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Self-cleaning and antibacterial of *E.coli* properties of TiO_2/SnO_2 composites thin films

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ABSTRACT

TiO_2/SnO_2 composites thin films containing 0 to 5% SnO_2 coated on glass substrate were prepared by sol-gel dip coating method. The prepared composites thin films were synthesized at the temperature of 500 °C for 2 h with a heating rate of 10 °C/min. The microstructure of synthesized TiO_2/SnO_2 composites thin films were characterized by XRD and SEM. The self-cleaning properties of TiO_2/SnO_2 composites thin films were evaluated by means of contact angle of water droplet on the films under UV irradiation. Finally, composites thin films were tested their antibacterial property by using *Escherichia coli form* (*E.coli*) under irradiation of UV light. The concentration of *E.coli* was evaluated by plating technique. The result showed that $TiO_2/1SnO_2$ composites thin film has highest self-cleaning properties (small contact angle, 6.4° for 60 min) and antibacterial of *E.coli* properties (80.67% for 3 h).

Keywords: Self-cleaning, Antibacterial, TiO_2/SnO_2, Composite thin films

1. INTRODUCTION

Titanium dioxide (TiO_2) is one of the basic materials in everyday life. It has been widely used as its potential applications. TiO_2 exists in three crystalline modifications: rutile, anatase, and brookite. Generally, TiO_2 is a semiconducting material which can be chemically activated by light. TiO_2 coating has been applied on glass in order to obtain various properties, which render the glass more useful, such as photodegradation of organic and inorganic pollutants, antibacterial and self-cleaning.

Many deposition techniques have been used to prepare TiO_2 and TiO_2 composites thin films, such as chemical vapor deposition [1], evaporation [2] magnetron sputtering [3], ion beam techniques [4] and sol-gel processes [5-7]. The sol-gel processes are particularly efficient in producing thin, transparent, multi-component oxide layers of many compositions on various substrates, including glass [8]. Nowadays, many studies have been devoted to further improve the self-cleaning and antibacterial properties of TiO_2 thin films by SnO_2 doping [9-11]. Also TiO_2 thin films show high self-cleaning and antibacterial properties under UV irradiation [11-15].

In this work, TiO_2/SnO_2 composites thin films were prepared by sol-gel method. Based on our previous studies, the amount of SnO_2 in the range of 0 to 5 mol% of TiO_2 is carried on. The effects of the SnO_2 doping into TiO_2 composites thin films on the microstructure, self-cleaning and antibacterial of *E.coli* properties were investigated.

2. EXPERIMENTAL

2.1 Preparation of TiO_2/SnO_2 composites thin films

TiO_2/SnO_2 composites thin films were prepared via sol-gel method. Firstly, $SnCl_4.5H_2O$ with fixed at 0, 1, 3 and 5 mol% of TiO_2 and Titanium (IV) isoproxide (TTIP) with fixed at 10 ml were mixed into 150 ml of ethanol (C_2H_5OH) and the mixture was vigorously stirred at room temperature for 15 min. The pH of mixed solution was adjusted to about 3-4 by 3 ml of 2 M nitric acid (HNO_3). Finally, it was vigorously stirred at room temperature for 30 min until clear sol was formed. The composites thin films were deposited on glass substrates by dip-coating process at room temperature with the drawing speed of dip-coater at about 1.25 mm/s. The coated samples were dried at room temperature for 24 h and calcined at the temperatures of 500°C for 2 h with a heating rate of 10°C/min.

For this work the SnO_2 doped TiO_2 composites thin films containing 0, 1, 3 and 5

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mol% were designated as TP, T1Sn, T3Sn and T5Sn, respectively.

2.2 Characterizations

The morphology of TiO_2/SnO_2 composites thin films were characterized by Scanning Electron Microscope (SEM) (Quanta 400). The phase composition was characterized using an x-ray diffractometer (XRD) (Panalytical X'pert MPD, Cu-K). The crystallite size was calculated by the Scherer equation, Eq. 1, [16-17].

$$D = 0.9\,\lambda / \beta\, cos\theta_B \tag{1}$$

Where D is the average crystallite size, λ is the wavelength of the Cu K_α line (0.15406), θ is the Bragg angle and β is the full-width at half-maximum (FWHM) in radians.

