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Original Article

Photoactivity and hydrophilic property of SiO_2 and SnO_2 co-doped TiO_2 nano-composite thin films

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Abstract

SiO_2 and SnO_2 co-doped TiO_2 nano-composite thin films were prepared by sol-gel method. The effects of film thickness and amount of SiO_2 and SnO_2 co-doping into TiO_2 nano-composite films on phase presence, crystallite size, photocatalytic reaction and hydrophilicity were investigated. Thickness of 3-coating layers (238 nm) seems to provide the highest photocatalytic activity. The crystallinity of anatase phases, crystallite sizes and photocatalytic reactions of SiO_2 and SnO_2 co-doped TiO_2 films decrease with an increase in SiO_2 content. It was found that more amount of SiO_2 addition seems to inhibit grain growth and the formation of anatase phase; especially when it was synthesized at temperature less than 600°C. The photocatalytic reaction seems to decrease with an increase in SiO_2 doping when the concentrations of SnO_2 in the composite films are fixed. It was apparent that $1SiO_2/1SnO_2/TiO_2$ composite film exhibits the highest photoactivity. Suitable amounts of SiO_2 and SnO_2 doping into the TiO_2 composite films tend to enhance the hydrophilic property of the films. It was also apparent that the $3SiO_2/3SnO_2/TiO_2$, $5SiO_2/5SnO_2/TiO_2$ and $10SiO_2/3SnO_2/TiO_2$ composite films exhibit super hydrophilic characteristics under UV irradiation for 30 min.

Key words: TiO_2 nano-composite film, $SiO_2/SnO_2/TiO_2$ film, photocatalytic activity, hydrophilic property, sol-gel

1. Introduction

TiO_2 photocatalyst has been used for many purposes such as environmental treatment, self-sterilization and self-cleaning surfaces. The surface of TiO_2 under UV or visible light irradiation exhibits hydrophilic property and can be applied for anti-fogging glasses. The superhydrophilicity, expressed in terms of zero degree of water contact angle, shows self-cleaning effect. Many studies have been reported on doping metal oxides to TiO_2 to improve efficiency of TiO_2 photocatalyst. The most popular oxides doped in TiO_2 are SiO_2(Guan *et al.*, 2003; Awate *et al.*, 2005; Annaoui *et al.*, 2006; Xu *et al.*, 2009) and SnO_2 (Liu *et al.*, 2002; Yang *et al.*, 2002; Chun *et al.*, 2004; Lin *et al.*, 2008). Doping SiO_2 in TiO_2 enhances hydrophilic property. It was found that addition of 40 mol% SiO_2 to TiO_2 can lower the contact angle of water since Ti-O-Si bonds increases the acidity which induces increasing hydroxyl content in the composite film (Guan *et al.*, 2003). However, addition of SiO_2 suppresses growth of TiO_2 during calcination and enhances thermal stability for

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the phase transformation of TiO_2 particles from anatase to rutile and SiO_2 also acts as carrier of TiO_2. Doping SnO_2 in TiO_2 films could also improve hydrophilicity and photocatalytic activity of composite films due to reduction of TiO_2 particles growth rate (Liu *et al.*, 2002). In order to prepare stronger films of TiO_2 or TiO_2 composite coated on substrates such as glass, metal and polymer, via sol-gel process, SiO_2 had been introduced as a buffer layer or mixed into TiO_2 and TiO_2 composite. In this study, SiO_2 was introduced on SnO_2/TiO_2 films since photocatalytic activity and hydrophilicity of composite SiO_2/SnO_2/TiO_2 films have yet to be reported. SiO_2 and SnO_2 co-doped TiO_2 nano-composite thin films were thus prepared by sol-gel method and coated on soda lime glass substrates by spin coating technique. This paper shows the effect of film thickness and concentration of SiO_2 and SnO_2 co-doped in TiO_2 nano-composite films on anatase crystallinity, crystallite size, photocatalytic reaction and hydrophilic property.

