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Effect of SiO_2 Content on the Microstructure and Photocatalytic Activity of TiO_2 Films on Ceramic Substrate

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ABSTRACT

TiO_2 films has been widely used and deposited on various substrates due to its potential application as a photocatalyst. However, on unglazed or glazed ceramic tiles, TiO_2 films on both substrates commonly resulted in a cracked morphology of the film. The cracks present usually lead to delamination and peel off of film from substrate and reduce its photocatalytic efficiency. Therefore, a binder needs to be added into the composition of TiO_2 sol in an effort to eliminate cracking when deposited on ceramic substrates. In this work, silica (SiO_2) powders were added into TiO_2 sol preparation as an additive to act as a binder, in order to improve the microstructure of TiO_2 films on unglazed ceramic tiles by sol-gel dip-coating. TiO_2 sol with different amount of SiO_2 (1, 3, 5 mol%) were utilized during film deposition. The crystalline phases were characterized by XRD, while film morphologies were analysed by SEM. The photocatalytic activity was evaluated by degradation of methylene blue under UV irradiation according to ISO 10678. The reduction of cracks formation was observed at a high amount of SiO_2 (5 mol%) added and resulted in lower thickness of the films. The reduced cracks and delamination of film ensures film to bind closely to the substrate hence reducing film thickness. The highest degradation observed is at 3 mol% SiO_2 where the microstructure consists of small cracks which promoted to more exposure of UV irradiation that enhanced the film's photocatalytic activity.

1. Introduction

TiO_2 is widely known for its photocatalysis [1], air and waste water purification [2], superhydrophilicity and self-cleaning properties [3,4]. Originally, TiO_2 nanosized particles were synthesized to remove organic pollutants in water [5,6] and now it can be immobilized by different deposition methods on different types of substrates such as glass [2,7-9], stainless steel [10-12] and ceramics substrates [4,13-15].

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However, past studies showed that it is difficult to deposit TiO_2 films onto ceramic tiles when they often resulted in cracks and peeling off of the film from the substrate. This problem is due to the tensile stress during annealing stage of the films processing [16,17]. Therefore, adding additives to function as a binder is a promising approach in an effort to produce a microstructure that is crack free with continuous layer covering the substrate, henceforth improving the properties of the TiO_2 films.

Silicon dioxide or silica (SiO_2) has been introduced into TiO_2 film to create a more durable TiO_2 film with improved morphology, mechanical stability and photocatalytic performance [2-4]. In most of these work, SiO_2 sol is synthesized using a precursor such as tetraethoxysilane (TEOS), which is then added into TiO_2 solution during the sol-gel process, which later resulted in TiO_2- SiO_2 composite films. The addition of SiO_2 improves the microstructure and mechanical stability of TiO_2 films as well as its photocatalytic performance [2,10,18]. Latthe *et al.,* [3] synthesized TiO_2- SiO_2 films deposited on polycarbonate substrate with SiO_2 content from 7 to 20 vol %. Addition of SiO_2 resulted in a smooth and crack-free morphology which contributes to high photocatalytic performance. Zhang *et al.,* [4] synthesized TiO_2- SiO_2 films and deposited on glazed ceramic tiles. The addition of SiO_2 had reduced the size of particle aggregates on the surface of the film which resulted in a uniform distribution of particles and smooth film. The reduced particle size and smooth film surface contributed to the high photocatalytic activity of TiO_2 films with the addition of SiO_2 and which is also in agreement with Aziz and Sopyan [2]. Aside from smooth and crack free morphology, it was also deduced that the addition of SiO_2 helps to create new catalytic active sites due to interaction between TiO_2 and SiO_2 [6]. This is due to the mixed metal oxide improves the ability of the surface adsorption and increases surface hydroxyl group of the photocatalyst [19].

