INFLUENCE OF SILVER INCORPORATION ON THE MICROSTRUCTURE AND CRYSTALLINITY OF TiO_2 COATINGS

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ABSTRACT: Silver titanium dioxide, Ag-TiO_2, has been exploited in various applications due to its self-cleaning properties, but has not been critically explored on unglazed ceramic tiles. In this study, Ag was incorporated into TiO_2 coating with Degussa as an additive in order to study the effect of 10 mol% Ag incorporation on the microstructure and crystallinity of the immobilized TiO_2. TiO_2 and Ag-TiO_2 coatings were deposited on glass slides and unglazed ceramic tiles through sol-gel dip-coating method. The coating morphologies and thickness were analyzed using Scanning Electron Microscope (SEM), while the crystalline phases and sizes were characterized using X-ray Diffraction (GAXRD). Results show that Ag incorporation influences the morphology of the coating, while insignificantly affects its crystallinity. With the Ag incorporation, the coating deposited is slightly thinner with an average coating's thickness of ~2μm on the glass slides and ~31μm on the unglazed ceramic tiles. Ag is also found to present throughout the coating structure. XRD analysis shows the presence of anatase and rutile, along with Ag and Ag oxides for the Ag-TiO_2 coating. This study offers a promising deposition technique for Ag-incorporated TiO_2 coating with Degussa P25 as an additive for an efficient design of self-cleaning ceramic tiles.

KEYWORDS: *Titanium Dioxide; TiO_2 Coating; Ceramic Tile; Sol-Gel; Antimicrobial*

1.0 INTRODUCTION

At present, TiO_2 has been doped with several dopants to enhance its photocatalytic and antimicrobial performance [1-2]. Silver (Ag) is well known for its oligodynamic effect and has been incorporated in TiO_2 for numerous applications to enhance its photocatalytic activity [3] and antimicrobial capability [1, 4]. Despite these overwhelming studies, however, there are still many remaining studies needed, especially regarding to the coating applications. The incorporation of Ag in TiO_2 coating was observed to influence the microstructure, phase transformation as well as grain growth of the TiO_2 coatings. Yu et al. [5] reported that the incorporation of silver salt has produced TiO_2 coating with a more mesoporous morphology, while Fu et al. [6] exhibited that the addition of Ag hindered cracking of the coating.

Moreover, some studies have shown that the addition of certain amount of Ag promote the anatase to rutile transformation [5, 7], while others show that Ag incorporation hinders or does not influence the TiO_2 crystallization [8]. Akgun et al. [7] also revealed that Ag incorporation has a depression effect on the average anatase grain growth as well as the anatase grain size. However, later work by Ubonchonlakat et al. [9] indicates a contradicting finding. Their study shows that the increment in anatase phase and the reduction in anatase crystallite size only occurred for the addition of 0.5 - 2% Ag content. The crystallite size increases when 3 - 5% Ag content is doped into the TiO_2. Another work carried out by Albert et al. [10] has indicated that the method used in incorporating Ag into the TiO_2 sol-gel film also affects the antimicrobial performance of the coating. Their work compared the antibacterial performance of Ag/TiO_2 sol-gel film prepared using two different methods used to incorporate the Ag; by co-deposition (adding Ag directly to the precursor sol) or by post-synthetic impregnation of the ready-made TiO_2 coating. The works revealed that the antibacterial performance of the co-deposited samples vanished after the first use despite their high and constant remaining silver content while the impregnated samples, which has lower silver content, shows long-lasting antibacterial performance.

Studies reported on TiO_2 coating with Ag incorporation are mostly executed on glass substrates, while the one done on unglazed ceramic

tiles is very limited. Furthermore, literature shows that immobilization of TiO_2 coating on unglazed ceramic tiles are usually accompanied by silica/glaze as the coating material [11]. The presence of silica has definitely influenced the interaction of TiO_2 with the ceramic material. Thus, a systematic study on the immobilization of pure TiO_2 coating on unglazed ceramic tiles, without the incorporation of silica, is believed to be vital in order to comprehend the interaction of TiO_2 with a pure ceramic substrate. Apart from this, the use of Degussa P25 as an additive in the TiO_2 coating to promote good TiO_2 film morphology, and crystal formation has been reported for other substrates [12]. However, it has not been systematically studied on unglazed ceramic substrates.