2. Experimental Details

2.1 Preparation of TiO_2 and composite TiO_2 thin films

TiO_2 thin films were prepared by sol-gel method in order to investigate the effect of film thickness. Titanium tetra-isopropoxide (TTIP) 9 ml was firstly dissolved in 145 ml ethanol, stirred at room temperature with a speed of 800 rpm for 30 min and pH of the mixed solution was adjusted to 3.5 with 2 M hydrochloric acid. Secondly, 1.6 ml distilled water was added to the solution, stirred for 30 min to achieve the mole ratio of TTIP:C_2H_5OH:H_2O = 1:82:3. The prepared solution so-called *clear sol* was kept at room temperature for 8 h before coating on a clean soda lime glass substrate (10x10x0.3 cm) by spin coating at a speed of 1700 rpm. Thirdly, the 1, 2 and 3- layered coating specimens were prepared and dried at room temperature for 24 h. Then the specimens were annealed at 500ºC for 2 h with a heating rate of 10ºC/min to obtain TiO_2 thin films.

The sols as the source of the composite $xSiO_2$/$ySnO_2$/TiO_2 films used for coating on soda lime glass substrates were prepared by dissolving certain amounts of TTIP and tetraethyl orthosilicate with 145 ml ethanol, stirred at room temperature at a speed of 800 rpm for 30 min before mixing with a hydrous stannic chloride. The prepared sols were kept at room temperature for 8 h before coating on clean soda lime glass substrates. The x and y in the $xSiO_2$/$ySnO_2$/TiO_2 system represented the mole percentage, respectively, of SiO_2 and SnO_2 doping in TiO_2 where x varied at 1, 3, 5 and 10 mol% SiO_2 and y varied at 1, 3, and 5 mol% SnO_2. Since it was found from our previous study that three layered coating films exhibit the highest photocatalytic activity, therefore, only three layered nano-composite films were prepared for $xSiO_2$/$ySnO_2$/TiO_2 system. The coated specimens were dried at room temperature for 24 h and then heat-treated at 600ºC temperature for 2 h to form anatase phase since this is the most effective temperature of amorphous TiO_2 - anatase phase transformation. We had found that anatase phase does not form at temperature below 600ºC.

2.2 Characterization and photocatalytic activity test

The phase and the crystallite size of TiO_2 and composite $xSiO_2$/$ySnO_2$/TiO_2 films were characterized using X-ray diffraction (XRD). The morphology, the film roughness and the crystallite size of TiO_2 films were observed using Atomic force microscopy (AFM). Dispersion of the TiO_2 phase in the films was observed by X-ray mapping images and Energy dispersive x-ray (EDX) attached to a Scanning electron microscopy (SEM) device. Photocatalytic activity was performed by means of degradation of methylene blue solution with a concentration of $1x10^{-5}$ M under UV irradiation with an intensity of 3.89 mW/cm^2 for 2, 4 and 6 h. The concentration of the tested solution was measured using Ultraviolet-Visible spectrophotometer (UV-Vis). The hydrophilic property of the composite films was also evaluated by measuring the water droplet contact angle under UV irradiation by a 36-W ultraviolet light.

3. Results and Discussion

3.1 Effect of film thickness

It was revealed from the XRD spectra of pure TiO_2 films calcined at 500ºC that only TiO_2 anatase phase was found except for those at 10 mol% of SiO_2 and SnO_2 doping where only amorphous phase of TiO_2 was formed. The dispersion of TiO_2 in the coated films was observed by X-ray mapping technique illustrated in Figure 1. The three- layer coated film exhibited the highest Ti-O dispersion density. From AFM analysis, we found that the thicknesses of single, double and triple layers are 54, 124 and 238 nm respectively. The surface roughness and TiO_2 grain size are listed in Table 1. It can be seen that the surface of triple-layer coated film is

