

# Investigation of superhydrophilic mechanism of titania nano layer thin film—Silica and indium oxide dopant effect

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**Abstract.** In this paper, TiO<sub>2</sub>–SiO<sub>2</sub>–In<sub>2</sub>O<sub>3</sub> nano layer thin films were deposited on glass substrate using sol–gel dip coating method. Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and water contact angle measurements were used to evaluate chemical structure, surface composition, hydroxyl group contents and superhydrophilicity of titania films. FTIR result indicated that Si–O–Si, Si–O–Ti and Ti–O–Ti bands formed in TiO<sub>2</sub>–SiO<sub>2</sub>–In<sub>2</sub>O<sub>3</sub> sample. According to XPS, the hydroxyl content for TiO<sub>2</sub>, TiO<sub>2</sub>–SiO<sub>2</sub> and TiO<sub>2</sub>–SiO<sub>2</sub>–In<sub>2</sub>O<sub>3</sub> films was calculated as 11.6, 17.1 and 20.7%, respectively. The water contact angle measurements indicated that silica and indium oxide dopant improved the superhydrophilicity of titania nano film surface especially in a dark place. The enhanced superhydrophilicity can be related to the generation of surface acidity on the titania nano film surfaces. In the present state, superhydrophilicity is induced by the simultaneous presence of both Lewis and Bronsted sites.

**Keywords.** TiO<sub>2</sub>; sol–gel method; surface acidity; superhydrophilicity.

## 1. Introduction

TiO<sub>2</sub> is a widely used photocatalytic and hydrophilic material, which has been employed in many promising industrial applications for its optical, electrical, chemical and hydrophilic properties (Ashkarran and Mohammadzadeh 2008; Aubry *et al* 2008; Novotna *et al* 2008). The superhydrophilicity of TiO<sub>2</sub> was actually discovered by chance in the work that was being carried out at the laboratories of TOTO Inc., in 1995. It is well known that superhydrophilicity is an intrinsic property of TiO<sub>2</sub> (Fujishima *et al* 2008). Superhydrophilicity is a phenomenon that occurs when TiO<sub>2</sub> film is irradiated with UV radiation. A very small contact angle appears on the hydrophilic surface ( $\theta \leq 5^\circ$ ). The water tends to spread completely across this surface rather than forming droplets. This makes the surface anti-fogging and easy washing (Kafizas *et al* 2009; Menga and Sun 2009; Taga 2009). The mechanism proposed behind this phenomenon is that the dissociative water molecules adsorb on the oxygen vacancies of the TiO<sub>2</sub> surfaces, resulting in an increase in the surface hydroxyl groups of the TiO<sub>2</sub> surfaces during UV light irradiation. When the UV light is turned off, the high wettability of the TiO<sub>2</sub> surfaces gradually disappears (Takeuchi *et al* 2005). Therefore, pure TiO<sub>2</sub> is limited for superhydrophilic application due to its alternative photo-induced efficiency with light changes. Recently, special attention has been focused on the structure modification of TiO<sub>2</sub> to improve its hydrophilic

performance. Machida *et al* (1999) first reported that the addition of 10–30 mol% of SiO<sub>2</sub> into a TiO<sub>2</sub> film yielded optimum photo-induced superhydrophilicity, which can be maintained for a certain time in a dark place. Ren *et al* (2004) also reported that SiO<sub>2</sub>–TiO<sub>2</sub> thin films have excellent superhydrophilicity and enhanced adhesion to the substrate. It was shown that the addition of SiO<sub>2</sub> not only improved the photoinduced superhydrophilicity of anatase but also its photocatalytic activity. Guan (2005) studied the relationship between photocatalysis and photohydrophilicity for self-cleaning applications of composite SiO<sub>2</sub>–TiO<sub>2</sub> films. He mentioned that the amount of SiO<sub>2</sub> in mixed SiO<sub>2</sub>–TiO<sub>2</sub> films had different influences on the photocatalysis and photohydrophilicity. An optimum photocatalytic activity could be obtained by adding 10–20 mol% of SiO<sub>2</sub> in the films, whereas addition of 30–40 mol% of SiO<sub>2</sub> yielded an optimum photohydrophilicity.

