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# Hydrophilic and Photocatalytic Properties of TiO<sub>2</sub>/SiO<sub>2</sub> Nano-layers in Dry Weather

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## ABSTRACT

his paper describes the changes in TiO2/SiO2 nanolayers properties induced by Ultraviolet- visible spectroscopy (UV) irradiation in terms of hydrophilicity/photocatalycity. The TiO<sub>2</sub>/SiO<sub>2</sub> nano particles were synthesized by the sol-gel method and deposited on soda-lime glass by dipcoating. X-ray diffraction (XRD) of the  $TiO_2$  particles showed that the nanoparticles were crystallized in anatase crystal structure with a crystallite size of  $\sim 12$  nm. The morphology and surface roughness of TiO<sub>2</sub> nanolayer were observed by scanning electron microscope (SEM) and atomic force microscopy (AFM) analysis. The surface roughness (Ra) for TiO<sub>2</sub>/Glass and TiO<sub>2</sub>/SiO<sub>2</sub> was measured  $\sim$  5 and 19 nm, respectively. The hardness of nanolayers on the glass was evaluated and scratch thickness for 1000 g sinker was measured ~150 nm. The self-cleaning properties were tested in dry condition (RH < 15%) under UV irradiation by evaluating the oleic acid photodegradation and monitoring the hydrophilic properties of the surface with a contact angle measurement. The result showed that contact angle of the layer decreases from 77 to 42° after 25 h UV irradiation. Fourier-transform infrared spectroscopy- Attenuated total reflectance (FTIR-ATR) showed the elimination of C=O bonds of oleic acid on the surface after UV light irradiation. Water droplet contact angle measurement on  $TiO_2$  nano-layer exhibited a less hydrophilicity after UV irradiation and the contact angle changed from 15 to 40°, which may be due to the low atmospheric humidity. Adding SiO<sub>2</sub> nanoparticles increases roughness of the nano-layer, from 5 to 19 nm, without a significant effect on the photodegradation rate of oleic acid. Prog. Color Colorants Coat. 14 (2021), 221-232© Institute for Color Science and Technology.

#### 1. Introduction

Photocatalyst materials have been noticeably used in the water purification [1, 2] and air deodorization systems [3-6]. Due to a high photocatalytic reaction rate, these products have been extremely used on the exterior surfaces especially glass and ceramics, and for self-cleaning applications [7, 8]. Self-cleaning property mainly depends on photocatalytic activity and surface wettability level, which can be developed by either hydrophilicity or hydrophobicity [9-13]. In the case of  $TiO_2$  nano-layers, hydrophilicity has already reported as a famous mechanism for self-cleaning [14, 15]. In fact, photoinduced hydrophilicity of  $TiO_2$  has been proposed through different mechanisms. Most challenges can be divided into three main categories; (1) generation of surface vacancies, (2) photo-induced changes in TiO<sub>2</sub> surface bonds, and (3) photocatalytic degradation of organic pollutants [16, 17]. By UV irradiation, the TiO<sub>2</sub> surface energy increases due to the adsorption of a hydroxyl group in oxygen vacancy. In this way, water droplet tends to spread widely over TiO<sub>2</sub> surface until the contact angle is reduced to less than 5° and a superhydrophilic surface is formed. This superhydrophilic property results in an easy washing and anti-fogging surface [18]. The decomposition of organic contaminants by TiO<sub>2</sub> photocatalytic activity is another mechanism of self-cleaning property. Since organic molecules are oxidized photocatalytically under light irradiation [19], the water droplet contact angle decreases until a clean surface appears [20].

Recently, considerable efforts have been made in the synthesis of hydrophobic nano-layers as a selfclean coating [20, 21]. Different methods and compounds have been employed to synthesize hydrophobic nano-layers [11, 22, 23]. For instance coating of SiO<sub>2</sub> by electrodeposion showed the high roughness and a perfect ability of hydrophobic on the surface [24, 25]. The main challenges in this field are chemical stability, large scale producible, high efficiency, and an acceptable lifetime. Chemical properties and roughness of a surface determine the contact angle of the water droplet. Some chemical groups on the surface decrease the surface energy, which makes the water surface repellent [26]. Water repellency retains droplets almost spherical on the superhydrophobic surfaces. This property results in less adhesion of the pollutant particles to the surface because of low surface energy. Thus, as the water droplet rolls over the surface, it tends to pick up dirt and dust easily [27].