Hence, this work was executed with the intention to characterize the effect of Ag incorporation on the microstructure and crystallinity of TiO_2 coating deposited via sol-gel dip-coating method with the presence of Degussa P25. It is hoped that by comprehending the interaction between Ag, Degussa P25, TiO_2 alkoxide sol, and the unglazed ceramic tiles, it will give some insights on how the characteristics of the ceramic substrate influence the TiO_2 deposition parameters and the coating properties. This will further lead to economical immobilization of TiO_2 coating on other types of ceramic substrates. This work is targeting to contribute towards the manufacturing of antimicrobial ceramic tiles.

2.0 METHODOLOGY

TiO_2 coatings were prepared by using titanium (IV) isopropoxide (TTiP) (97%, Sigma Aldrich Co.) and Degussa P25 (99.5%, Sigma-Aldrich) as the titanium precursors, ethanol (C_2H_5OH), hydrochloric acid (37%, HCl) and deionized water. For the incorporation of silver, silver nitrate ($AgNO_3$) (Merck) was chosen as the Ag precursor while Acetonitrile (CH_3CN) (Merck) is added as a stabilizer for silver nitrate in this work.

2.1 Substrate Preparation

Two types of substrates; glass slides (20 mm × 10 mm × 2 mm; surface roughness of 0.02 ± 0.005 μm) and unglazed ceramic tiles (20 mm × 10 mm × 5 mm; surface roughness of the ceramics tile is 5.50 ± 0.20 μm) were used in the present study. A notch was made on the surface of the substrate by using a diamond pen (for glass slide), or a diamond saw (for unglazed ceramic tile) for getting fractured cross-sectional

analysis. Subsequently, all the substrates underwent a surface cleaning process that involved 10 minutes ultrasonication in acetone, ethanol, and deionized water, sequentially. Following that, the substrates were oven dried for two hours at 110°C.

2.2 TiO_2 Sols Preparation

For this work, sol-gel technique was employed to prepare the TiO_2 sol. Briefly, ethanol and deionized water was mixed and then stirred for 30 minutes. HCl was then added to maintain the pH < 2. Next, a solution of TTiP and ethanol was added dropwise to the above solution and dispersed by stirring for 1 hour. Then, 50 g/L of Degussa P25 powder was added slowly into the prepared sol under continuous stirring to prevent agglomeration. To examine the effect of silver incorporation to the coating microstructure and crystallinity, the same solution was prepared with the incorporation of 10 mol% Ag from a mixture of $AgNO_3$ and acetonitrile. This sol is labelled as Ag-TiO_2 sol.

2.3 TiO_2 Coating Deposition

A mechanical dip coater set at a speed of 30 mm/min and an immersion time of 5 s was utilized for the dip-coating procedure. After the dipping process, the samples were set aside for 24 hours in the drying cabinet. Subsequently, the samples were heated at 110°C for 30 minutes to prevent the cracking of the coating and the collapsing of the mesoporous TiO_2 structured during high thermal treatment process. This procedure was repeated for five times and followed by a heat treatment at a ramp rate of 2°C/min to 500°C for one soaking hour.

2.4 Coating Characterization

The TiO_2 and Ag-TiO_2 coatings' morphology, thickness, and elemental mapping were examined using Scanning electron microscope (SEM) coupled with an Energy-Dispersive X-ray Spectrometer (EDX) (JEOL model JSM-6010PLUS/LV). Prior to this analysis, the samples were gold-coated due to its non-conductive properties. For the cross-sectional analysis, the samples were fractured along the pre-created notch. The coating thickness, t_{ave}, was measured by averaging the thickness measured at four points along the coating cross-section. The crystallinity of the coating was studied by using X-ray diffraction (PANalytical X'PERT PRO MPD Model PW 3060/60) at a grazing angle of 4° with Cu Kα radiation (λ = 1.54060A°). The XRD generator was set at 30 mA and 40 kV. The average crystallite sizes were estimated by application of Scherrer's formula for the most intense diffraction peaks, anatase (101) at 25.3° and rutile (110) at 27.5° where

$$L = \frac{k\lambda}{\beta\cos\theta} \quad (1)$$

where L is the mean size of the crystalline (nm), k is a Scherrer coefficient, λ is the wavelength of x-rays, β is the full width at half the maximum intensity in radian (FWHM) and θ is the Bragg angle.