In addition, Liu *et al* (2009) and Houmard *et al* (2007, 2008) studied the superhydrophilicity of TiO<sub>2</sub>–SiO<sub>2</sub> composite thin film. They confirmed that the addition of SiO<sub>2</sub> has a significant effect on the superhydrophilicity of TiO<sub>2</sub> thin film. Guan (2005) and Guan *et al* (2006) suggested that the addition of SiO<sub>2</sub> might increase the surface acidity of TiO<sub>2</sub>–SiO<sub>2</sub> films, which would improve the hydroxyl content at the surface of composite films, resulting in enhanced superhydrophilic properties. Recently, Skorb *et al* (2008) investigated the addition of In<sub>2</sub>O<sub>3</sub> on the hydrophilicity of TiO<sub>2</sub> thin film. They reported that the formation of TiO<sub>2</sub>–In<sub>2</sub>O<sub>3</sub> composite film with 20–30 mol % of In<sub>2</sub>O<sub>3</sub>, yields optimum hydrophilicity.

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However, the superhydrophilic properties of  $\text{TiO}_2\text{-SiO}_2\text{-In}_2\text{O}_3$  sol-gel derived thin films have not been investigated yet. In the present study,  $\text{TiO}_2\text{-SiO}_2\text{-In}_2\text{O}_3$  thin films were prepared by the sol-gel dip coating method on glass substrates. Then, the additional effect of  $\text{SiO}_2$  and  $\text{In}_2\text{O}_3$  on the superhydrophilic mechanism of  $\text{TiO}_2$  thin film was investigated.

## 2. Experimental

### 2.1 Materials

The following materials were used to make nanofilm: Acetyl acetone (Sigma Aldrich, purity  $\geq 99\%$ ), TBOT (Sigma Aldrich, purity 97%), absolute ethanol (EtOH, Merck, purity  $\geq 99.5\%$ ), acetic acid (Sigma Aldrich, purity  $\geq 99.7\%$ ), deionized water, tetraethylorthosilicate (TEOS, Sigma Aldrich, purity  $\geq 99.0\%$ ), hydrochloric acid (Sigma Aldrich, purity 37%) and salt indium (III) chloride (Sigma Aldrich, purity 98%).

### 2.2 $\text{TiO}_2\text{-SiO}_2\text{-In}_2\text{O}_3$ nanofilm preparation

$\text{TiO}_2$  precursor sol was prepared by dissolving tetrabutyl orthotitanate in ethanol and acetyl acetone. Acetic acid was dissolved in deionized water and ethanol, and then added to the first solution during stirring. The stirring of each solution was carried out for 30 min and then the solutions were mixed ultrasonically for another 30 min. Acetyl acetone was added to slow the speed of hydrolysis and condensation reactions and form a stable sol.

Tetraethylorthosilicate was dissolved in a solution containing absolute ethanol and deionized water. Droplets of hydrochloric acid were added to this solution and refluxed at  $70^\circ\text{C}$  for 2 h. The resulting mixture was aged for 24 h to obtain  $\text{SiO}_2$  sol.

The  $\text{In}_2\text{O}_3$  precursor sol was prepared by dissolving the desired amount of precursor salt indium (III) chloride in ethanol and hydrochloric acid. The precursor solutions were mixed together in a certain quantity. In order to make comparisons, the following sol solutions (films) were prepared from pure  $\text{TiO}_2$ ,  $\text{TiO}_2\text{-SiO}_2$  and  $\text{TiO}_2\text{-SiO}_2\text{-In}_2\text{O}_3$ . The mol ratio of  $\text{TiO}_2 : \text{SiO}_2 : \text{In}_2\text{O}_3$  was taken as 4 : 1 : 0.2.