In much self-cleaning applications porous or fibrous substrate such as glass fiber and cotton are used. Van der Waals and electrostatic forces are the same force between the surface and pollutant particles when they adhere to the surface [28, 29]. Usually, UV light irradiation results in hydrophilic surfaces; however, the surface energy is decreasing with passing time. It has been reported that UV light irradiation can change the wettability of ZnO film surface between hydrophobicity and hydrophilicity [30, 31]. Moreover, some reports show that humidity of the atmosphere affects the hydrophilicity/hydrophobicity of the surfaces [32].

In this research, the  $TiO_2$  /SiO<sub>2</sub> nanolayers on the glass surface have been synthesized by the sol-gel

method. Self-cleaning property of the nano-layers was characterized by hydrophilic property and photocatalytic degradation of oleic acid as a fatty oil under UV light irradiation in a dry condition (RH ~15%). The Hashimoto model is used to explain the behavior of surface nano-layers of the TiO<sub>2</sub> and SiO<sub>2</sub> on the glass surface.

### 2. Experimental

To prepare a solution of TiO<sub>2</sub> nanoparticles, TIPT (tetra isopropyl orthotitanate) (purity>99%, Merck) was dissolved in a mixture of ethanol and hydrochloric acid by a volume proportion of 1.5:10:1, respectively. In addition, TEOS (tetraethyl orthosilicate), ethanol and hydrochloric acid (Merck) were used as precursors of SiO<sub>2</sub> sol in the sol-gel process with a weight proportion of 18.9:75:1.2, respectively. The prepared solutions were stirred for 2.5 hours and a transparent and homogeneous sol was obtained. Soda-lime slide glasses were cleaned by soap liquid, distilled water, acetone and ethanol, respectively. The synthesized sol was deposited on the substrates using a dip-coating method. The speed of dipping and withdrawing of the slide glasses from the solution was 4.5 mm/s. At the end, the coated glass was annealed at 500 °C for 2 hours, and a uniform TiO<sub>2</sub> and SiO<sub>2</sub> nano-layers were formed on the surface. A clean glass without any coating is named G, TiO2/glass named T-G and TiO<sub>2</sub>/SiO<sub>2</sub>/glass named T-S-G. 1T-G and 3T-G is referred to the glass samples coated by TiO<sub>2</sub> for 1 and 3 times, respectively.

SEM images of the nano-layers were characterized by a KYKY machine (EM 3200 model), and these images were analyzed by Nano Measurement software to determine nano-particle size distribution. Surface roughness and morphology of nano-layers were evaluated by atomic force microscopy (AFM) using an Auto Probe CP Park Scientific instrument in a contact mode with the Si<sub>3</sub>N<sub>4</sub> tip. To determine the crystal structure of nano-layers some portion of the solution was dried and heated by the same method as the preparation of the nano-layers. XRD spectrum was measured by a Cu K<sub>a</sub> radiation at 40 kV voltage and 30 mA current (X'PertPro). UV-Visible transmission spectra of the nano-layers were measured by a doublebeam Jasco spectrophotometer (model 7800). The thickness of the nano-layers was obtained by cross section field emission SEM images (FE-SEM, Mira 3-XMU model).

To evaluate the photocatalytic activity of the  $TiO_2$ nanolayer a solution of 1 wt.% oleic acid in ethanol was used. Glass surface,  $TiO_2$ , and  $TiO_2$ -SiO<sub>2</sub> nanolayers were coated by the oleic acid solution named O-G, O-T-G, and O-T-S-G, respectively. 2O-T-G refers to the  $TiO_2$  nano-layer on the glass sample, which was used for photodegradation of oleic acid 2 times. The chemical bonds of oleic acid on  $TiO_2$  nano-layer before and after UV irradiation were detected by Fourier transform infrared spectroscopy using the attenuated total reflectance accessory (FTIR-ATR: Bruker Equinox 55). Hardness of the  $TiO_2$  nano-layer was evaluated by a scratch test.