On the other hand, adding SiO_2 has created a gateway for high thermal temperature treatment for TiO2 films. Aziz and Sopyan [2] synthesized TiO_2- SiO_2 thin films deposited on glass substrate via spin-coating with different SiO_2 content. It was found out that amorphous-to-anatase and anatase-to-rutile transformation shifts towards higher temperature up to 900˚C as SiO_2 composition increases compared to without SiO_2 addition which is at 650˚C. This occurrence is also in agreement with Tobaldi *et al.,* [18] which synthesized TiO_2 - SiO_2 powders and stated that the bigger crystal structure of SiO_2 blocking and suppressing the TiO_2 densification and crystal growth thus making it possible to heat treat TiO_2 at temperatures higher than 500˚C [20].

Based on the review conducted, it should be highlighted that most work reviewed on the effect of SiO_2 on TiO_2 films were deposited on glass and steel substrates. The works involved prior synthesization of SiO_2 sol using SiO_2 precursor such as TEOS, which is later mixed into the TiO_2 sol. Therefore, it is of our interest to study the potential of TiO_2-SiO_2 film on ceramic substrate, mainly on unglazed ceramic tile to initiate works for antimicrobial application. In our work, SiO_2 powders is used as SiO_2 source which is directly added into the TiO_2 sol prior ageing process. This is an effort to improve the film's microstructure in which is crack free with uniform layer and fully covering the surface of the substrate. This will also contribute to the photocatalytic activity of the films by degradation of methylene blue. In this paper, the effect of SiO_2 amount added on the microstructure and photocatalytic activity of TiO_2 film on unglazed tile is reported.

2. Methodology

2.1 Preparation of TiO_2 Films

The method of making TiO_2 sol with SiO_2 are as follows. Titanium(IV) isopropoxide (TTIP) (Sigma Aldrich Co.) was used as TiO_2 source. Ethanol was used as solvent, hydrochloric acid as catalyst and water for hydrolysis. Separate sols, sol A and sol B, were prepared with water, ethanol and

hydrochloric acid in sol A and TTIP and ethanol in sol B. Next, sol B were added dropwise into sol A. 2.5g of Degussa P25 was added as the anchor for the growth of TiO_2. Silica fumed powder was added in different amounts (1, 3, 5 mol%) to study the effect of SiO_2 on the films. Then, the solution was kept at room temperature for 48 hours for ageing process.

The films were prepared by dip-coating using above prepared TiO2 sol on glass and unglazed ceramic tile with a withdrawal rate of 0.5mm/s and 5s dwelling time. The coated substrates were oven dried at 110˚C for 30 minutes. The dipping step was repeated for 5 dipping times. Then the films were heat treated at 500˚C for 1 hour with heating rate of 2˚C/min.

2.2 Characterization of TiO_2 Films

The crystal phase composition of the TiO2 films deposited on unglazed tile was studied by Glancing Angle X-ray diffraction (GAXRD) method in the 2θ range of 10˚-80˚ at a grazing angle of 4˚ by using the PANalytical X'PERT PRO MPD Model PW 3060/60 with Cu Kα of 1.54060Å and generator settings at 30 mA and 40 kV. The average crystallite size, L, were calculated at strongest XRD line [(101) at 25˚], [(110˚) at 27˚] by Scherrer's equation [21]:

$$L=K\lambda/\beta\cos\theta$$

Film surface microstructure was examined by Scanning electron microscope (JEOL model JSM-6010PLUS/LV). Film thickness was determined by cross-section SEM analysis.

2.3 Photocatalytic Activity

Degradation of methylene blue (MB) was performed following the ISO 10678:2010 [22]. The samples were exposed under UV radiation (Sankyo Denki, 20 W, intensity, Ep = 124.34 W/m^2) for 24 hours in order to decompose any possible remaining organic contaminants by photocatalytic oxidation. Then, the samples were immersed in 25 mL of 10ppm aqueous MB solution each one and left in the dark for another 24 hours for pre-adsorption of substrates. This process is necessary because the substrates tend to absorb the dye molecules. After the pre-adsorption of substrates, the adsorbed solution was replaced by a new solution (25 mL, 10ppm) and the samples were exposed to UV-light (Sankyo Denki, 20 W, intensity, E_p = 124.34 W/m^2). The degradation of MB was measured every 1 hour for 5 hours using a spectrophotometer (SHIMADZU UV-1700, cell length, d = 10 mm) by determining the absorption spectrum at 664nm wavelength. A reference sample (blank) was kept in the dark and the absorption spectrum was also measured at the same time interval.