3.0 RESULTS AND DISCUSSION

3.1 Microstructure Analysis

Figure 1 displays the surface and cross-sectional morphology of TiO_2 and Ag-TiO_2 coatings deposited on glass slides. It can be seen that TiO_2 coatings on the glass slide (Figure 1(a)i) produced uniform sponge-like structure of coating with rougher surface. The sponge-like structure is a typical morphology of Degussa P25 [13]. The microstructure also consists of small agglomerates that distributed randomly throughout the surface. The agglomerates are the aggregates of Degussa P25 nanoparticles covered with TiO_2 crystallites developed from TTiP sol hydrolyzation and condensation [14]. In contrast, Ag-TiO_2 coatings produced uniform coatings with smoother surface and with fewer but larger agglomerates distributed randomly across the surface (Figure 1(a)ii). This result is in contrast to Yu et al. [5] that reported rougher morphology when higher amounts of silver were incorporated in TiO_2 coating deposited on silicon wafer at 500°C. Likewise, Zhao and Chen [15] also reported rougher Ag/TiO_2 coating compared to TiO_2 coating deposited on glass slides via sol-gel dip-coating method. The difference in coating morphology of this work compared to the findings in the literature is attributed to the addition of Degussa P25 in the TiO_2 coating that is well known to produce mesoporous coating structure with agglomerates that leads to rougher TiO_2 coatings [12, 16].

The cross-sectional morphology of the five dipping times of TiO_2 and Ag-TiO_2 coatings on glass slides (Figure 1(b)) shows two distinguish layers that belong to the coating and the substrate respectively. Both coatings exhibit a brittle coating (due to the addition of Degussa P25) with an average thickness of 2.3 ± 0.4 μm for TiO_2, and 2.2 ± 0.8 μm for Ag-TiO_2 coating, respectively. Since both type of coatings yield almost equal average thickness, this suggests that Ag does not influence the TiO_2 coating thickness in this work.

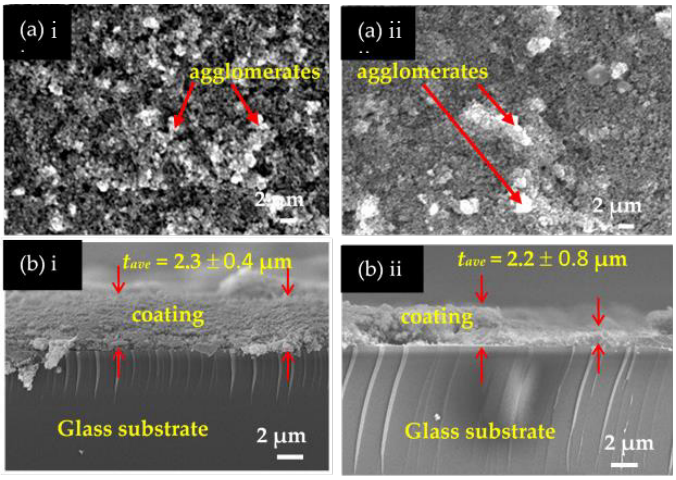

Figure 1: (a) Surface and (b) cross-sectional morphology of (i) TiO_2 coating, and (ii) Ag-TiO_2 coating, deposited on glass slides

The surface and cross-sectional morphology of TiO_2 and Ag-TiO_2 coatings on unglazed ceramic tiles are displayed in Figure 2. The surface morphology of TiO_2 coating on the unglazed ceramic tiles consist of a uniform surface with visible pores (Figure 2(a)i). Few agglomerates that distributed randomly on the surface can also be seen in the coating. The surface of Ag-TiO_2 coating shows almost similar morphology but with much larger pores and agglomerates. Voids can also be spotted in the coating.