Degradation of oleic acid on the glass surface in a dry condition (RH ~15%) under UV-(A) irradiation (9 mW/cm<sup>2</sup>, 370 nm) was determined by contact angle measurement using a Dino-Light Digital Microscope (model 2011). The images were analyzed by Adobe Illustrator software, and the contact angle experimental error is  $\pm 2^{\circ}$ . To evaluate the surface energy changes of the nano-layers before and after UV irradiation, two liquids (deionized water and ethylene glycol) were used for the measurements. To determine an accurate contact angle value for droplets, 5 measurements on different locations of the nano-layers surface were performed in a dry condition (RH~15%). The surface energy was determined using the average contact angle value ( $\theta$ ) by the following equation (Eq. 1) [33, 34]:

$$(1 + \cos\theta) \gamma_{l} = 2 (\gamma_{s}^{d} + \gamma_{l}^{d})^{1/2} + 2 (\gamma_{s}^{p} + \gamma_{l}^{p})^{1/2}, \qquad (1)$$

where,  $\gamma_1$  is total surface tension. Dispersive and polar components for water and ethylene glycol,  $\gamma_1^d$  and  $\gamma_1^p$ , are given in Table 1 [35]. Then, both parameters  $\gamma_s^d$ and  $\gamma_s^p$  can be obtained for surface of the nano-layers. Finally, total surface energy for each surface was estimated by Young's equation (Eq. 2):

$$\gamma_{\rm s} = \gamma_{\rm s}^{\rm d} + \gamma_{\rm s}^{\rm p}. \tag{2}$$

Test liquids	$\gamma_{l}$ (mJm <sup>-2</sup> )	$\gamma_{l}^{p} (mJm^{-2})$	$\gamma_l^d (mJm^{-2})$
Deionized water	72.8	51.0	21.8
Ethylene glycol	48.0	19.0	29

#### 3. Results and Discussion

Figure 1 shows SEM images of the surface of nanolayers on the glass with their particle size distribution. Figure 1(a) indicates that there are many small particles on the surface with a size of smaller than 60 nm. The histogram of the particle size of 1T-G is demonstrated in Figure 1(b). Accordingly, the mean particle size is  $\sim 28$ nm. For 3T-G the process of TiO<sub>2</sub> coating was repeated 3 times continuously (without any annealing after each coating). Figure 1(c) shows the SEM image of the 3T-G surface. In this case, the surface morphology is approximately the same as 1T-G. It appears that the size of the biggest particle on the surface is about 60 nm. The average particle size on the 3T-G surface is  $\sim 29$  nm (Figure 1(d)). In Figure 1(e), the nano-granular distribution on the surface looks more spherical and is concentrated in the range of 20-30 nm. In this condition, the average particle size is estimated to be 23 nm (Figure 1(f)). Since the process of pre-coating of the SiO<sub>2</sub> layer on the glass surface was not continued by a heating process, the condensation and gelation process of it was interrupted by dipping in TiO<sub>2</sub> sol. Due to this, the composition of it may be different. However, a precoating of SiO<sub>2</sub> or increasing the number of dips has not made a considerable effect on the particle size distribution of the surface. It can be concluded that SEM images confirm the formation of a uniform TiO<sub>2</sub> nanolayer on the glass surface.

AFM results of the surface of 1T-G is shown in Figure 2(a). It exhibits some granularities that makes the surface roughness (Ra) about 5 nm. While in the T-S-G sample in Figure 2(b), the surface roughness (Ra) is about 19 nm. In fact, the deposition of SiO<sub>2</sub> buffer layer increases the surface roughness [24, 25, 36]. It seems that the real surface area of the coating increased by the pre-coating of the SiO<sub>2</sub> layer. The nano-granular particles on surfaces are in the range of 30-50 nm. As a result, the particle size distribution obtained from SEM is almost in agreement with the AFM images. Since the SEM images of 1T-G and 3T-G surfaces were very similar to each other, the AFM analysis of 3T-G sample was ignored.