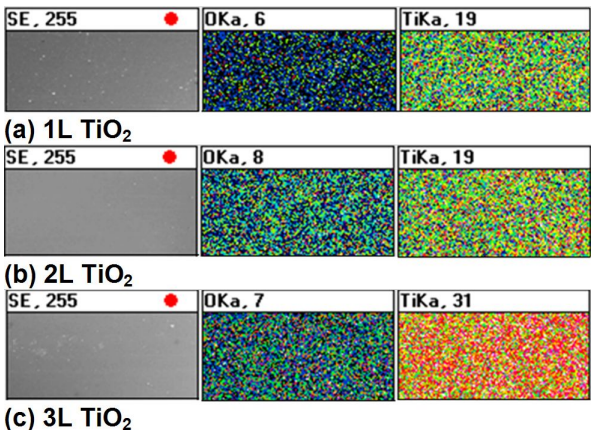

Figure 1. Effect of thickness of TiO_2 films calcined at 500ºC on Ti and O distributions for (a) single, (b) double, and (c) triple layers.

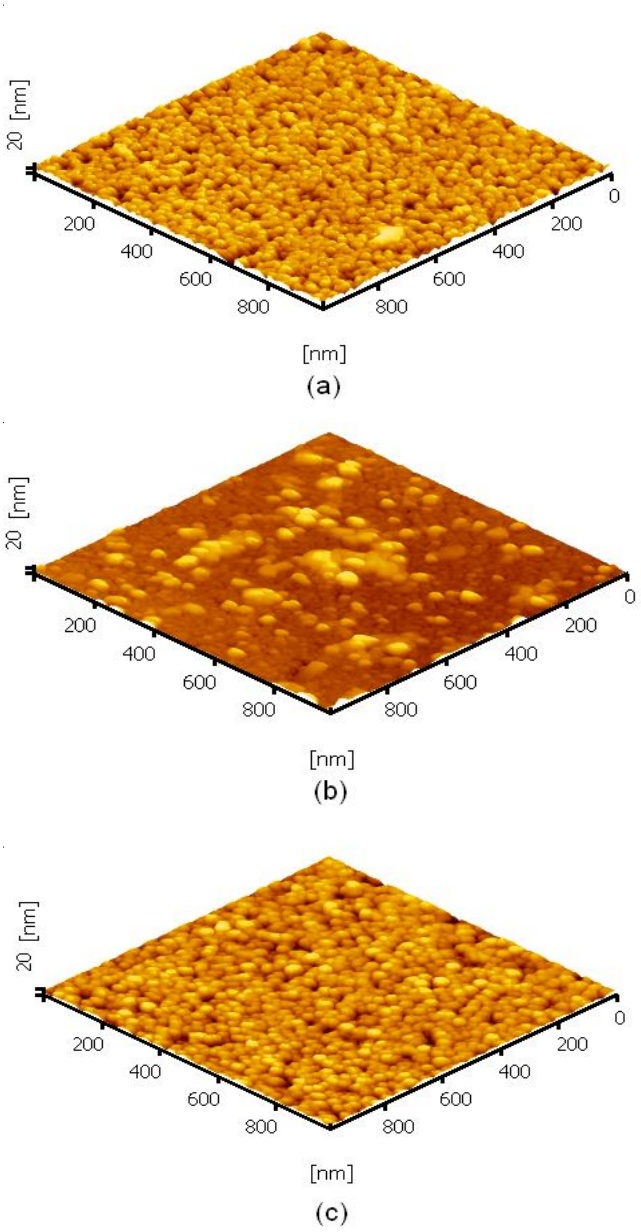

Figure 2. Illustration of AFM images of TiO_2 films calcined at 500ºC for (a) single, (b) double and (c) triple layers.

smoother than those of single and double layers. The surface smoothness seems to correlate to the crystallite or grain size and the closed size distribution of TiO_2 film as shown in Figure 2.