2.3 Photocatalytic activity

The photocatalytic properties were evaluated by the degradation of methylene blue (MB), under UV irradiation using 110W of black lamps. Thin films with an area of 26 x 30 cm^2 was soaked in a 4 ml MB with a concentration of 1×10^{-6} M and kept in a chamber under UV irradiation for 0, 1, 2, 3, 4, 5 and 6 h. After that the supernatant solutions were measured for MB absorption at 665 nm using a UV-Vis spectrophotometer (UV-Vis) (GENESYS™10S). The degradation of the MB was calculated by C/C_0 [18]. Where C_0 is the concentration of MB aqueous solution at the beginning and C is the concentration of MB aqueous solution after exposure to a light source.

2.4 Self-cleaning properties

The self-cleaning properties of TiO_2/SnO_2 composites thin films was evaluated by measuring the contact angle of water droplet on the thin film with and without UV irradiation using 110 W of black lamps under an ambient condition at 25 °C. Water droplets were placed at 3 different positions for one sample and the averaged value was adopted as the contact angle [18].

2.5 Antibacterial properties

The antibacterial properties of TiO_2/SnO_2 composites thin films against the bacteria *Escherichia coli* (*E.coli*) were prepared by used 1 ml of 10^3 CFU/ml concentration of *E.coli* dropped on composites thin films (26 x 26 cm^2) that placed in Petri dish plate and then exposed to UV irradiation using 110 W of black lamps for 0, 1, 2 and 3 h. Then, pour the Macconkey Agar liquid into the bottom of a Petri dish plate and rotate the plate gently to distribute the agar evenly, and allow the agar to harden (about 10 min).

Finally, it was incubated at 37 °C for 24 h. After incubation, the number of viable colonies of *E.coli* on each Macconkey agar plate was observed and disinfection efficiency of each test was calculated comparing to that of control [19]. The *E.coli* survival rate was calculated according to the following equation, Eq. 2, [20].

$$E.\ coli \text{ survival rate} = N/N_0 \tag{2}$$

Where N_0 and N are the average number of live *E.coli* cells per milliliter in the flask of the control and thin films.

3. RESULT AND DISCUSSION

3.1 Characterizations

Figure 1 shows the XRD patterns of TiO_2/SnO_2 thin films composed of various mol ratios of SnO_2 to TiO_2 were 0, 1, 3 and 5 mol%. X-ray diffraction peak at 25.5° corresponds to characteristic peak of crystal plane (1 0 1) of anatase at 27.6° in thin films. According to the XRD patterns, all sample constituted of pure anatase phase. Sn-compound phase was not detected here due to a very small amount of SnO_2 doping.

The average crystallite size of thin films was determined from the XRD patterns, according to Scherer equation. The average crystallite size of TiO_2/SnO_2 thin films composed of various mol ratios of SnO_2 to TiO_2 were 0, 1, 3 and 5 mol% are 20.7, 8.3, 9.2 and 14.6 nm, respectively. It was apparent that SnO_2 added in TiO_2 has significantly effect on crystallite size. It was found that TiO_2 doped with 1 mol% of SnO_2 (T1Sn) show the smallest crystallite size.

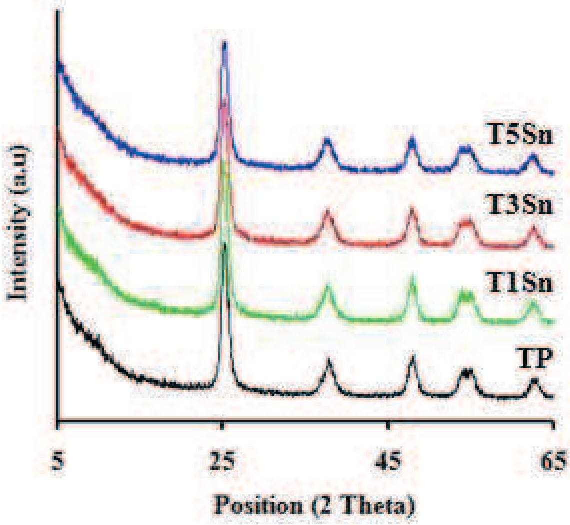
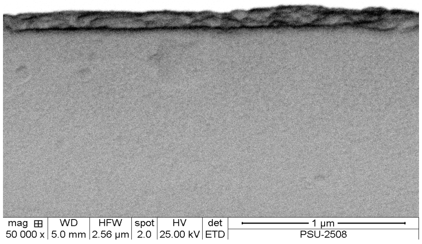
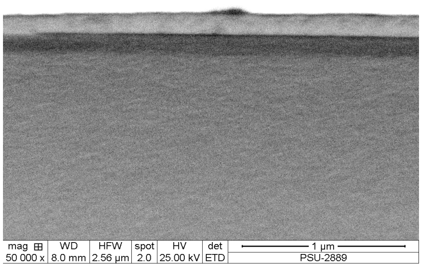
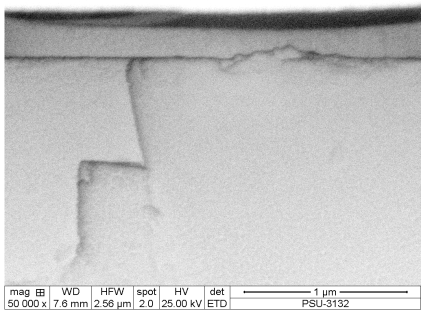