The specific degradation rate R, was calculated from Eq. (1).

$$R = \frac{\Delta A_\lambda \times V}{\Delta t \times \varepsilon \times d \times A} \quad (1)$$

where ΔA_λ is the absorption difference from one time interval to another, V is the volume of MB solution, Δt is the time difference, ε is the MB molar extinction coefficient at 664nm, d is the measuring cell length used at the spectrophotometer and A is the contact area from the MB solution and the catalyst.

The degradation rate, R, of the irradiated and dark samples makes it possible to calculate the specific photocatalytic activity, P_{MB} by Eq. (2).

$$P_{MB} = R_{irr} - R_{dark} \quad (2)$$

Finally, the photonic efficiency, ζMB can be calculated using Eq. (3).

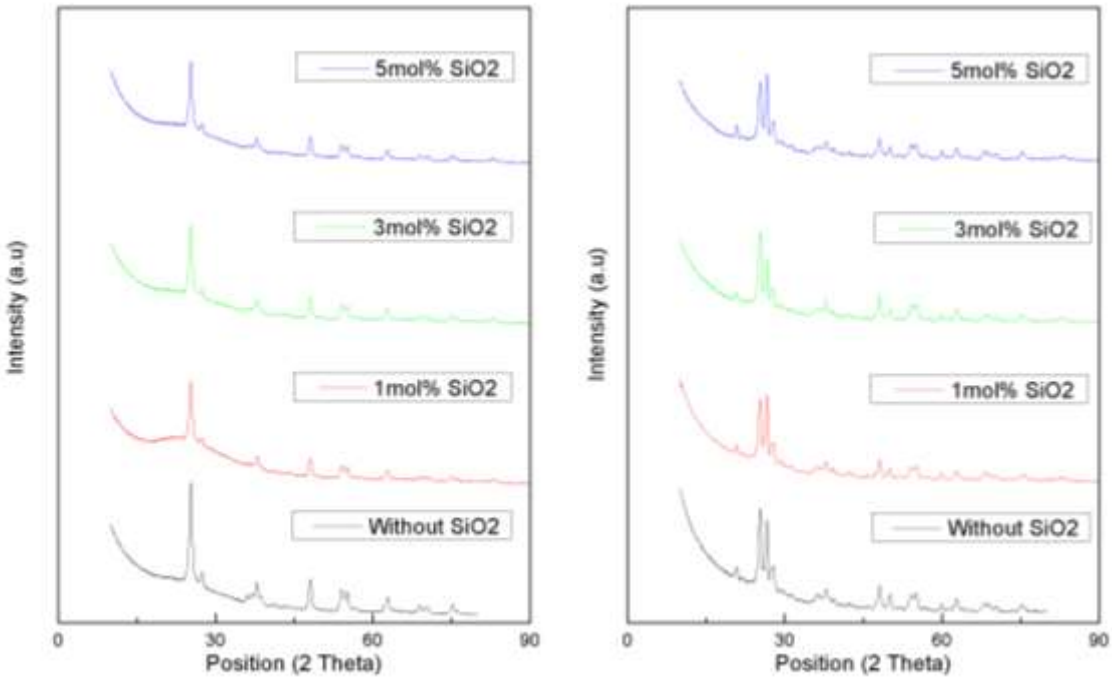
$$\zeta_{MB} = \frac{P_{MB}}{E_p} \times 100 \quad (3)$$

where E_p is the UV radiation intensity.