Table 1 shows the result of photocatalytic decolourization of methylene blue by TiO_2 films with different film thickness treated under UV irradiation for 6 h. It was apparent that the film thickness has an effect on the photocatalytic activity, i.e., photocatalytic reaction increases with an increase in film thickness from single layer to triple layer due to higher photo-induced electron density transferred from the surface of TiO_2 (Figure 1).

The water droplet contact angles on TiO_2 films measured after exposure to natural light irradiated for 30 min are listed in Table 1. These have been found to be on the decrease with increasing coated thickness; i.e. it was 5º for the triple-layer coated film and were 6º and 13º for the single and double layers respectively. With increasing number of coating cycle, and hence the coated thickness, the photo-induced electron density at TiO_2 surface increases and more hydroxyl is produced resulting in a decrease in contact angle.

3.2 Effect of SiO_2 and SnO_2 co-doped concentration

The XRD spectra of pure TiO_2 and SiO_2 and SnO_2 co-doped composite films calcined at 600 ºC illustrated in Figure 3a revealed that SiO_2 reduces growth rate of TiO_2 anatase phase. The higher concentration of SiO_2 added the more reduction in the anatase crystallinity and the crystallite size of the composite films (Table 2). As can be observed, at 10 mol% SiO_2 doping, only the amorphous phase of TiO_2 was formed. Figure 3b shows the effect of SnO_2 dosage on the anatase phase and the crystallite size. It was found that addition of 1~5 mol% SnO_2 with fixed SiO_2 content rendered a slight effect on the growth of anatase crystalline. However 10 mol% or more SnO_2 doping tended to hinder the TiO_2 growth. Introduction of Sn^{4+} in the composite sol at pH~ 3.5

Table 1. Effect of thickness and TiO_2 film coating synthesized at 500ºC on surface roughness, photocatalytic decolourization of methylene blue performed after 6h UV irradiation and contact angle measured under 30 min natural light

Items	Number of coating cycles		
	1	2	3
Film thickness (nm)	54	125	238
Roughness (nm)	3.8	3.4	3.0
TiO_2 grain size (nm)	24.6	11.6	16.2
Decolourization (%)	34.48	61.00	78.05
Contact angle (º)	6.0	13.0	5.0

Table 2. Effect of SiO_2 and SnO_2 co-doped in TiO_2 composite films heat-treated at 600ºC on crystallite size determined by using Scherrer equation (Xu *et al.*, 2009).

SiO_2 content (mol %)	Crystallite size (nm)		
	SnO_2 content (mol %)		
	1	3	5
1	17.92	25.09	17.92
3	12.54	15.68	15.68
5	10.46	12.54	12.55
10	7.83	8.20	12.70
Pure TiO_2		17.91	

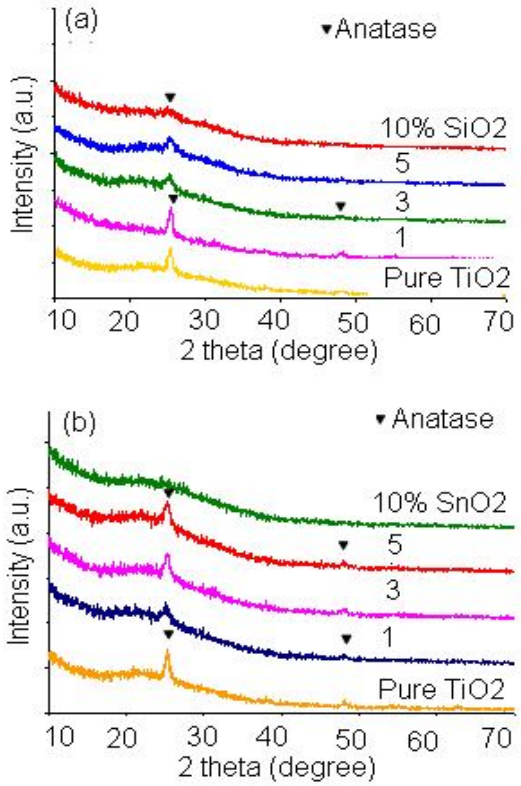

Figure 3. Effect of SiO_2 (a) and SnO_2 (b) on transformation of anatase phase of TiO_2 composite films calcined at 600ºC.