Fig.1 XRD pattern of TiO_2/SnO_2 composites thin films

The cross-sectional morphologies was observed with SEM. Figure 2 shows cross-sectional morphologies of TiO_2/SnO_2 composites thin films prepared by sol-gel method and dipped coating on the glass substrate with the 50,000 magnifications. It was found that the thickness of all composites thin films in the range of 0.25 to 0.50 μm and their surface are dense and very smooth.







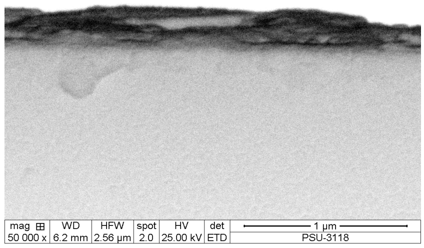


Fig.2 SEM image of TiO_2/SnO_2 composites thin films with the 50,000 magnifications

3.2 Photocatalytic activity

The photocatalytic degradation of MB by using TiO_2/SnO_2 thin films under UV irradiation is show in Figure 3. It was apparent that SnO_2 added in TiO_2 has significantly effect on photocatalytic reaction under UV irradiation compared with undoped SnO_2. For TiO_2 doped with SnO_2 thin films, it was found that the photocatalytic activity decreases with increases SnO_2 doping. The MB degradation percentage of thin films under UV irradiation is shown in Table 1. It was found that MB degradation percentage of thin films under UV irradiation for 6 h are 39.6, 58.1, 53.3 and 47.5% for 0, 1, 3 and 5 mol% of SnO_2 doping, respectively. It was found that $TiO_2/1SnO_2$ thin films show the best photocatalytic activity.

3.3 Self-cleaning properties

Self-cleaning properties of thin films based on hydrophilic phenomenon can be considered in terms of contact angle of water droplets on the thin films. The contact angles of water droplets TiO_2/SnO_2 composites thin films coating on the glass substrate measured after UV irradiation for 0, 10, 30 and 60 min are shown

Figure 4. It was apparent that SnO_2 added in TiO_2 has significantly effect on hydrophilic properties under UV irradiation [11], with the hydrophilic properties increases with add SnO_2 doping.

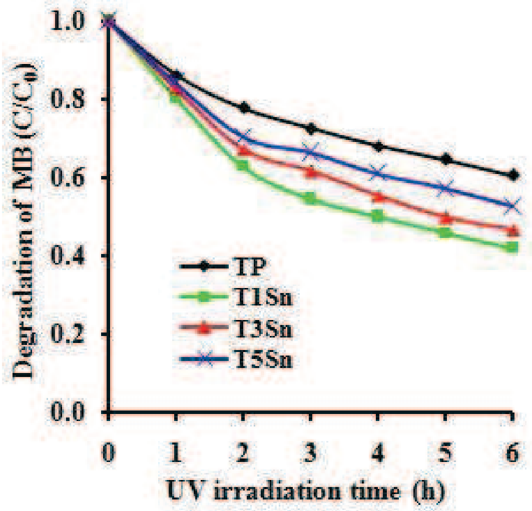


Fig.3 The photocatalytic activity of TiO_2/SnO_2 thin films

Table 1 The degradation percentage of MB of TiO_2/SnO_2 thin films

SnO_2	UV irradiation time (h)					
mol%	1	2	3	4	5	6
0	13.8	22.3	27.6	31.9	35.4	39.6
1	19.6	37.2	45.5	50.0	54.3	58.1
3	17.2	32.9	38.5	44.7	50.2	53.3
5	15.8	29.9	33.6	39.0	42.8	47.5