Before coating, soda-lime glass substrates ( $75 \times 25\text{mm}$ ) were ultrasonically cleaned in acetone and then dipped in absolute ethanol for 5 min, after which a thorough wash was carried out. The nano films were obtained by a dip coating method and drawn with the speed of 5 cm/min. The gel films were air dried for 15 h, and then heat-treated at  $500^\circ\text{C}$  for 2 h in air. The thickness of the films was increased by repeating the cycles from withdrawing to heating. This procedure was carried out six times. The average thickness of each layer was measured as 86 nm according to Guan (2005) method.

### 2.3 Characterization

Surface functional groups of nanofilm were characterized by Fourier transform infrared spectroscopy (JASCO FT/IR-689 Plus). Surface properties of the film samples were analysed using X-ray photoelectron spectroscopy (XPS, JEOL) with Mg  $K\alpha$  source (1253.6 eV). The X-ray source was operated at 10 kV for a current of 10 mA. The calibration of binding energy of the spectra was performed with C 1s core level peak at a binding energy of  $\sim 284.6$  eV (Sharma *et al* 2006). The O 1s 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 thin films 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  $1\mu\text{L}$  micro-injector. The water contact angle was averaged from 5 measurements. UV-Vis was irradiated to the surface of the samples by xenon lamp (300W, 300–500 nm). Prior to the photo induced super-hydrophilicity measurements, samples were stored in a drying oven at  $120^\circ\text{C}$  for overnight. In addition, the hydrophilic-hydrophobic conversion of films after storage in a dark place was investigated.

## 3. Results and discussion

### 3.1 FTIR

The characterizations of functional groups on the films are important to understand the photoinduced super-hydrophilicity on the surface. The film was measured in transmission configuration in the  $4000\text{--}400\text{ cm}^{-1}$  spectral range with a resolution of  $4\text{ cm}^{-1}$ . Figure 1 shows FTIR spectra of  $\text{TiO}_2\text{-SiO}_2\text{-In}_2\text{O}_3$  thin film. The peak at about  $3400\text{ cm}^{-1}$  is assigned to the stretching modes of O–H bonds and is related to surface adsorbed water. The peak at  $1600\text{ cm}^{-1}$  is attributed to the bending vibration of bonds, which is assigned to the chemisorbed water (Takeuchi *et al* 2006). The peak at  $1050\text{ cm}^{-1}$  is assigned to the stretching vibration of Si–O–Si bond. The Si–O–Ti stretching mode appears at about  $950\text{ cm}^{-1}$  (Park and Kim 2007). The peak at

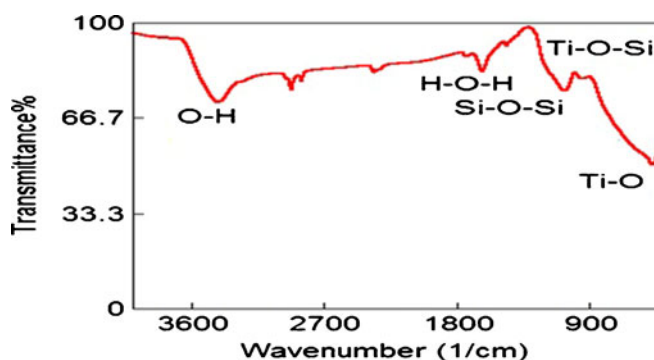


Figure 1. FTIR spectra of  $\text{TiO}_2\text{-SiO}_2\text{-In}_2\text{O}_3$  film.

about  $450\text{ cm}^{-1}$  is due to the stretching vibrations of Ti–O–Ti and Ti–O bonds (Jensen *et al* 2005).

We assume that some  $\text{In}^{3+}$  cations substitute  $\text{Ti}^{4+}$  cations in the titania framework by forming Ti–O–In–O–Ti bonds; however, the identification of such species is very difficult. Because, only few  $\text{In}^{3+}$  species can be inserted in the titania framework, and the ionic radius of  $\text{In}^{3+}$  is 94 pm (hexacoordinated), which, compared with the  $\text{Ti}^{4+}$  of 74.5 pm (hexacoordinated), is too high to expect a large substitution. Gonzalez *et al* (2008) reported the formation of Ti–O–In–O–Ti bonds in  $\text{TiO}_2\text{--In}_2\text{O}_3$  film according to signal shift in the Raman spectra of  $\text{TiO}_2$ .

