Self-cleaning Properties of TiO₂-SiO₂-In₂O₃ Nanocomposite Thin Film

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TiO_2 -SiO_2 -In_2O_3 nanocomposite thin film was deposited on the glass substrates using a dip coating technique. The morphology, surface composition, surface hydroxyl groups, photocatalytic activity and hydrophilic properties of the thin film were investigated by AFM, XPS, methyl orange decoloring rate and water contact angle measurements. The hydroxyl content for TiO_2, TiO_2-SiO_2 and TiO_2-SiO_2-In_2O_3 nanocomposite films was calculated to be 11.6, 17.1 and 20.7%, respectively. TiO_2-SiO_2-In_2O_3 film turned superhydrophilic after 180-min irradiation with respect to pure TiO_2 and TiO_2-SiO_2 thin films. The photocatalytic decomposition of methyl orange for TiO_2, TiO_2-SiO_2 and TiO_2-SiO_2-In_2O_3 thin films was measured as 38.19, 58.71 and 68.02%, respectively. The results indicated that SiO_2 and In_2O_3 had a significant effect on the hydrophilic, photocatalytic and self-cleaning properties of TiO_2 thin film.

Key Words : Sol-gel processes, TiO_2, Self-cleaning

Introduction

The self-cleaning property of TiO_2 thin films has become an interesting subject in recent years. The self-cleaning property has been known to be a combined effect of the two photoactive characteristic properties of TiO_2 thin films: super-hydrophilicity and photocatalysis.[1-3] The photocatalytic 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 TiO_2 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] Thus, the photocatalytic and hydrophilic properties of TiO_2 coated glass allow the water to easier wash away deposited particles.

TiO_2 thin films on glass substrates are widely used in various applications such as mirrors, window glasses, light bulb, automobile windshields and optical lenses.[6,8]

However, TiO_2 thin film exhibits hydrophilicity and photocatalysis under the ultraviolet light irradiation.

In practical applications, the ultraviolet light irradiation on the TiO_2 surface does not always occur. Therefore, it is desirable that the TiO_2 retain its hydrophilic and photocatalytic property for a long time in a dark place. This is a main purpose in this research.

Machida[9] indicated that the addition of silica to titania (10-30 mol % SiO_2) and formation of TiO_2 -SiO_2 composite film, improved the hydrophilicity of TiO_2 especially in a dark place. Guan[4] investigated the effect of SiO_2 on the self-cleaning property of TiO_2 thin films. He showed that the addition of SiO_2 has a significant effect on the superhydrophilicity, photocatalysis and therefore self-cleaning properties of titania thin films. Shchukin[10] and Sviridov[11] investigated the effect of In_2O_3 on the photocatalytic and hydro-

philic properties of TiO_2 thin films. They showed that the addition of In_2O_3 has a noticeable effect on the photocatalytic and hydrophilic and then self-cleaning properties of titania thin films.

However, the self-cleaning properties of the TiO_2-SiO_2-In_2O_3 sol-gel derived thin films have not been investigated yet. In the present study, TiO_2-SiO_2-In_2O_3 thin films were prepared by the sol-gel dip coating method on the glass substrates. Then, hydrophilic, photocatalytic and self-cleaning properties of the thin films were investigated.

Experimental

First, TiO_2 and SiO_2 sol solutions were made. The procedure for the preparation of TiO_2 and SiO_2 sol solutions is as described in detail in our earlier published work.[12]

In the following, the In_2O_3 precursor sol was prepared by dissolving the desired amount of the precursor salt indium (III) chloride in ethanol and hydrochloric acid. Then, the solutions were mixed together in a certain quantities. In order to make a comparison, the following sol solutions (films) were prepared from pure TiO_2, TiO_2-SiO_2 and TiO_2-SiO_2-In_2O_3. The mol ratio of TiO_2:SiO_2:In_2O_3 was taken as 4:1:0.2.

Before coating, soda-lime glass substrates were ultrasonically cleaned in acetone and ethanol for 15 and 20 min, respectively. The cleaned glass was then immersed into the sol and withdrawn speed of 5 cm/min. In this way the substrate glass was covered with a thin layer of film. The film was naturally dried in the air and the coating operation was repeated again. The coated sample was then heat treated at 500 ºC for 2 h.

The thickness of the films was increased by repeating the cycles from withdrawing to heating. This procedure was

carried out six times. According to the Guan method,[4] the average thickness of the film was estimated to be ~490 nm.