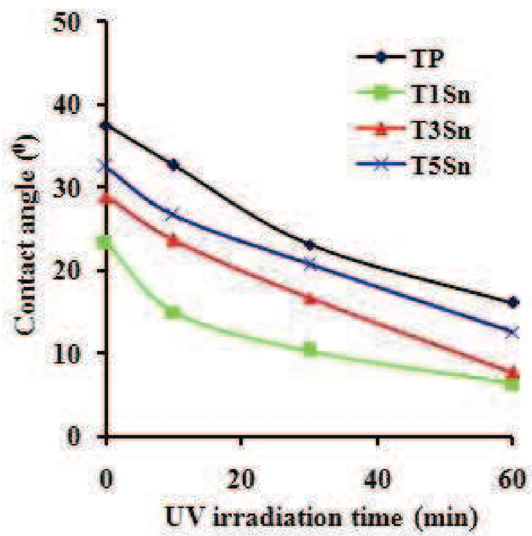


Fig.4 The contact angle of water droplets TiO_2/SnO_2 composites thin films

We should note here that the TiO_2/SnO_2 composites thin films on hydrophilicity for 60 min under UV irradiation prior to measurement are shown in Figure 5**.** It found that the contact angle for water is 16.2° for the pure TiO_2 thin films, and 6.4°, 7.8°, 12.6° for the TiO_2/SnO_2 composites thin films with SnO_2 doping 1, 3 and 5 mol%, respectively.

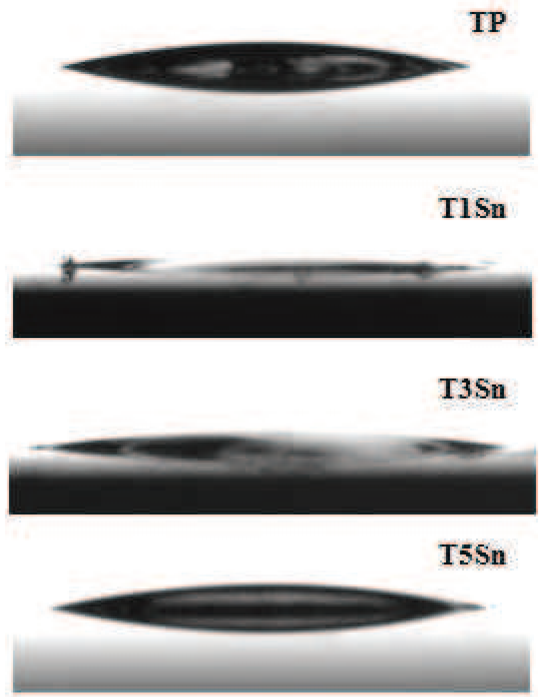


Fig.5 Image of water droplet contact angle measured after UV irradiation for 60 min

3.4 Antibacterial properties

Figure 6 present the *E.coli* survival rate after testing under UV irradiation of TiO_2/SnO_2 composites thin films, showing decrease in *E.coli* survivals with irradiation time. The result indicated that TiO_2 doped with 1% SnO_2 composites thin films exhibited higher antibacterial properties compared to TiO_2 doped with 0, 3 and 5% SnO_2 composites thin films, respectively.

The *E.coli* kill percentage of TiO_2/SnO_2 composites thin films under UV irradiation is show in Figure 7. It was found that the *E.coli* were killed of composites thin films under UV irradiation for 3 h are 30.33, 80.67, 49.33 and 43.67% for TiO_2 doped with 0, 1, 3 and 5% SnO_2 composites thin films, respectively. The photo of viable bacterial colonies (red spots) on synthesized TiO_2/SnO_2 composites thin films treated with UV irradiation for 0, 1, 2 and 3 h are illustrated in Figure 8.