### 3.2 XPS

X-ray photoelectron spectroscopy (XPS) is employed to study the core level spectra and to reveal the elemental composition of the sample. The core level XPS spectra of C 1s, Ti 2p, O 1s, Si 2p and In 3d of  $\text{TiO}_2\text{--SiO}_2\text{--In}_2\text{O}_3$  films are shown in figure 2. The binding energy peaks corresponding to Ti 2p, Si 2p and In 3d spectra indicated the chemical states of Ti, Si and In to be  $\text{Ti}^{4+}$ ,  $\text{Si}^{+4}$  and  $\text{In}^{+3}$ , respectively.

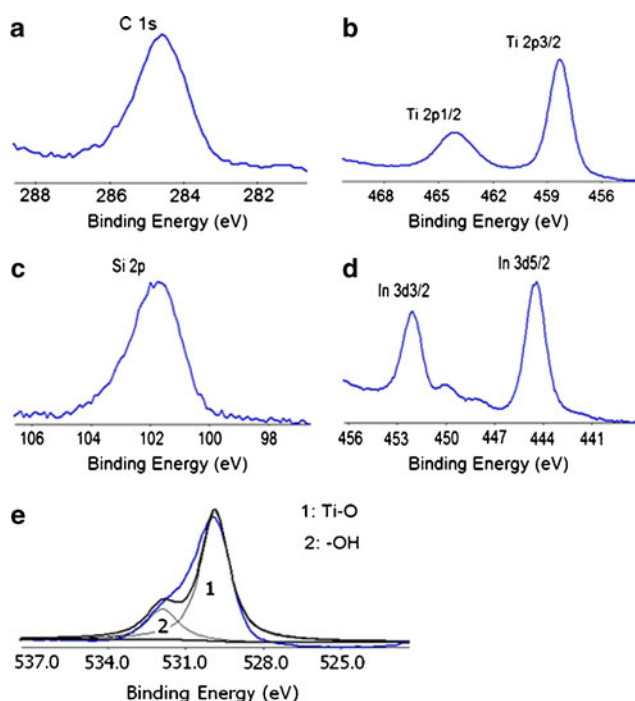
Quantitative analysis of the elements present in the films has been performed by measuring the area under the peak divided by its atomic sensitivity factor. The % composition of each element can be calculated by following relation:

$$\%X_i = \frac{X_i(AP)/X_i(ASF)}{\sum_i X_i(AP)/X_i(ASF)} \times 100, \quad (1)$$

where  $X_i$  is the element present in the films, AP the area under the peak and ASF the atomic sensitivity factor. Quantitative % elemental composition of Ti, O, Si and In are shown in table 1.

In addition, it is well known that XPS is one of the most useful methods of measuring the hydroxyl groups content on the film surfaces. Surface hydroxyl groups are an important factor in maintaining the hydrophilicity of  $\text{TiO}_2$  thin film especially in a dark place (Guan 2005).

Figure 2e shows the high resolution XPS spectra for the O 1s region for composite  $\text{TiO}_2\text{--SiO}_2\text{--In}_2\text{O}_3$  film. The O 1s region includes two peaks. One peak is attributed to the Ti–O (529.90 eV) in  $\text{TiO}_2$  and the composite, while the other one is assigned to the hydroxyl group (531.90 eV) (Yu *et al* 2002). The hydroxyl content (%) is the ratio of the area of 531.90 eV peak to the total area of the two O 1s peaks. The hydroxyl content for  $\text{TiO}_2$ ,  $\text{TiO}_2\text{--SiO}_2$  and  $\text{TiO}_2\text{--SiO}_2\text{--In}_2\text{O}_3$  film was calculated as 11.6, 17.1 and 20.7%, respectively. The amount