changes the surface charge of TiO_2 sol particles to be more positive and distances them from each other by electrostatic repulsive potential which leads to smaller size of TiO_2 formed in the composite thin films.

Figure 4 shows the effect of SiO_2 concentration doped in TiO_2 composite films at fixed concentrations of SnO_2 (1, 3 and 5 mol %) on photocatalytic decolourization kinetics of methylene blue solution. It was found that the more SiO_2 content the less was the degradation rate. This is because SiO_2 doping has an influence on the hindrance of anatase crystal growth, leading to a low degree of anatase crystallinity. Although higher concentration of SiO_2 resulted in reduction of crystallite size of the composite films (Table 2), in this case it cannot promote the photocatalytic acitivity. The effect of SiO_2 and SnO_2 co-doped in the composite TiO_2 films on photocatalytic degradation of methylene blue at 6 h-UV irradiation, summarized in Figure 5 and Table 3, confirmed the result discussed above for 1~3 mol% SnO_2 addition. Similar to the 1~3 mol%SiO_2 doping, higher amount of SnO_2 addition at fixed concentrations of SiO_2 (1~3 mol%) resulted in a decrease in degradation rate due to prohibition of anatase crystal growth similar to the effect of SiO_2. It was also found that $1SiO_2/1SnO_2/TiO_2$ composite film exhibited the highest activity.

The effect of SiO_2 and SnO_2 co-doping on hydrophilicity of the TiO_2 composite films in terms of water contact