The cross-sectional morphology of TiO_2 and Ag-TiO_2 coatings on unglazed ceramic tiles are shown in Figure 2(b). Two layers indicating the substrate and the coating are well identified for both coatings. The ceramic substrate at the bottom layer is observed to comprise of a lot of pores while the coating produced shown a denser layer in contrast. It can also be seen that both TiO_2 and Ag-TiO_2 coatings exhibits the presence of cracks, with Ag-TiO_2 coatings having bigger cracks. The use of Degussa P25 yields a high viscosity sol that produces a thicker, non-uniform coating that is likely to generate cracks [17]. The TiO_2 coating has an average thickness of 35 ± 14.4 μm, while Ag-TiO_2 coating has an average thickness of 31.5 ± 16.5 μm. This shows that a thicker coating is formed on the unglazed ceramic tiles compared to the ones on glass slides.

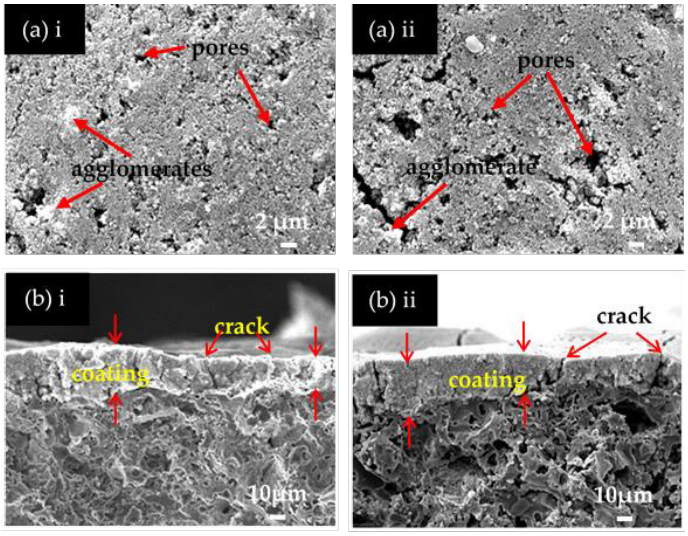

Figure 2: (a) Surface and (b) cross-sectional morphology of (i) TiO_2 coating, and (ii) Ag-TiO_2 coating, deposited on unglazed ceramic tiles

Figure 3 displays the SEM Cross-sectional morphology and the EDX spectrum of five dipping times of Ag-TiO_2 coating on unglazed ceramic tiles. The figure displays that the coating consists of Ti, O, and Ag, while the ceramic tile substrate mostly consists of Fe, O, Si, Ca, Al, Na, and Mg. It can be seen that Ag is detected on each part of the coating (top, middle, and bottom) with top and middle parts having more Ag compared to the bottom part. Thus, it can be deduced that Ag is present throughout the coating. Figure 3 also exhibited that Ag is not detected in the unglazed ceramic tile substrate. This demonstrated that Ag does not diffuse into the ceramic substrate during the coating deposition. It is also observed that silicon is detected at the bottom part of the coating. This is due to the interface physical locking between the ceramic substrate and the deposited coating. Trace of Ti is also detected on the ceramic tile layer, due to the coating chips that resided on the fractured surface.