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

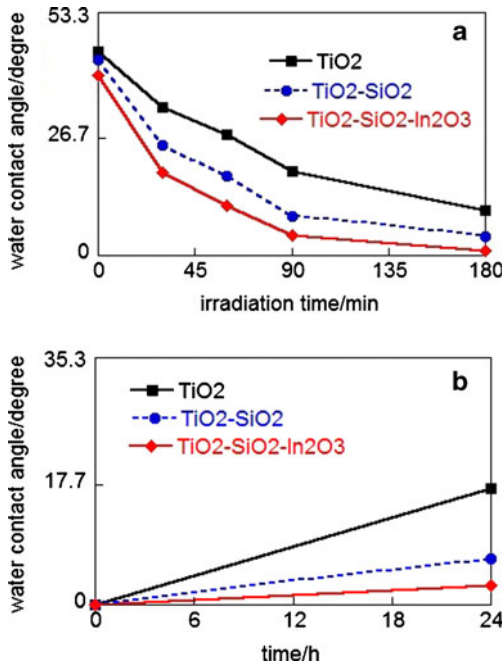
of the hydroxyl group from the chemisorption of water molecules on the  $\text{TiO}_2$  surface is enhanced by the presence of  $\text{SiO}_2$  and  $\text{In}_2\text{O}_3$ . Although some water is easily adsorbed on the surface of the film samples, the physically adsorbed water on the film samples is desorbed under the ultra-high vacuum condition of the XPS system (Yu *et al* 2002). Therefore, the XPS spectra only show chemisorbed water. This difference in the hydroxyl density is discussed in relation to the results of superhydrophilicity in the following section.

### 3.3 Water contact angle measurements

Figure 3 shows the water contact angle measurements on the nanofilm surfaces after 180 min of irradiation and storage in a dark place for 24 h. The water contact angle of the film surface which consists of only  $\text{TiO}_2$  is  $10.3^\circ$ ,  $\text{TiO}_2\text{--SiO}_2$  is  $4.3^\circ$  and  $\text{TiO}_2\text{--SiO}_2\text{--In}_2\text{O}_3$  is  $1.1^\circ$ . After storing films in a dark place for 24 h, the water contact angle goes up to  $17.1^\circ$  for  $\text{TiO}_2$ ,  $6.7^\circ$  for  $\text{TiO}_2\text{--SiO}_2$  and  $2.9^\circ$  for  $\text{TiO}_2\text{--SiO}_2\text{--In}_2\text{O}_3$ . The results indicate that with the formation of  $\text{TiO}_2\text{--SiO}_2\text{--In}_2\text{O}_3$  composite film, the water contact angle on the film surface increases very slowly and superhydrophilicity can be maintained for a long time in a dark place due to highest hydroxyl content on the film surface. With the increase of adsorbed hydroxyl groups on the film surface, van der Waals forces and hydrogen bond interactions between water molecules and hydroxyl group will increase (Yu *et al* 2001). Then, water can easily spread on the surface and the hydrophilicity can be maintained for a long time in a dark place.

**Table 1.** Chemical composition of film surfaces (%atomic)

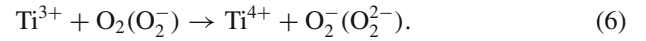
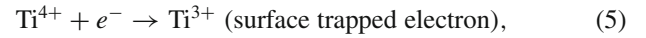
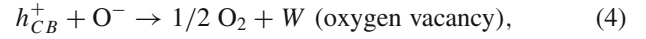
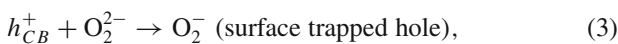
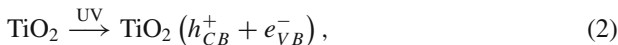
Element	Ti	O	Si	In
State	2p	1s	2p	3d
ASF	1.8	0.66	0.27	3.9
$\text{TiO}_2$ (%element)	29.12	70.88	-	-
$\text{TiO}_2\text{--SiO}_2$	24.29	65.83	9.88	-
$\text{TiO}_2\text{--SiO}_2\text{--In}_2\text{O}_3$	22.84	64.47	8.48	4.21