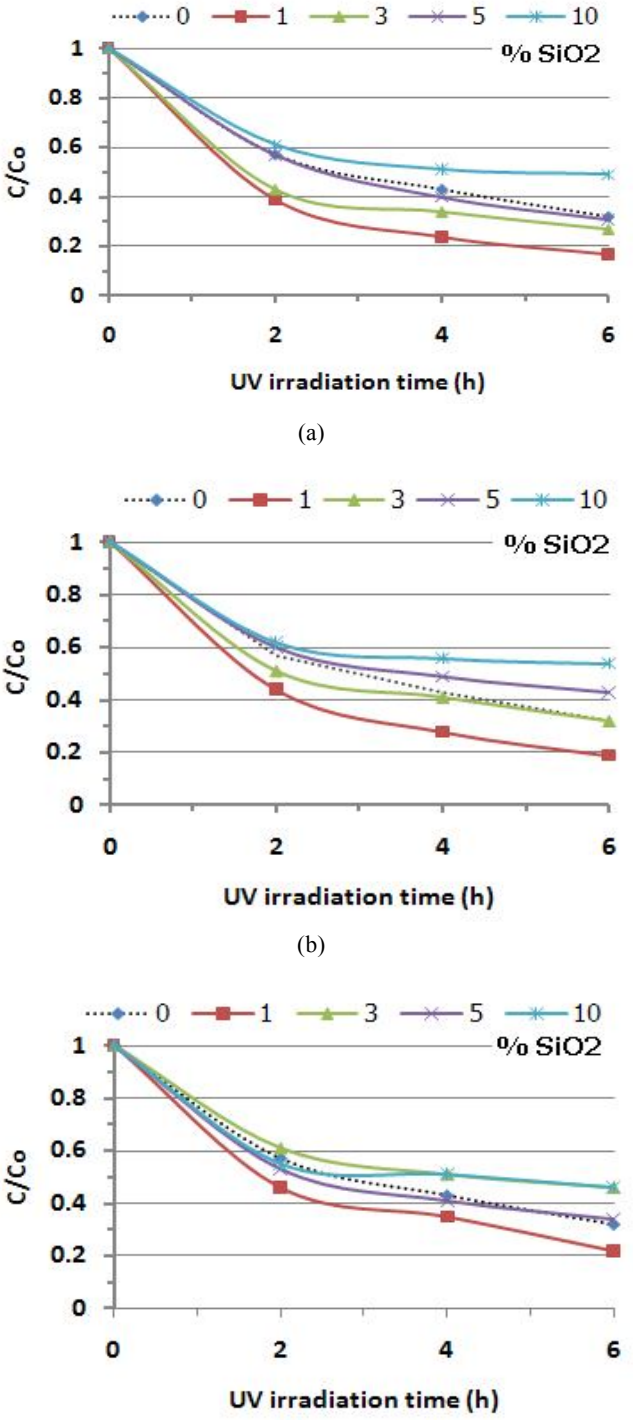

Figure 4. Effect of SiO_2 concentration doped in composite TiO_2 films at fixed concentration of SnO_2, (a) 1 mol%, (b) 3 mol % and (c) 5 mol%, on photocatlytic decolourization kinetics of methylene blue solution.

angles measured against UV irradiation time is shown in Figure 6. It was apparent that contact angles depend on the crystallite size as listed in Table 2 and Figure 7. The smaller the crystallite size the more hydrophilicity of the films. The

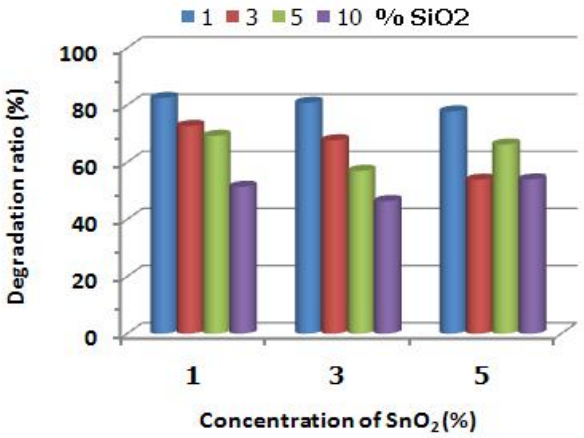

Figure 5. Effect of the concentration of SiO_2 and SnO_2 co-doped in TiO_2 composite films calcined at 600ºC on photodegradation of methylene blue under 6 h UV irradiation.

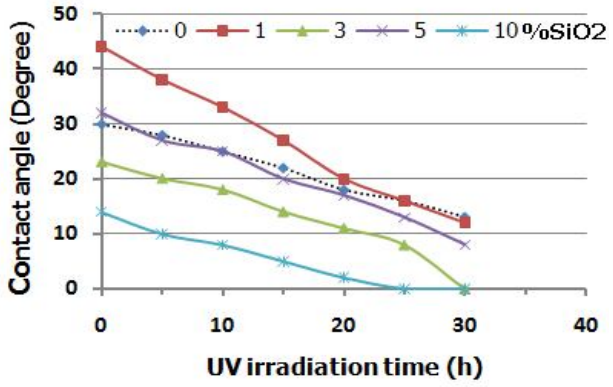

Figure 6. Relationship between contact angles of $xSiO_2/3SnO_2/TiO_2$ films and UV irradiation time.

Table 3. Effect of SiO_2 and SnO_2 co-doped in TiO_2 composite films heat-treated at 600ºC on photocatalytic decolourization of methylene blue performed by 6 h UV irradiation.