3. Experimental Results

3.1 Characterization of TiO_2 Films

Figure 1 shows XRD pattern of TiO_2 film with different SiO_2 content on glass slides and unglazed tiles. XRD patterns show all samples exhibit a mixture of anatase and rutile crystalline phase after 1 hour heat treatment at 500˚C. Peaks identified as anatase (1 0 1) are at 25.33˚, 37.90˚ and 48.05˚ while rutile (1 1 0) is at 27.50˚, 41.28˚ and 54.00˚. Note that for films on unglazed tile, crystalline peak observed at 26.65˚ represents quartz which is attributed to the substrate's element.



(a) (b)

Fig. 1. XRD pattern of TiO_2 films on (a) glass (b) unglazed tile

It was observed as the amount of SiO_2 is increased, the intensity of anatase peak decreased at 25.3˚ for both substrates. This observation is much more obvious with films on glass slides. Besides that, the reduction of rutile peak intensity at 54.0˚ was similarly detected. With the increasing content of SiO_2, the intensity of anatase peak decreases. This implies that with the existence of SiO_2, the crystal growth and arrangement of TiO_2 is suppressed and retarded resulting in low crystallinity phase [2,20,23]. The addition of SiO_2 has a suppressive effect on the growth of TiO_2 since the SiO_2 or Ti-O-Si bond blocks the contact among TiO_2 particles and inhibits grain growth during calcination process.

Table 1 shows the crystallite sizes of anatase phase without and with SiO_2 addition. In this study, the addition of SiO_2 into TiO_2 films did not significantly change the crystal size of TiO_2 anatase.

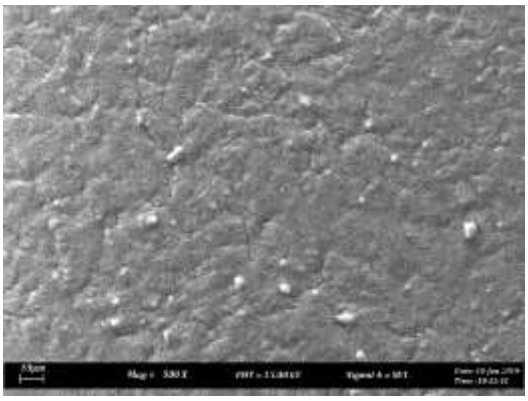
Nevertheless, there are findings that claimed crystallite size of anatase becomes smaller with the addition of SiO_2 due to the suppressive effect of SiO_2 on TiO_2 grain growth [4,6,10,18]. The SiO_2 matrix behaves as a barrier, thus reducing the coarsening of anatase by preventing titania particles from coming into mutual contact and therefore delaying the growth of anatase crystal size [24].

Table 1
Anatase crystallite size of TiO_2 coating without and with SiO_2 addition

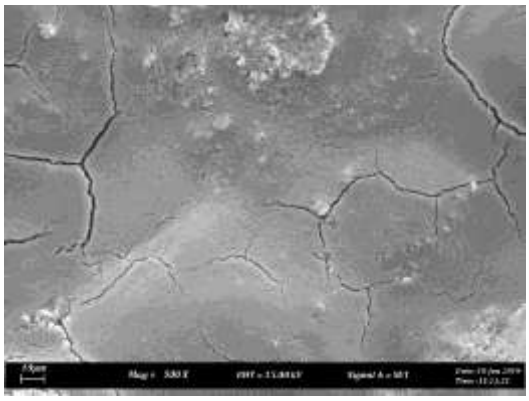
SiO_2 Addition	Anatase crystallite size (nm)	
	Glass	Unglazed tile
Without SiO_2	17.28	19.21
1 mol %	19.20	21.60
3 mol %	19.20	17.28
5 mol %	17.28	19.20