**Figure 3.** Water contact angle on film surfaces (a) under irradiation and (b) dark place.

### 3.4 Superhydrophilic mechanism

Several papers on the studies on superhydrophilic mechanism of  $\text{TiO}_2$  have been published (Diebold 2003; Kontos *et al* 2007). When  $\text{TiO}_2$  is irradiated with UV light ( $\lambda < 380$  nm), photoexcited electrons and positive holes are produced in conduction and valence bands, respectively. These photogenerated carriers migrate to the  $\text{TiO}_2$  surface and the photogenerated holes react with the lattice oxygen of  $\text{TiO}_2$  and are trapped by the lattice oxygen. The lattice oxygen, after trapping a hole ( $\text{O}^-$ ), may be further oxidized by a second hole to form a neutral O radical. By coupling two neutral radicals, an  $\text{O}_2$  molecule is produced. Then, an oxygen molecule is ejected and an oxygen vacancy is created at the  $\text{TiO}_2$  surface. Water molecules may travel into the oxygen vacancy sites, which then leads to dissociative adsorption of the water molecules on the film surface. This process causes an increase in the hydroxyl content on the illuminated  $\text{TiO}_2$  surfaces. Meanwhile, the photogenerated electrons react to  $\text{Ti}^{+4}$  cations and reduce the  $\text{Ti}^{+4}$  cations to  $\text{Ti}^{+3}$  states. In air,  $\text{Ti}^{+3}$  cations (surface trapped electrons) tend to react immediately with  $\text{O}_2$  adsorbed on the surface to form  $\text{O}_2^{2-}$  or  $\text{O}_2^{-2}$  ions. In other words, the photogenerated electrons do not directly play an important role in surface hydrophilic conversion (Diebold 2003; Kontos *et al* 2007). In general, the formation processes of defective sites on the  $\text{TiO}_2$  surface can be expressed as follows:



It is assumed that the formation of oxygen defects occurs more readily at doubly coordinated lattice oxygen sites (bridging oxygens) than at triply coordinated sites. It is well known that bridging site oxygen is more reactive than the usual three-fold coordinated oxygen (Diebold 2003). In addition, it is reasonable to consider that the dissociative water adsorption occurs more readily on the bridging oxygen site. Watanabe *et al* (1999) evaluated the wettability measurement under UV irradiation on the (110) and (001) surfaces of single rutile crystal. They showed that the (110) surface displays higher hydrophilicity than the (001) surface due to bridging oxygen sites (Watanabe *et al* 1999).

If  $\text{TiO}_2$  film is stored in a dark place, the surface of the film is converted to a hydrophobic state. The regeneration of the hydrophobic surface is due to either adsorption of organic contaminants or by the release of water molecules, which can be due to adsorption of oxygen molecules, creating a hydrophobic surface.

It is well accepted that the sol-gel derived thin films have polycrystalline structure (rather than single crystal structure) and the bridging site oxygen may not be enough. So, releasing more oxygen vacancies during fabrication of composite films can enhance the hydrophilicity due to the formation of structural changes. The enhanced hydrophilicity of composite film can be explained as follows:

Metal oxides are well known to have surface acidity. A popular hypothesis is proposed by Tanabe *et al* (1974) about surface acidity. This hypothesis attributes acidity to the charge imbalance that develops along  $M_1\text{-O-}M_2$  heterolinkages (where  $M_1$  and  $M_2$  are different cations). Such a charge imbalance is related to the differences in cation valence and coordination number at the site of substitution of the minor component cation, which is assumed to retain its original coordination number when entering the host environment while surrounding oxygen atoms are in the host coordination.

The charge imbalance must be satisfied. The charge imbalance is calculated for each individual bond to the dopant cation and multiplied by the number of bonds to the cation.

In the structure of  $\text{TiO}_2\text{-SiO}_2\text{-In}_2\text{O}_3$ ,  $\text{TiO}_2$  is the main oxide. In single oxides, the coordination number of Ti is 6, Si is 4 and In is 6, whereas the coordination number of oxygen in the single oxides are 3, 2 and 4, respectively.  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{In}_2\text{O}_3$  form single oxide particles in the films.

