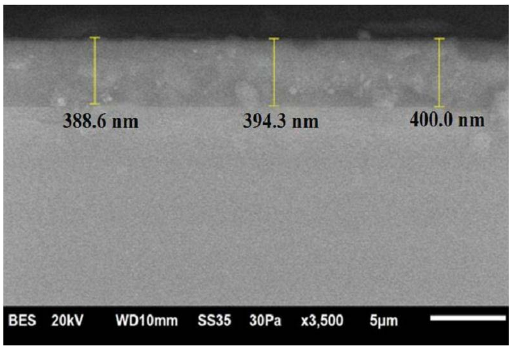

Figure 2. SEM micrographs showing the cross section of the film thickness on glass substrate.

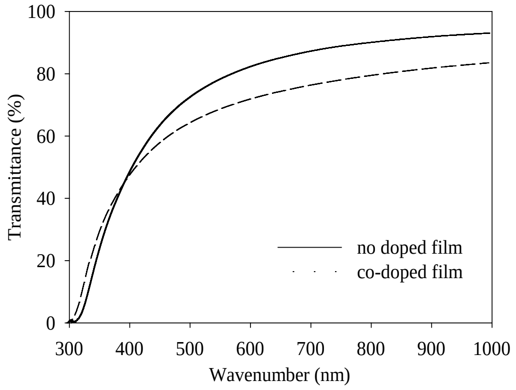

Figure 3. The UV-Vis transmittance spectra of the transparent films of un-doped and co-doped TiO_2-SiO_2 thin films.

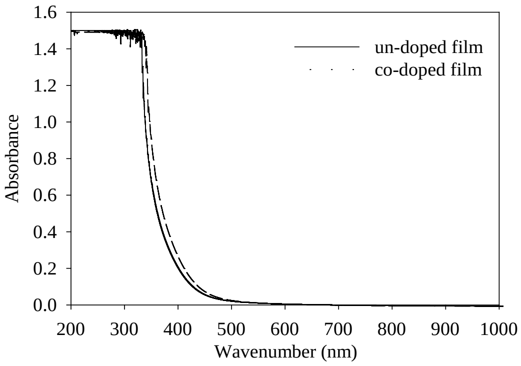

Figure 4. The UV-Vis absorption spectra of coated TiO_2-SiO_2 thin films.

and co-doped TiO_2-SiO_2 thin films. The absorption edge of un-doped is limited only to ultraviolet light region, whereas the absorption threshold values of co-doped photocatalyst is extended up to the visible light range. The energy band gap (Eg) is determined by the formula [14], Eg = 1239.8/ λ, where λ (nm) is the wavenumber of the absorption edge in the spectrum. The energy band gap of un-doped and co-doped TiO_2-SiO_2 thin films was 3.08 and 2.88 eV, respectively.

3.2. Photocatalytic Activity

The formaldehyde degradation activity of the prepared photocatalytic films was determined and shown in **Figure 5**. In dark condition, the formaldehyde adsorbed onto the all films within 30 min and approached equilibrium after 50-60 min. Under light irradiation, in both cases of indoor and outdoor conditions, all co-doped samples, demonstrate higher photocatalytic efficiencies than that of the un-doped photocatalysts. This could be