The structural evaluation of the  $TiO_2$  powder, prepared with the same method as  $TiO_2$  nano-layer, was obtained by the XRD spectrum in Figure 3. It can be observed that all peaks in the XRD spectrum are corresponding to the standard spectrum of the anatase crystal structure of  $TiO_2$ . Among  $TiO_2$  crystalline phases, the anatase phase is a well-known as the most active photocatalytic one [15, 37, 38]. In addition, the  $TiO_2$  layer in the anatase phase usually works as a superhydrophilic surface [39, 40]. By using the Debye-Scherrer formula for (101) anatase peak the crystallite

size is calculated about 12 nm. Since the average particle size obtained by SEM and AFM is bigger than the crystallite size measured by XRD, it is concluded that each particle is composed of some crystallites.



Figure 1: SEM images and particle size distribution of nano-layers on the glass surface; (a) and (b) 1T-G, (c) and (d) 3T-G, (e) and (f) double layers T-S-G.



Figure 2: AFM images and surface topography of (a) 1T-G and (b) double layers T-S-G.



Figure 3: XRD pattern of TiO<sub>2</sub> powder in anatase crystal structure.

Figure 4 displays UV-Visible transmittance spectra of 1T-G, 3T-G, and T-S-G samples. It indicates that the transmittance of the coated samples in comparison with the bare substrate is more than  $\sim 60\%$  in the visible region. The interference of light by the nano-layer interfaces has made some fluctuations in the spectra.

Self-cleaning property of the nano-layers was characterized by hydrophilic property and photocatalytic degradation of oleic acid as a fatty oil under UV light irradiation in a dry condition (RH ~15%). Figure 5(a) shows the results of water contact angle measurements on G, T-G, and T-S-G surfaces under UV light irradiation. One can note that after 25 hours of UV irradiation, the contact angle of the water droplet with the bare slide glass surface increases from 28 to 54°, while for T-G sample it changes from 15 up to 40°. Compare to a bare slide glass, clearly can be seen the TiO<sub>2</sub> nano-layer enhanced the surface hydrophilicity even at the beginning of the irradiation. The result of the T-S-G sample shows contact angle changes from 10° to 20° by UV irradiation for 25 hours. It confirms the enhancement of hydrophilicity by ~34° contact angle reduction for the T-S-G sample compared to bare slide glass.



Figure 4: UV-Visible spectrum of transparent nano layers at different number of dips.



**Figure 5:** Contact angle of water droplet on the surface versus UV light irradiation time; (a) G, T-G and T-S-G surface. Each contact angle is an average of 3 measurements, and the experimental error of the measurements is ±1 degree. Schematic of TiO<sub>2</sub> surface bonds (b) stable state, (c) environment with high humidity under UV irradiation, and (d) environment with low humidity under UV irradiation.

UV irradiation has effect on the TiO<sub>2</sub> surface layer, which increases the hydrophilicity of the surface. This means the reduction of contact angle of water droplets on the surfaces [41, 42]. According to the Hashimoto model [43], it is due to the adsorption of water molecules on the surface. UV irradiation causes the adsorbed water molecules to make some bonds on the surface, and the less stable hydroxyl groups are created on the surface of TiO<sub>2</sub>. Another reason for hydrophilicity on the surface is due to the high surface energy of the TiO<sub>2</sub> layer. The layer covered with the less stable hydroxyl groups has a higher surface energy than that of the surface with the hydroxyl groups initially [15, 44]. Therefore, it can be concluded that the chemisorption of atmospheric water molecules in oxygen vacancies results in hydrophilicity.