It is necessary to mention that during annealing of films at 500 ºC, it is possible that some ions (sodium or calcium) penetrated from glass substrate to the thin films and the effect on film properties. To resolve this problem, before thin film preparation, a thin layer of SiO_2 was deposited on glass substrates. This layer was acted as barrier layer. The thickness of this layer was measured around 56 nm.

The surface morphology of the film was observed by atomic force microscopy. The surface properties of the thin film samples were analyzed by X-ray photoelectron spectroscopy (XPS, JEOL) using Mg Ka source (1253.6 eV). The X-ray source was operated at 10 kV for a current of 10 mA. Spectra were calibrated with respect to the C1s peak at 284.6 eV.[13] The O1s peak of films was deconvoluted using a Gaussian-20% Lorentzian function after subtraction of the background by the Shirley method.

The photo induced super-hydrophilicity of the nanofilm was evaluated by measuring the contact angle of a water droplet on the film surfaces. A droplet was injected on to the surface using a 1 μL micro-injector. The water contact angle (WCA) was averaged from five measurements. UV-vis was irradiated to the surface of the samples by Xe lamp (power 300W, wavelength 300-500 nm). In the part of photo induced super-hydrophilicity measurements, samples were stored in a drying oven at 120 ºC for overnight before use. In addition, the hydrophilic-hydrophobic conversion of films after storage in a dark place was investigated.

The photocatalytic activities of films under UV-vis irradiation were evaluated by the decoloring rate of methyl orange ($C_{14}H_{14}N_3SO_3Na$). Methyl orange was also used as a model organic compound to measure the photoreactivity in other studies.[14,15]

One sample of thin film (surface area 6 cm^2) was horizontally placed at the bottom of the testing cell containing 25 mL (2×10^{-5} M) methyl orange solution. The solution was irradiated with an Xe lamp (300W, wavelength 300-500 nm) under ultrasonic stirring.

After irradiation, the light absorbance of the methyl orange solution was measured using a UV-vis spectrophotometer at 464 nm, which is the maximum absorption of methyl orange.[16] Then, the decoloring rate of the methyl orange, was used to quantify the photocatalytic activities of thin films, and calculated using following equation:[17]

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

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

Results and Discussion

AFM was used to characterize the surface morphology, particle size, and surface roughness of pure and composite films. Figure 1 shows AFM images of TiO_2 and TiO_2-SiO_2-In_2O_3 thin films. It can be seen from the Figure 1 that films have granular microstructure. The average size of particles in the TiO_2 and TiO_2-SiO_2-In_2O_3 thin films are approximately 78 nm and 45 nm, respectively. In addition to particle size, AFM gives the surface roughness. The root mean
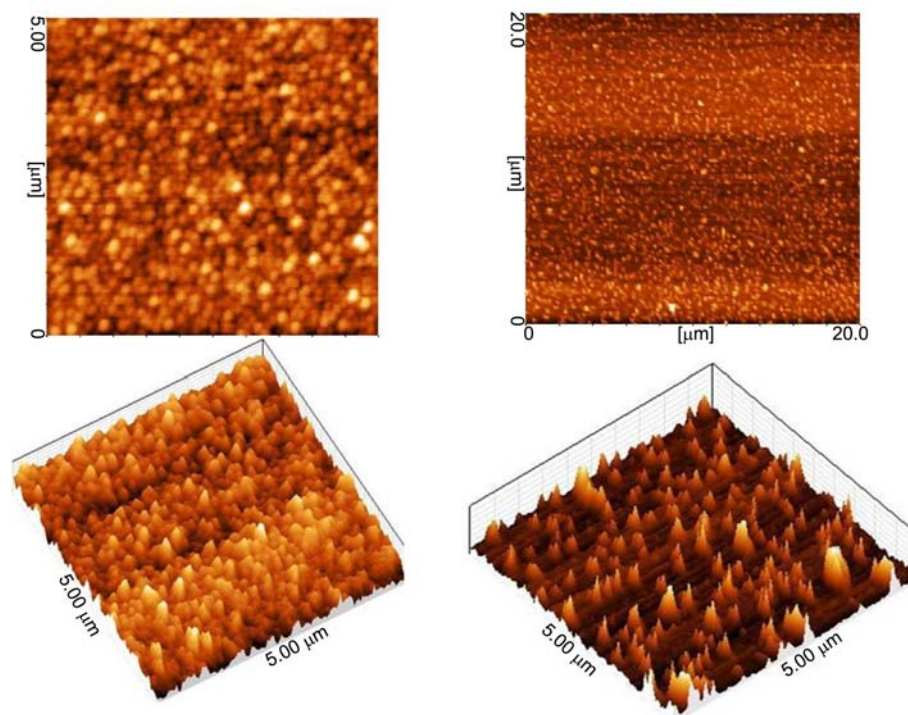