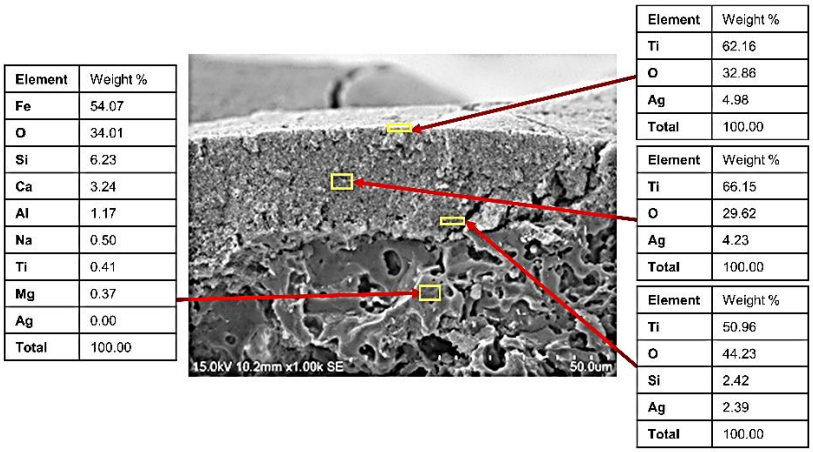

Figure 3: SEM Cross-sectional morphology and EDX spectrum of Ag-TiO_2 coating at 5 dipping times deposited on an unglazed ceramic tile

3.2 GAXRD Phase Analysis

Figure 4 summarizes the GAXRD diffractograms of the TiO_2 and Ag-TiO_2 coatings on glass and unglazed ceramic tile, respectively. The uncoated glass substrate and the unglazed ceramic tile diffraction patterns are also shown for comparison. Similar XRD patterns are obtained for both TiO_2 and Ag-TiO_2 coatings, regardless of the substrate's type. Figure 4(a) shows that the uncoated glass substrate is amorphous. It also displays that the TiO_2 and Ag-TiO_2 coatings produced on the glass slide exhibits the presence of a mixture of anatase and rutile TiO_2 crystal phases. Three main anatase peaks are identified at 2θ of 25.3° (101), 38° (004), and 48°(200) (JCPDS No. 01-070-7348). The rutile peaks are detected at 27.5° (110), 36°, and 41° (JCPDS No. 01-072-4813). Therefore, this implies that the incorporation of 10 mol% Ag and type of substrate does not affect the crystallization of TiO_2 coating. This result is in contrast to the earlier findings by Yu et al. [5] and Akgun et al. [7] that demonstrated the addition of Ag has promoted the anatase to rutile transformation. The reason lies on the addition of Degussa P25. In this study, Degussa P25 (commercial TiO_2 nanoparticles consisting of both anatase and rutile) has been added into the TiO_2 sol. Therefore, the anatase and rutile present are mostly attributed by Degussa P25, and less by the TiO_2 sol, whereas in Akgun et al. [7] and Yu et al. [5] the TiO_2 crystals are solely formed from the sol.

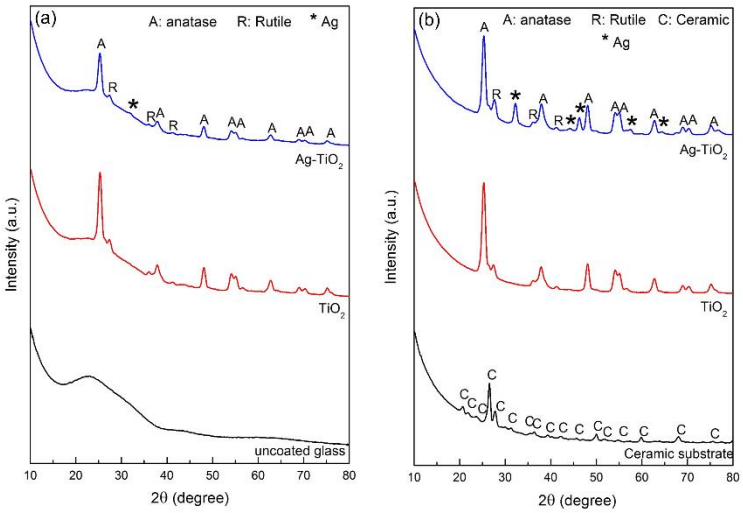

Figure 4: GAXRD diffractograms of TiO_2 and Ag-TiO_2 coatings coated at 5 dipping times deposited on (a) glass substrate and (b) unglazed ceramic tile

In Figure 4(a) also, only one broad peak with a weak intensity was detected at 32.3° for the Ag-TiO_2 coating on the glass slide. This peak is assigned to Ag_2O (111) (JCPDS 41-1104). No obvious peaks ascribed to metallic Ag (Ag^0) at around 38.3° (111) and 44.3° (200) are visible. The Ag^0 peak around 38.3° was probably masked by the TiO_2 anatase peak as discussed by others [5, 18]. Therefore, the presence of Ag^0 in the Ag-TiO_2 coating on the glass slide is inconclusive. However, the EDX elemental mapping supports the existence of Ag^0. Furthermore, the presence of Ag^0, Ag^+, and Ag^{2+} on the Ag incorporated TiO_2 surfaces have been reported in literature [19].