There are some reports on reversible wettability of ZnO film surface between hydrophobicity and hydrophilicity under UV irradiation [30, 31]. In addition, it has been reported that the content of the solution can change the wettability of the porous surface [45]. On the other hand, the humidity of the atmosphere has a direct effect on the hydrophilicity of surfaces [32]. There are some reports showing the rate of contact angle decrease for TiO<sub>2</sub> coating under UV irradiation depends on the relative humidity (% RH). For the irradiated samples in the low humid condition, the rate of contact angle is decreasing. The lowest

humidity used in that report is 20%, which has the lowest rate of hydrophilicity [32].

It appears that in a very low humid atmosphere (RH < 20%) the mechanism is different. When UV photons encounter to the TiO<sub>2</sub> surface, they are absorbed by surface bonds such as Ti-O-Ti and Ti-OH [16, 46]. Due to this, the hydroxyl groups may diffuse over the surface, or it would be released. If the humidity in the atmosphere is not enough during the UV light irradiation, the hydroxyl groups are willing to be released from the surface to the atmosphere. Then the concentration of Ti-O-Ti bonds on the surface overcome that of Ti-OH bonds. In this case, the water droplet tends to be more spherical and surface hydrophilic property decreases [16]. This process can be performed for bare slide glass, as in Figure 5(a), it shows that the contact angle of the glass surface increases from 28 to 54° with UV-irradiation in dry condition (RH~15%). In the case of T-S-G, due to the coating condition, the TiO<sub>2</sub> nano-layer was influenced by the SiO<sub>2</sub> buffer layer and the enhancement of contact angle is less than 1T-G.

The surface energy of nano-layers was calculated using the contact angle values of two kinds of liquids, water and ethylene glycol [35]. The results of surface energy are shown in Tables 2 and 3. It can be observed that the surface energy of T-G and 3T-G decreases after UV irradiation. Since surface energy almost decreases after UV irradiation, droplets tend to be spreading out on the surface [9]. Therefore, hydrophobicity behavior can be observed.

Figure 5(b), (c) and (d) demonstrate a schematic of TiO<sub>2</sub> surface bonds under UV light irradiation as a function of humidity. It's based on the model proposed by Irie et al. [43]. It shows how H<sub>2</sub>O molecules of atmosphere react on the surface under UV light irradiation and change hydrophilicity/hydrophobicity of the surface. Additionally, Simonsen et al. [32] attributed a linear correlation to TiO<sub>2</sub> hydrophilicity in different humidities. As the environment of Yazd city is almost dry, the average humidity of the environment was about 15% during the experiments. As a result, a less hydrophilic property on these three samples may be attributed to the low humidity. Since there are a low concentration of H<sub>2</sub>O molecules in the atmosphere, by irradiation of UV light the adsorbed H<sub>2</sub>O molecules on the surface are released and make the surface less hydrophilic. Off course it can decrease the surface energy of the surface.

The behavior of oleic acid on the  $TiO_2$  nano-layer under UV light irradiation was investigated too. Figure 6 indicates water contact angle measurements on the O-G, O-T-G and O-T-S-G surface under UV light irradiation in RH~15%. On O-G surface the contact angle has changed from 42 to 74° after 25 hours exposure to UV light. Since there is no photocatalyst coating for the O-G sample, decreasing the hydrophilicity of it under UV light can be explained in Figure 5 (d). This phenomenon can be interpreted in another way; when the surface is irradiated by UV light an active oxidation environment is produced. It can be supposed that in an oxidative environment more hydrophilic groups such as -CO and -OH react on the surface, and these are oxidized to the gaseous products such as CO<sub>2</sub> and H<sub>2</sub>O, respectively. Therefore, the organic compound or other hydrophobic groups are exposed on the surface. This would be the increase in water contact angle [47]. In the case of O-T-G sample, the contact angle of the surface reduces from 77 to  $42^{\circ}$ after 25 hours of UV irradiation. This effect can be explained by the photodegradation of oleic acid through the photocatalytic property of the TiO<sub>2</sub> nanolayer. Although, the mechanism of photodegradation of oleic acid by TiO<sub>2</sub> involves some complicated challenges, some reactions and intermediates were detected [48, 49]. Due to UV irradiation, the C=O and C-O-H bonds of oleic acid are attacked by hydroxyl radicals and they are eliminated [50]. On the other hand, hydroxyl radicals existing on the surface accelerate the degradation of oleic acid. While the mechanism is explained in Figure 5(d), it may slow down the reduction of contact angle on the surface because of low humidity. The reactions happened during photodegradation of oleic acid are explained at equations 3 to 8:

$$\operatorname{TiO}_2 + h\nu (\mathrm{UV}) \longrightarrow \operatorname{TiO}_2 \left( e_{CB}^- + h_{VB}^+ \right)$$
(3)

Samples	$\gamma_s^{p}$ (mJm <sup>-2</sup> )	$\gamma_s^d (mJm^{-2})$	$\theta_{\rm W}$	$\theta_{EG}$	E (mJm <sup>-2</sup> )
T-G	81.87	2.22	15	12.5	84.0
3T-G	83.14	2.06	13	12	85.20
T-S-G	83.84	2.14	10	7.5	86.0

**Table 2:** Surface energy (E) and Contact angel ( $\theta$ ) of samples before UV irradiation.

**Table 3:** Surface energy (E) and Contact angel ( $\theta$ ) of samples after 25 h UV irradiation.

Samples	$\gamma_s^{p}$ (mJm <sup>-2</sup> )	$\gamma_s^d (mJm^{-2})$	$\theta_{\rm W}$	$\theta_{EG}$	E (mJm <sup>-2</sup> )
T-G	64.69	2.14	40	33	66.83
3T-G	64.42	3.32	36	30	67.74
T-S-G	78.40	2.48	20	16	80.88

$$O_2 + e^- \rightarrow O_2^{--} \tag{5}$$

Oleic acid  $+ OH \rightarrow$  products (6)

Oleic acid  $+ \theta_2^{-} \rightarrow \text{products}$  (7)

Oleic acid +  $O_2 \rightarrow H_2O + CO_2$ . (8)

The above discussion phenomenon can be confirmed from the SEM images of O-G surface morphology in Figure 7(a) and (b), before and after 25 hours UV irradiation. According to Figure 7(a), it can be observed that dip-coating of oleic acid makes a uniform layer on the glass surface. UV irradiation removes the uniformity on the surface and makes some large particles the size of 300-400 nm on the surface (Figure 7(b)). They are probably composed of droplets of oleic acid. These nano-micro structures enhance the roughness and make some obstacles among the glass surface and the water droplets. Therefore, as irradiation time passes, water repellency on the O-G surface increases. Figure 7(c) demonstrates the SEM image of the O-T-G surface before UV irradiation. TiO<sub>2</sub> hydrophilic property causes oleic acid to be distributed on the surface as granules. The droplets size on the surface is in the range of 100-200 nm. The initial contact angle of water on the surface is large. According to Figure 7(d), a few oleic acid droplets can be observed on the surface, which confirms the photodegradation of oleic acid by TiO2 after 25 hours UV

irradiation. As OH and  $O_2^-$  have accelerated the photodegradation process, the water droplet contact angle is decreased and a clean surface is developed. In fact, UV irradiation changed the concentration of hydrophobic and hydrophilic groups on O-G and O-T-G surfaces. So, it is evident that UV irradiation can increase the difference between the water droplet contact angle of the O-G and O-T-G surfaces.

Figure 8 shows the FTIR spectra of oleic acid bonds on the O-T-G surface before and after 25 hours of UV irradiation. It is evident that the C=O bond in COOH species disappeared after UV irradiation [42]. The adsorption peak at 1710 cm<sup>-1</sup> is assigned to the C=O stretching mode for the dimeric COOH group [46]. Due to the photocatalytic reaction of the  $TiO_2$ nano-layer, the intensity of the symmetric and asymmetric vibration peaks of oleic acid at 2854 and 2923  $\text{cm}^{-1}$  (Figure 8 8(b)) is reduced [51]. It can be observed that the peak of stretching mode at 1710 cm<sup>-1</sup> disappeared after UV irradiation. It can be concluded that the remaining alkyl chains on the surface prevented the enhancement of hydrophilicity. In addition, due to the dry atmosphere and low concentration of hydroxyl radicals, the photocatalytic degradation takes more time. As oleic acid is decomposed on the surface photocatalytically, the water droplet contact angle is decreased continuously. Therefore, a combination of these two effects happened on the surface [23, 52].