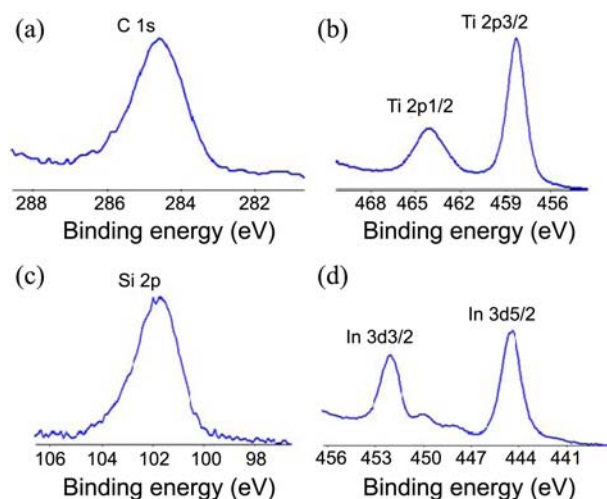**Figure 1.** 2D and 3D of AFM images: (left) TiO_2 and (right) TiO_2-SiO_2-In_2O_3 films.

Figure 2. High-resolution XPS spectra of (a), C 1s, (b) Ti 2p, (c) Si 2p and (d) In 3d.

Table 1. Water contact angle on the film surfaces

Film	TiO$_2$	TiO$_2$-SiO$_2$	TiO$_2$-SiO$_2$-In$_2$O$_3$
Contact angle (°) before irradiation	46.1	44.3	40.8
Contact angle (°) after 30 min irradiation	33.6	24.9	18.7
Contact angle (°) after 60 min irradiation	27.4	17.9	11.2
Contact angle (°) after 90 min irradiation	19.1	8.9	4.6
Contact angle (°) after 180 min irradiation	10.3	4.3	1.1
Contact angle (°) after 210 min irradiation	7.4	1.7	
Contact angle (°) after 240 min irradiation	4.6		
Contact angle (°) In a dark place for 24 h	17.1	6.7	2.9

square roughness values (Rrms) of TiO$_2$ and TiO$_2$-SiO$_2$-In$_2$O$_3$ films are 5.43 and 3.8, respectively.

Figure 2 shows high resolution XPS scan spectra for TiO$_2$-SiO$_2$-In$_2$O$_3$ thin film. The Ti 2p, Si 2p and In 3d spectra indicated the chemical states of Ti, Si, and In to be Ti^{4+}, Si^{4+} and In^{3+}, respectively. Therefore, the XPS spectrum confirms that the film contains titania, silica and indium oxide.

XPS is one of the most useful methods to measure the hydroxyl groups content on film surfaces. In literature, the O 1s peak was often believed to be composed of several different oxygen species, such as lattice oxygen, oxygen on reduced titanium (Ti^{3+}), oxygen connected to surface carbon species, hydroxyl groups and adsorbed water.[18] In the present study, the obtained XPS peaks were assigned to lattice oxygen (Peak 1) and surface hydroxyls (Peak 2), for convenience, and their contents were estimated by deconvolution using two pseudo-Voigt functions as shown in the Figure 3.

The hydroxyl content for TiO$_2$, TiO$_2$-SiO$_2$, and TiO$_2$-SiO$_2$-In$_2$O$_3$ thin films was calculated 11.6, 17.1 and 20.7%, respectively. The hydroxyl content (%) is the ratio of the area of peak 2 to the total area of the two O 1s peaks. This difference in the hydroxyl density is discussed in relation to the results of hydrophilic and photocatalytic properties in the
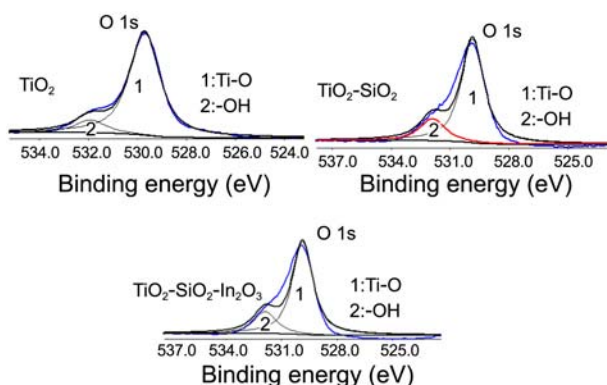

Figure 3. High-resolution O 1s spectra of thin films.

following sections.