Figure 4(b) shows the unglazed ceramic tile substrate that consists of crystalline phases mixture which are designated to the ceramic constituents (labelled as C). Similar to Fig. 4(a), three main anatase peaks are identified at 2θ of 25.3° (101), 38° (004), and 48°(200) (JCPDS No. 01-070-7348) while the rutile peaks are detected at 27.5° (110), 36°, and 41° (JCPDS No. 01-072-4813). The figure also exhibits that Ag-TiO_2 coating on unglazed ceramic tile shows five diffraction peaks that belong to Ag^0 and Ag-containing phases (Ag^+ and Ag^{2+}). Although the strongest Ag^0 peak around 38.3° was not certain due to the overlapping with the anatase peak, the presence of peaks around 44.2°and 64.3° support the existence of Ag^0 (ascribed to 200 and 220 phase planes, respectively) (JCPDS No. 004-0783 or JCPDS No. 87-0720). The other Ag peaks detected are ascribed to Ag_2O (111) at 32.3° (JCPDS 41-1104) and other Ag-containing phases (the peaks at 46.3° and 57.6°). The

existence of Ag oxide in the coating is resulted from thermal decomposition of $AgNO_3$ during the calcination process, which followed according to the scheme: $AgNO_3 \rightarrow Ag_2O \rightarrow Ag$ [18]. Thus more Ag^+ exist since $AgNO_2$ is not photoreduced to Ag^0 prior to the decomposition. The chemical state of Ag, which depend on the heat treatment temperature and the amount of Ag incorporated [7], influenced the photocatalytic and antimicrobial performance of the TiO_2 coating. Moreover, there are no ceramic peaks observed at five dipping times of TiO_2 coating deposited on the unglazed ceramic tiles. This indicates that five dipping times is adequate to coat the entire ceramic tile surface.

Table 1 lists the average crystallite size of five dipping of TiO_2 and Ag-TiO_2 coatings after heat treatment at 500°C. Both anatase and rutile sizes do not change significantly with the addition of Ag. Hence, this result shows that the incorporation of Ag into the TiO_2 coating does not influence the TiO_2 grain growth. This result, which contradicting to the earlier studies by Akgun et al. [7], is attributed to the used of Degussa P25 as discussed in the GAXRD analysis.

Table 1: Average Crystal size of TiO_2 and 10 mol% Ag-TiO_2 (in nm)

Substrate	Coating	Anatase	Rutile	Silver
Glass	TiO_2	11.53	14.47	-
	Ag-TiO_2	11.53	14.47	7.31
Unglazed ceramic tile	TiO_2	10.81	12.41	-
	Ag-TiO_2	11.53	11.58	15.30

4.0 CONCLUSION

The deposition of TiO_2 and Ag-TiO_2 coatings on glass slides and unglazed ceramic tiles has been accomplished by sol-gel dip-coating method. This work exhibited that the incorporation of 10 mol% Ag does affect the morphology and thickness of the TiO_2 coatings, but not its crystallinity. XRD result exhibits that TiO_2 crystals, metallic Ag and Ag-containing phases essentially present on the surface of Ag-TiO_2 coatings, regardless of substrate type. Since the Ag chemical state depends on the heat treatment temperature and the amount of Ag incorporated, which further affect the TiO_2 coating performance, thus, it is suggested that subsequent works on evaluating the TiO_2 antimicrobial activity on ceramic tiles should be focusing on optimizing the Ag content in the TiO_2 sol.

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