Figure 6: Contact angle of water droplet on the surface versus UV light irradiation, O-G, O-T-G, O-T-S-G and 2O-T-G surface.



Figure 7: SEM images of (a) O-G before, (b) O-G after 25 UV irradiation, (c) O-T-G before and (d) O-T-G after 25 h UV irradiation.



Figure 8: C=O bonds in FTIR-ATR spectra of oleic acid on O-T-G surface; (a) before and (b) after 25 h UV irradiation.

Repetitive degradation of oleic acid confirms the stability of the photoactivity of the  $TiO_2$  nano-layer. Figure 6 displays the variation of contact angle measurement on 2O-T-G, which changes from 63 to 42° after 20 hours of UV irradiation. Furthermore, a 30° reduction of contact angle measurement on O-T-S-G with the same photodegradation rate as an O-T-G sample during 25 hours UV irradiation can be observed. It seems that the  $TiO_2$  nano-particles play the main role in the photodegradation of oleic acid on the

O-T-S-G surface. Although, it was expected that  $SiO_2$  nano-particles reduce the photodegradation rate of oleic acid, it was observed that the process takes the same time as pure  $TiO_2$  layer and the contact angle value reached to 29° after 50 hours UV irradiation. This effect was performed as a result of the initial hydrophilicity and the synergetic effect [49]. In fact, the role of  $SiO_2$  in the composite is improving hydrophilicity and decreasing photoactivity or vice versa [42].



Figure 9: FE-SEM images; cross-section of (a) 1T-G, (b) 3T-G and (c) scratch thickness on 1T-G surface.

Thickness of the  $TiO_2$  nano-layers were measured 75 and 85 nm for 1T-G and 3T-G samples, respectively, based on the cross-section FE-SEM images (Figures 9(a) and (b)). It was observed that there is a compact layer stick to the substrate. Therefore, there is no linear correlation between the number of dips and thickness of the nano-layers.

To evaluate the hardness of the  $TiO_2$  nano-layers, the Elkometer was employed to perform a scratch test. The process of scratching was performed for different sinkers until the surface of 1T-G was scratched. Figure 9(c) shows the scratch on the 1T-G surface, which is created by 1000 gr sinker. It is evident that scratch thickness is about 150 nm. Therefore, the  $TiO_2$  nanolayer should have an enhancement to get enough resistance against hard scratching and proper adherence to the substrate [14].

#### 4. Conclusions

 $TiO_2$  nanolayer was successfully deposited on the glass surface. The nanolayer was characterized by SEM, XRD, AFM, UV-Visible spectroscopy and water droplet contact angle measurements. The results of water droplet contact angle measurements under UV light irradiation confirm that the humidity can act as a key factor in hydrophilicity of the TiO<sub>2</sub> nanolayer. It may make a negative effect on the self-cleaning property. The Hashimoto model was used to explain this effect at the low humid conditions. Adding SiO<sub>2</sub> nanolayer under the TiO<sub>2</sub> layer enhances the hydrophilicity because of the increase in the roughness and surface area of the nanograins. The photocatalytic property of the TiO<sub>2</sub> layer was examined by a thin layer of oleic acid. It was shown that UV irradiation on the oleic acid/TiO<sub>2</sub> layer reduces the droplet contact angle and it was attributed to the photocatalytic property of TiO<sub>2</sub> layer. The FTIR-ATR analysis of oleic acid before and after photodegradation indicates the elimination of the C=O bond. Finally, the stability of photodegradation and hardness of the TiO<sub>2</sub> nanolayer were satisfied by repetitive photodegradation of oleic acid and scratch test, respectively.

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