Table 1 presents the results for the water contact angle on the thin film surfaces under irradiation and storage in a dark place. As shown in the Table 1, TiO$_2$-SiO$_2$-In$_2$O$_3$ thin film turned super-hydrophilic after 180 min under light irradiation, meanwhile the contact angle of the TiO$_2$ changed slightly throughout the measurement.

As seen in the Table 1, during storage in a dark place, the water contact angles of the TiO$_2$-SiO$_2$-In$_2$O$_3$ thin film increased slightly over time and super-hydrophilicity was maintained for a long time. Whereas, the water contact angles of the TiO$_2$ thin film increased with time and the surface of the film is converted to a hydrophobic state. Therefore, the hydrophilic- hydrophobic conversion rate is slower for TiO$_2$-SiO$_2$-In$_2$O$_3$ than pure TiO$_2$ film.

According to the water contact angle results, addition TiO$_2$ thin film with SiO$_2$ and In$_2$O$_3$ improves superhydrophilicity under irradiation and in a dark place. This phenomenon is described in the following.

As we have previously shown, Lewis acidity is present in the structure of TiO$_2$-SiO$_2$ thin film which is due to the appearance of excessive positive charges.[12] Therefore, hydroxyl groups are adsorbed on to the thin film surfaces. The hydroxyl group is an important factor in maintaining the superhydrophilicity of TiO$_2$ thin film especially in a dark place.[19] Therefore TiO$_2$ shows higher hydrophilicity with the presence of SiO$_2$ than in pure TiO$_2$.

In addition, Gonzalez *et al.*[20] indicated that during In$_2$O$_3$ addition into TiO$_2$, it is possible that In^{3+} cations replace Ti^{4+} cations in the TiO$_2$ structure. This phenomenon cause's charge imbalance which can be calculated according to Pauling's rules 2 [21] as shown in the following:

For Ti^{4+} ions, S = +4/6, for In^{3+} ion, S = +3/6.

Thus, charge difference for one bond is (+4/6 × 2 + +3/6) + (−2) = −1/6, and the total charge imbalance for all bonds

(six bond) is $6 \times (-1/6) = -1$.

In this case, Bronsted acidity is present, which is due to the appearance of an excessive negative charge. Therefore, H_3O^+ ions are adsorbed on the composite film surfaces which induce enhanced molecular or dissociative water adsorption and lead to the super-hydrophilic properties of composite films. Then, superhydrophilicity is induced by the conjoint presence of both kinds of acidic sites (Lewis and Bronsted sites) in the nanocomposite thin films. Therefore, TiO_2-SiO_2-In_2O_3 nanocomposite film due to very high surface acidity showed the lowest water contact angle both under irradiation and storage in a dark place in comparison to other films.

The photo-catalytic activities of thin films were characterized by the degradation of methyl orange. As shown in the Figure 4, 38.19, 58.71 and 68.02% of the methyl orange is degraded after 3 h of irradiation in the presence of TiO_2, TiO_2-SiO_2 and TiO_2-SiO_2-In_2O_3 thin films. It is obvious that TiO_2-SiO_2-In_2O_3 thin film shows the highest photocatalytic activity in comparison to others. This state can be attributed to the surface chemistry of the films which discuss in the following.

The photocatalytic activity of TiO_2 has been studied intensively for a number of years by many groups, and it is fairly well understood. Because TiO_2 is a semiconductor, the ultraviolet light can excite pairs of electrons and holes. The photogenerated electrons then react with molecular oxygen (O_2) to produce superoxide radical anions (O^{2-}), and the photogenerated holes react with water to produce hydroxyl radicals. These radicals work together to decompose organic compounds.[22,23]