Figure 2 shows SEM surface images of TiO_2 films with different amount of SiO_2 on glass slides and unglazed tiles. It was observed that on glass, Figure 2(a) to 2(d), showed a smooth surface of the films produced in contrast to the films deposited on unglazed tile, Figure 2(e) to 2(h). This is due to the nature of the substrates in which glass has a smoother surface than unglazed tile [17]. It is more clearly observed when comparing films without SiO_2 addition where TiO_2 film on glass showed a smooth coating while on unglazed tile showed cracks as shown in Figure 2(a) and 2(e) respectively. Referring to the effect of SiO_2 addition on the microstructure of TiO_2 film, it is seen that the microstructure of films deposited on unglazed tile is much more affected compared to films on glass substrate. For example, films with 1 and 3 mol % SiO_2 on unglazed tile showed more cracks in contrast to film with 5 mol % SiO_2. With 5 mol % SiO_2, the formation of cracks is reduced and no agglomerates were seen. The size of agglomerates on the surface of the film reduces with an increase of SiO_2 addition and particles present are less visible. This result is in agreement with the report that SiO_2 benefits the dispersion of TiO_2 particles [4]. In the case of sol-gel coated films, Latthe *et al.,* [3] reported that the capillary forces might have generated during drying process which provides cracks and propagation on the surface of the films and in this case, 1 and 3 mol% of SiO_2 was not sufficient to avoid the propagation. However, Aziz and Sopyan [2] claimed that the cracked surface may result in more exposure to UV irradiation and which will enhance the film's photocatalytic activity.

Without SiO_2



(a)



(e)