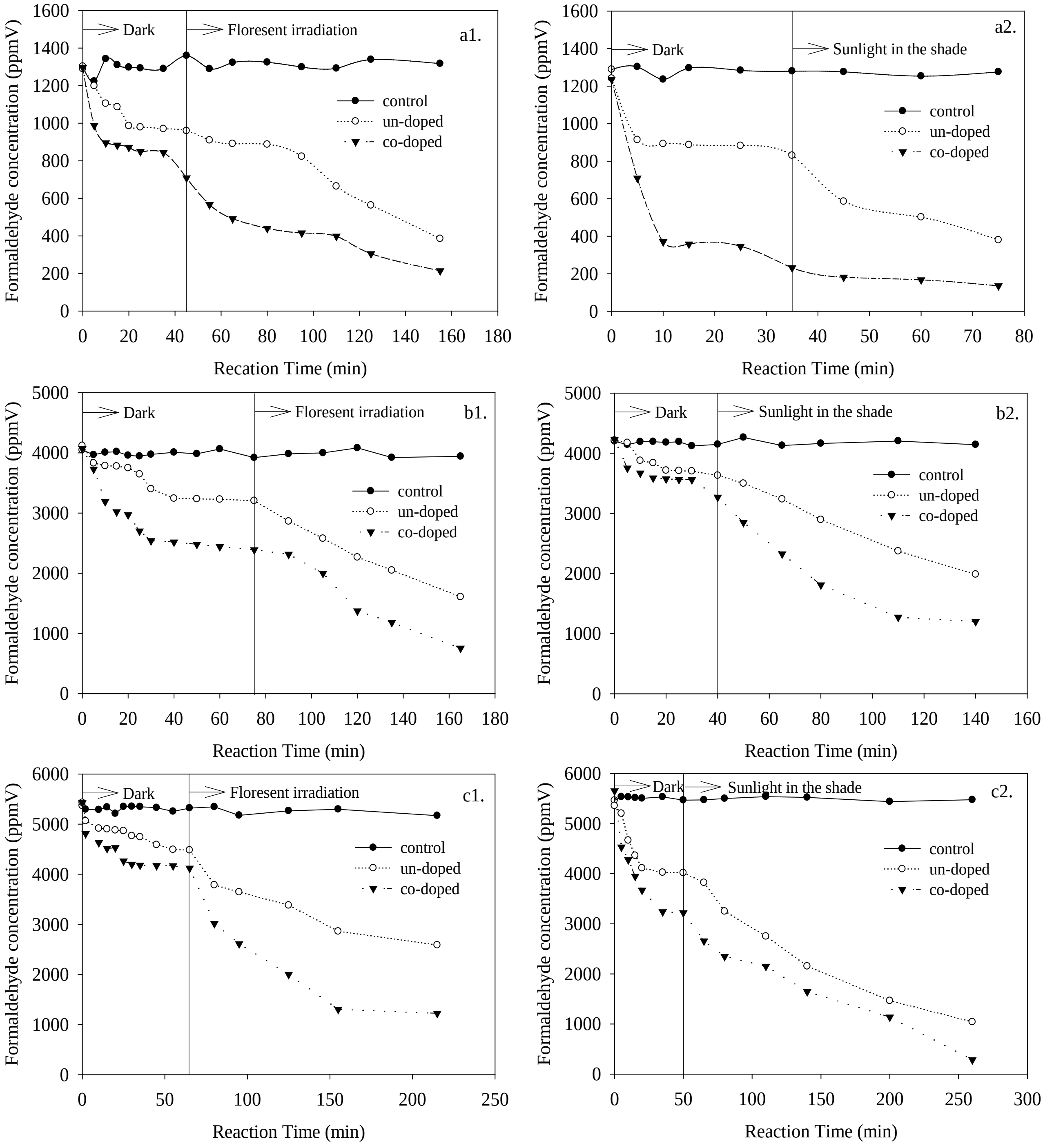

Figure 5. Photocatalytic decomposition profiles of gaseous formaldehyde by control (no photocatalyst) and photocatalysts chambers with different initial formaldehyde concentration a) 1,000 ppmV, b) 3,000 ppmV and c) 5,000 ppmV and different light source of irradiation.

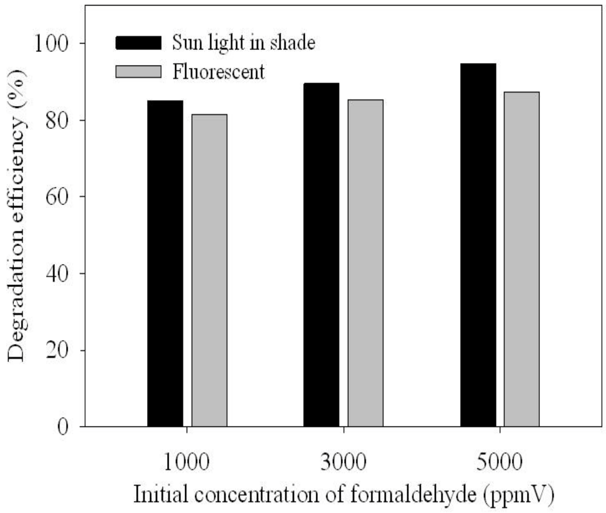

Figure 6. The photocatalytic efficiencies of the co-doped TiO_2-SiO_2 thin films with different of initial formaldehyde concentration.

attributed to the effect of the synergistic role of co-dopants in narrowing TiO_2 band gap.

It is generally accepted that a dopant level can form above the valence band for the substitutional nitrogen, and below the conduction band for Fe^{3+} doping, both of which could decrease the band gap of TiO_2 and improve the photocatalytic activity in the visible light region [15]. On the other hand, the co-doping of nitrogen and Fe^{3+} ion inhibits the recombination of the photogenerated electron and hole [16]. The effect of light source on the formaldehyde degradation efficiency is illustrated in **Figure 6**. It is clearly observed in the figure that the formaldehyde degradation efficiency of sun light in shade is higher than that of fluorescent irradiation due tothe higer light intensity [17].

4. Conclusion

The co-doped TiO_2-SiO_2 thin films were synthesized by using PTA sol as the TiO_2 source. The prepared films showed the average thickness of 394 ± 5 nm. The band gap energy of undoped and co-doped photocatalysts was 3.08 and 2.88 eV, respectively. The co-doping of Fe^{3+} and N,S ion into TiO_2 photocatalysts showed the highest photocatalytic activity of formaldehyde degradation. Under the sunlight in the shade condition, with the initial concentrations of formaldehyde of 1000, 3000 and 5000 ppmV, the efficiencies of formaldehyde degradation were 94.7%, 89.5% and 85.1%, respectively. For the fluorescent irradiation, with the same formaldehyde initial concentrations, the photocatalytic activities were 87.4%, 85.3% and 81.5%, respectively. Both iron ions and nitrogen species could lead to a narrowing of the band gap of TiO_2. In addition, the co-doping of nitrogen and Fe^{3+} ion inhibits the recombination of the photogenerated electrons and holes.

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