It is possible that at the interfaces of  $\text{TiO}_2$  and  $\text{SiO}_2$ ,  $\text{Si}^{+4}$  cations (ionic radius, 40 pm) replace  $\text{Ti}^{+4}$  cations (ionic radius, 74.5 pm) in titania structure as it is indicated by FTIR results, because of the existence of Si-O-Ti vibration in the FTIR spectrum (Guan 2005). This phenomenon causes charge imbalance which can be calculated according to Pauling's



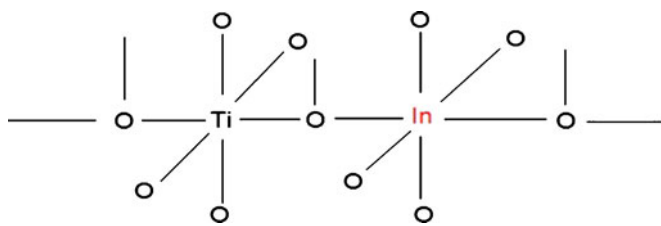


Figure 4. Structural model of Ti–O–In bond.

rules 2 (Carter and Norton 2007). Thus, the strength of the bonds can be calculated as follows:

For  $\text{Ti}^{4+}$  ions,  $S = 4/6 = +4/6$ , for  $\text{Si}^{4+}$  ion,  $S = +4/4 = +1$ .

Charge difference for one bond is  $(+4/6 \times 2 + 1) + (-2) = +1/3$ , and the total charge imbalance for all bonds (four-bond) is  $4 \times (+1/3) = +4/3$ .

In this case, Lewis acidity is present, which is due to the appearance of an excessive positive charge. These charge imbalances must be satisfied. Therefore, hydroxyl groups are adsorbed on the composite film surfaces.

In addition, it is possible that at the interfaces of  $\text{TiO}_2$  and  $\text{In}_2\text{O}_3$ ,  $\text{In}^{3+}$  cations (ionic radius 94 pm) replace  $\text{Ti}^{4+}$  cations (ionic radius 74.5 pm) in the titania structure by forming Ti–O–In–O–Ti bonds as shown in figure 4 (Gonzalez *et al* 2008). This phenomenon causes charge imbalance which can be calculated as follows:

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

Thus, charge difference for one bond is  $(+4/6 \times 2 + 3/6) + (-2) = -1/6$ , 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,  $\text{H}_3\text{O}^+$  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.

In the present state, it is clear that superhydrophilicity is induced by the conjoint presence of both kinds of acidic sites (Lewis and Bronsted sites).

In summary,  $\text{TiO}_2$ – $\text{SiO}_2$ – $\text{In}_2\text{O}_3$  composite film is expected to have an acidity property because of the excess of positive and negative charges. In fact, it is expected to display very high acidity. Also, it is well accepted that surface acidity is an important factor in maintaining the superhydrophilicity of  $\text{TiO}_2$  thin film, especially in a dark place.

#### 4. Conclusions

$\text{TiO}_2$ – $\text{SiO}_2$ – $\text{In}_2\text{O}_3$  nano film was prepared on a glass surface by the sol–gel method. The superhydrophilic mechanism of  $\text{TiO}_2$  with the addition of  $\text{SiO}_2$  and  $\text{In}_2\text{O}_3$  was investigated. The water contact angle measurements showed

that the superhydrophilicity of  $\text{TiO}_2$ – $\text{SiO}_2$ – $\text{In}_2\text{O}_3$  nanofilm can be maintained for a long time. The enhanced superhydrophilicity can be related to the generation of surface acidity. In the present state, superhydrophilicity is induced by the concurrent presence of both kinds of acidic sites (Lewis and Bronsted sites). Therefore, hydroxyl groups and  $\text{H}_3\text{O}^+$  ions are adsorbed on the composite film surface which induce enhanced molecular or dissociative water adsorption and lead to the super-hydrophilic properties of composite film.

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