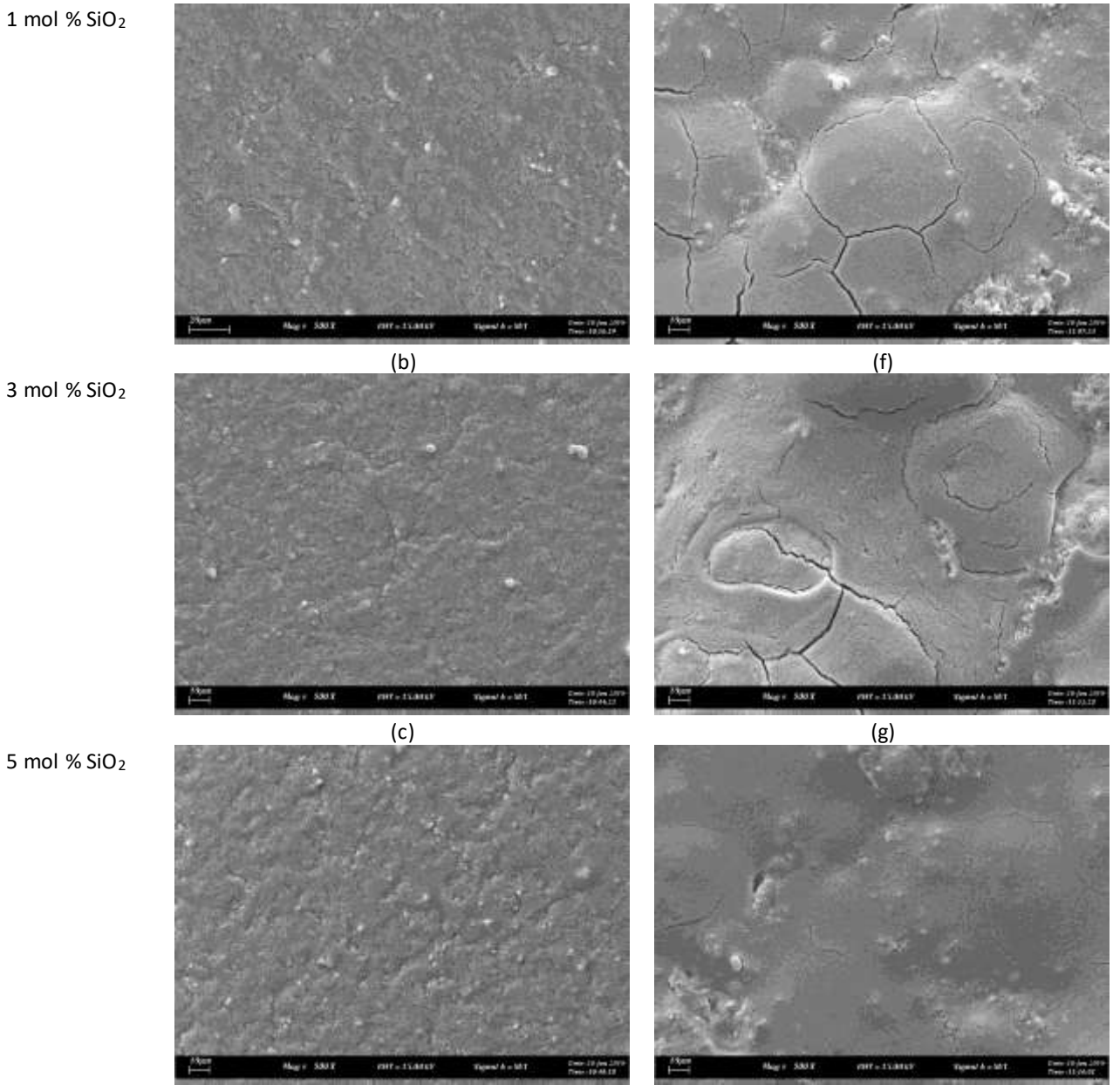


Fig. 2. SEM surface image of TiO_2 films without and with SiO_2 on (a-d) glass (e-h) unglazed tile

Figure 3 shows cross-sectional SEM images of TiO_2 films with different amount of SiO_2 on glass and unglazed tile at 5 dipping times. It is clearly seen that the film's thickness on unglazed tiles is greater than glass. The greater thickness is due to the nature of ceramic substrate utilized. The rougher surface of the tile would ensure better hold onto the TiO_2 colloids during dip-coating until heat treatment [17]. In contrast to the smooth surface of the glass when dip-coated, TiO_2 colloids slip from the surface due to gravity. The average thickness of TiO_2 films on glass slides without SiO_2, 1 mol % SiO_2, 3 mol % and 5 mol % SiO_2 is 1.94, 2.59, 2.90 and 1.21 µm respectively. While on unglazed tile, the film's average thickness is 15.10, 17.77, 17.37 and 14.62 µm for films without SiO_2, 1 mol %, 3 mol % and 5 mol % SiO_2 respectively. The decrease in thickness with an increased addition of SiO_2 is due to the reduced cracks of the film, creating a denser and more compact microstructure. This indicates the film with 5mol % SiO_2 addition is more tightly bonded with both substrates. This finding is also similar to Shi *et al.,* [25] which stated a lower film thickness will create more compact and high adhesion and hardness of films, while greater film thickness creates a looser microstructure resulting

in lower adhesion and hardness. Furthermore, a lower film thickness will have a better advantage such as lower surface roughness, better film adhesion to substrate and good mechanical stability of the film [26-29].