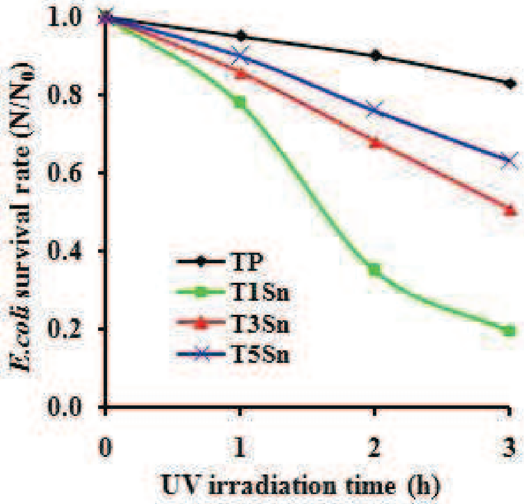


Fig.6 Antibacterial activity of TiO_2/SnO_2 composites thin films

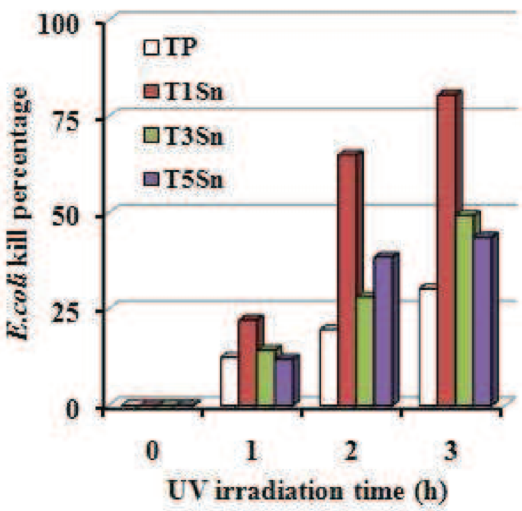


Fig.7 The *E.coli* kill percentage of TiO_2/SnO_2 composites thin films

It is very obvious that the cell walls and cell membranes were damaged when microbial cells came into contact with TiO_2/SnO_2 composite thin films being activated by UV light. In this sense, the photo-generated hydroxyl (OH°) and super oxygen (O_2^-) radicals acted as powerful oxidizing agents which react with peptidoglycan (poly-*N*-acetylglucosamine and *N*-acetylmuramic acid) of bacterial cell wall [21]. Figure 9 shows an image of the *E.coli* cell wall and membrane damages of $TiO_2/1SnO_2$ composite thin film treated with UV irradiation for 3 h.

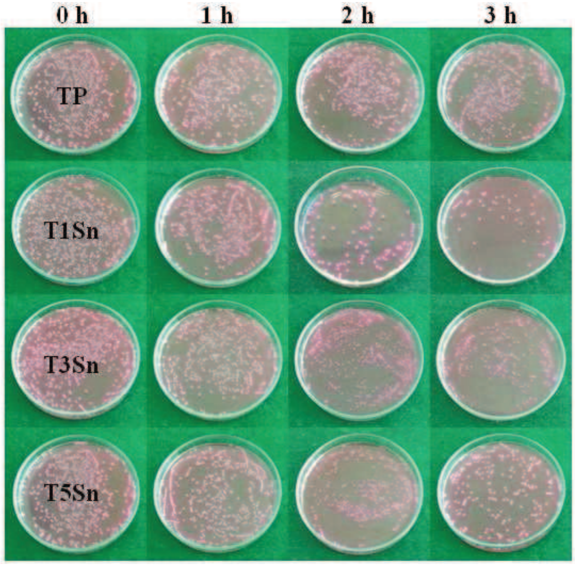


Fig.8 Photo of viable *E.coli* colonies (red spots) on synthesized TiO_2/SnO_2 composites thin films

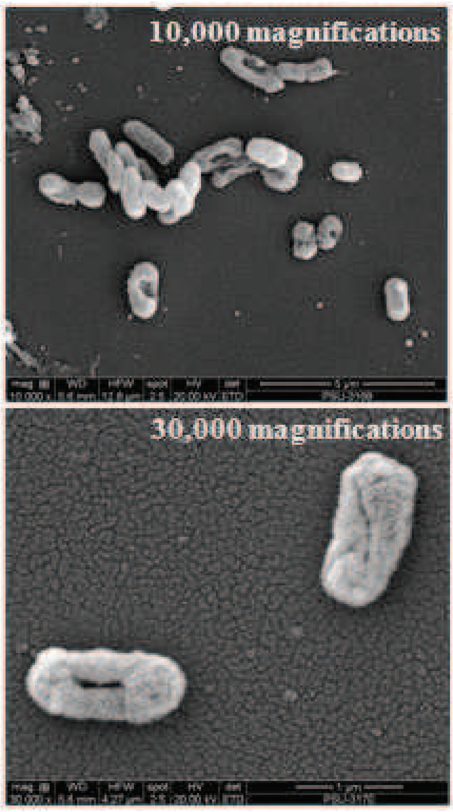


Fig.9 SEM image of the *E.coli* cell wall and membrane damages of $TiO_2/1SnO_2$ composite thin film treated with UV irradiation for 3 h

4. CONCLUSION

In this work, TiO_2/SnO_2 composites thin films were prepared by sol-gel method and dipped coating on glass substrate. It was found that SnO_2 affects to self-cleaning and antibacterial of *E.coli* properties. It can be note that $TiO_2/1SnO_2$ composites thin film has highest self-cleaning properties (small contact angle, 6.4° for 60 min) and antibacterial of *E.coli* properties (80.67% for 3 h).

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