On the other hand, OH^- groups can trap more photogenerated holes and improve the separation of electrons and holes[24,25] which results in the enhancement of photocatalysis. As already discussed, surface acidity is presence in the TiO_2-SiO_2-In_2O_3 thin film. Surface acidity is very important to adsorbed hydroxyl groups on the TiO_2 film surface.[19] These hydroxyl groups can improve photocatalytic activity in two ways: (1) fabrication of hydroxyl radicals and (2) inhibition of electron hole recombination. Then, methyl orange is attacked by hydroxyl radicals and generates inorganic radicals or some other intermediates. Eventually, methyl
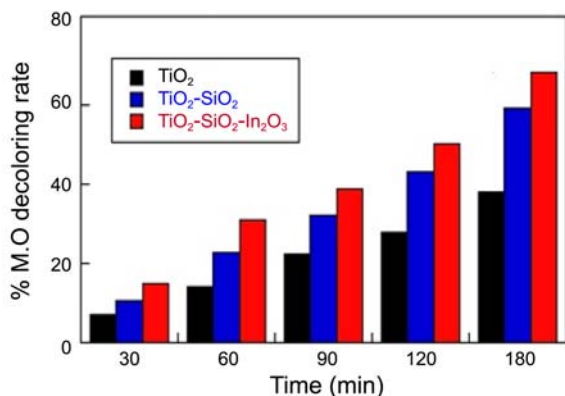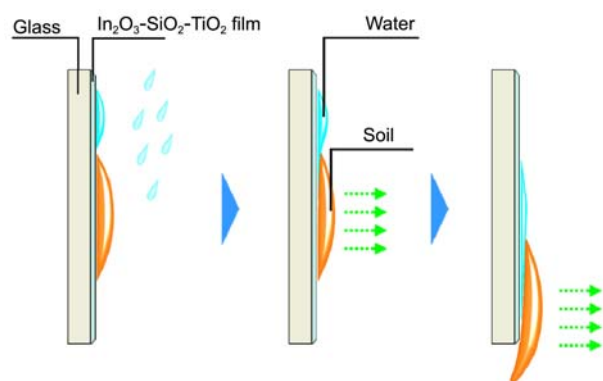

Figure 5. Self-cleaning effect of TiO_2-SiO_2-In_2O_3 nanocomposite film.

orange and intermediate compounds are oxidized into CO_2, SO_4^{2-}, and NO^{3-}.[26]

Photoactive characteristics, hydrophilicity and photocatalysis, reinforce each other to achieve the self-cleaning effect. The synergetic effect of photocatalysis and hydrophilicity can be explained as follows: There is a layer of chemisorbed water on the film surface due to hydrophilicity. The chemisorbed water or hydroxyl groups can further adsorb water by Van der Waals forces and hydrogen bonds. So the contaminant adsorbed on the surface can be easily removed by the spreading water and the glass exhibits a self-cleaning effect. However, a surface containing only a hydrophilic property cannot always maintain the self-cleaning effect. Photocatalysis can decompose the organic compounds on the TiO_2 surface and convert a hydrophobic state to a hydrophilic state. We can deduce that photocatalysis plays an important role in maintaining the self-cleaning effect in two ways: (1) decomposing the organic compounds into H_2O, CO_2.... (2) Recovery of the hydrophilicity with decomposition of the organic compounds. Figure 5 shows self-cleaning effect of TiO_2 nanocomposite thin film.

In fact, hydrophilicity and photocatalysis support each other to maintain the self-cleaning effect. The TiO_2-SiO_2-In_2O_3 nanocomposite film shows both the best hydrophilicity and the best photocatalytic properties in comparison to others. Then, it is concluded that the TiO_2-SiO_2-In_2O_3 nanocomposite film shows the best self-cleaning effect.

Conclusions

In this research, TiO_2-SiO_2-In_2O_3 nanocomposite thin film was prepared by a sol-gel dip coating method. Water contact angle measurements and photocatalytic methyl orange degradation indicated that the addition of SiO_2 and In_2O_3 improved the self-cleaning effect of TiO_2 thin film surfaces. This effect can be attributed to (1) by enhancing electron–hole pair separation and inhibiting their recombination, the SiO_2 and In_2O_3 addition enhances charge pair separation efficiency in the nanocomposite TiO_2 thin film (2) by increasing the hydroxyl group density and hydroxyl radicals on the TiO_2 surface, nanocomposite thin film improves both superhydrophilicity and photocatalytic activity of TiO_2 thin

Figure 4. Methyl orange degradation after 3 h irradiation.

film. It is concluded that SiO_2 and In_2O_3 addition improves the self-cleaning effect of TiO_2 thin film. Therefore, we suggest that TiO_2-SiO_2-In_2O_3 sol-gel derived nanocomposite thin film would be more useful than pure TiO_2 film in exhibiting self-cleaning effects for practical applications such as optical instruments.

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