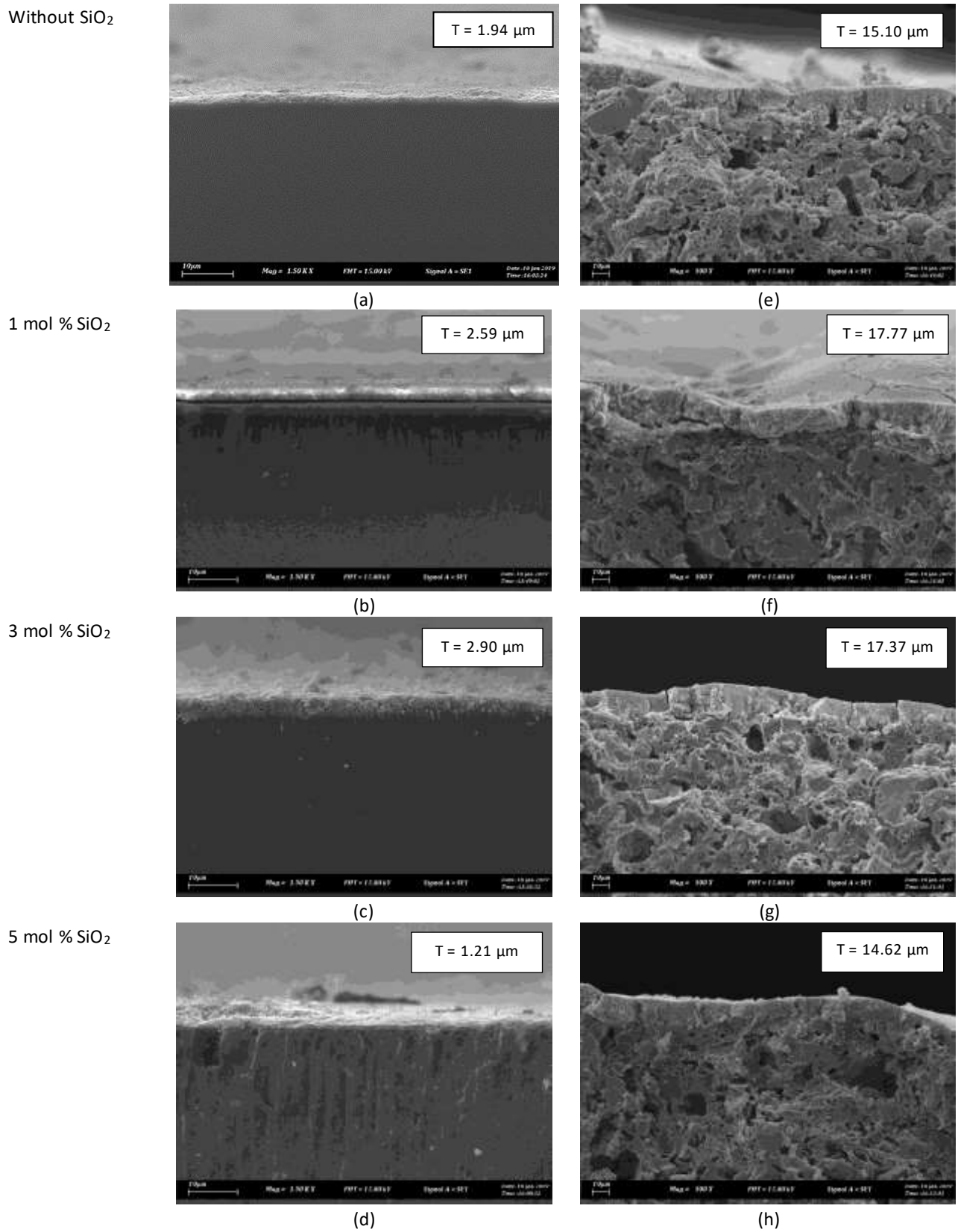
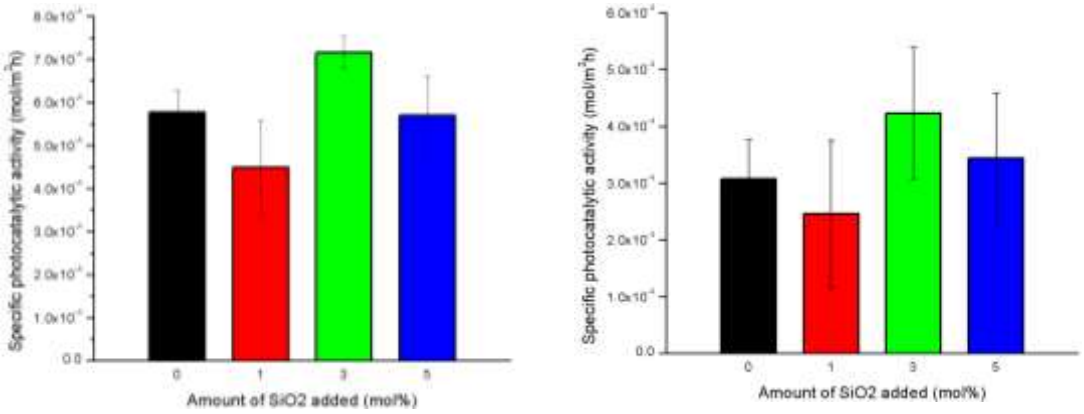