SiO_2 content (mol %)	Photocatalytic decolourization (%)		
	SnO_2 content (mol %)		
	1	3	5
1	82.51	80.83	77.80
3	72.69	67.72	53.94
5	69.24	56.97	66.24
10	51.44	46.42	53.98
Pure TiO_2		68.06	

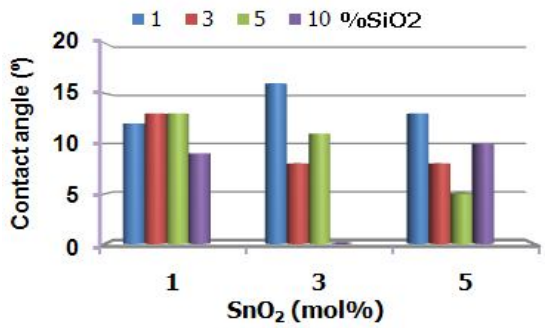

Figure 7. Contact angles of $xSiO_2/ySnO_2/TiO_2$ films under 25 min UV irradiation time

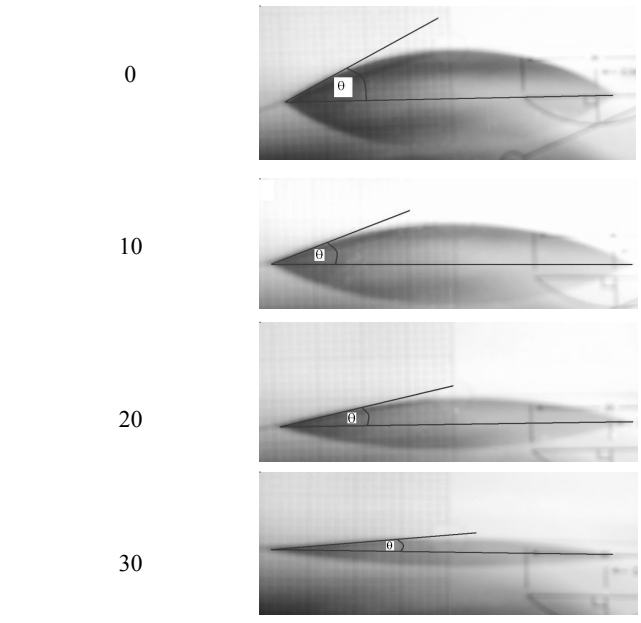

Figure 8. Images of contact angles of $3SiO_2/SnO_2$ / TiO_2 film under 0-30 min UV irradiation

$10SiO_2/3SnO_2/TiO_2$ film exhibited superhydrophilicity (contact angle = 0º) indicating self-cleaning effect of the composite film. For longer UV irradiation time of 30 min, $3SiO_2/3SnO_2/TiO_2$ and $5SiO_2/5SnO_2/TiO_2$ films also exhibited superhydrophilic property. Figure 8 illustrates images of water contact angles at 0~30 min-UV irradiation times. It confirms that contact angle decreases with increasing UV irradiation time as shown in Figure 6.

4. Conclusions

According to the results, we can conclude that:

1. The thickness of the 3-coating layers (238 nm) provided the highest photocatalytic activity and hydrophilicity.

2. Crystallinity of anatase phase and crystallite sizes of SiO_2 and SnO_2 co-doped TiO_2 films decreases with incresing SiO_2 content while they have been slightly influenced by 1~3 mol% SnO_2 doping.

3. Photocatalytic reaction of composite film decreases with increasing SiO_2 content as SnO_2 concentration is fixed to 1~3 mol% and vice versa, i.e., the reaction decreases with increasing SnO_2 content as SiO_2 concentration is fixed to 1~3 mol%.

4. It was found that $1SiO_2/1SnO_2/TiO_2$ composite film exhibits the highest activity.

5. Suitable amount of SiO_2 and SnO_2 co-doping tends to enhance hydrophilic property. The $3SiO_2/3SnO_2/TiO_2$, the $5SiO_2/5SnO_2/TiO_2$ and the $10SiO_2/3SnO_2/TiO_2$ composite films exhibited superhydrophilicity (self-cleaning effect) under UV irradiation for 30 min.

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