Fig. 3. Cross-sectional image of TiO_2 films on (a-d) glass (e-h) unglazed tile

3.2 Photocatalytic Activity

The specific photocatalytic activity, P_{MB}, is shown in Figure 4. The P_{MB} is the standard expression of photoactivity according to ISO 10678. The presence of SiO_2 clearly improved the photocatalytic activity of TiO2 films. For instance, the P_{MB} for TiO_2 film without SiO_2 addition on glass substrate is 57.65e-5 mol/m^2h, while with 3 mol % addition, the P_{MB} is higher at 71.61e-5 mol/m^2h and with 5 mol % is at 57.02e-5 mol/m^2h. Comparably on unglazed tile, the P_{MB} for TiO_2 films without SiO^2 added is 30.70e-5 mol/m^2h, while with 3 mol % and 5 mol % SiO_2 addition the P_{MB} increased up to 42.30e-5 and 34.40e-5 mol/m^2h respectively. Therefore, it was determined that the highest methylene blue degradation is when adding 3 mol% of SiO_2 on both substrates.



(a) (b)

Fig. 4. Specific photocatalytic activity, P_{MB}, of TiO_2 films on (a) glass (b) unglazed tile

The enhanced photocatalytic activity is attributed to the microstructure and unique physicochemical properties of TiO_2-SiO_2 composite oxides. Films with 3 mol % SiO_2 has higher photocatalytic activity as compared to films with 5 mol % on both substrates. The clear difference in photocatalytic activity is due to the exposure area of the TiO_2 films to UV irradiation which is related to its microstructure. The cracked surface of 3 mol % SiO_2 films resulted in high surface area to be exposed to the UV irradiation and generate more charge carriers as also observed by Aziz and Sopyan [2]. The higher surface area caused larger amounts of methylene blue to be adsorbed on the surface hence resulting a higher degradation rate resulted in increased photocatalytic capacity [30].

Furthermore, crystallinity of anatase phase also affects the photocatalytic activity of TiO_2 films. From Figure 1, it is observed that the intensity of anatase peak at 25.3˚ for TiO_2 film with 3 mol % SiO_2 addition is higher than 5 mol % SiO_2 addition. This indicates that the anatase present is more dominant in 3 mol % than 5 mol % SiO_2 added. Aziz and Sopyan [2] reported that less TiO_2 anatase content means less photocatalytic centre. The higher amount of SiO_2 would hinder the TiO_2 particles from interacting with organic molecules and decelerate photocatalytic activity. Therefore, it was determined that 3 mol % of SiO_2 addition is the suitable amount to enhance the photocatalytic activity of TiO_2 film.

4. Conclusions

TiO_2-SiO_2 composite films was synthesized and deposited on glass and unglazed tile to study the effect of SiO_2 on the microstructure and photocatalytic activity of TiO_2 films. A higher amount of SiO_2 need to be added in order to reduce the cracks of films deposited on unglazed tile. However, with higher amount of SiO_2 added, it decreases the photocatalytic activity of TiO_2 film due to smaller

surface area exposed to UV irradiation. The optimized addition of SiO_2 is at 3 mol % with the highest degradation of MB which is 71.61e-5 and 42.30e-5 mol/m^2h on glass and unglazed tile respectively. With 3 mol % SiO^2, cracks were observed when the film is deposited on unglazed tile, nevertheless, the cracks open up to more surface area exposed by the UV irradiation hence the high photoactivity.

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