EFFECT OF DEGUSSA P25 CONTENT ON THE DEPOSITION OF TiO_2 COATING ON CERAMIC SUBSTRATE

M.A. Musa[1,2], J.M. Juoi[1], Z.M. Rosli[3], N.D. Johari[1] and T. Moriga[4,5]

[1]Fakulti Kejuruteraan Pembuatan,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[2]Faculty of Engineering and Technology,
Multimedia University, Jalan Ayer Keroh Lama, 75450, Melaka, Malaysia.

[3]Fakulti Teknologi Kejuruteraan Mekanikal dan Pembuatan,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[4]Department of Chemical Science and Technology,
Graduate School of Advanced Technology and Science,
Tokushima University, 2-1 Minami-Josanjima, 770-8506 Tokushima, Japan.

[5]Tokushima-UTeM Academic Centre,
Tokushima University, 2-1 Minami-Josanjima, 770-8506 Tokushima, Japan.

Corresponding Author's Email: [1]jariah@utem.edu.my

Article History: Received 13 January 2018; Revised 16 June 2018; Accepted 23 September 2018

ABSTRACT: TiO_2 coatings were deposited on unglazed ceramic tiles to study the property of its antimicrobial activity. Here, the effect of TiO_2 nanoparticles content (Degussa P25) on the TiO_2 coatings' characteristics was investigated. TiO_2 sol containing 25, 50, and 100 g/L Degussa P25 were deposited few times on ceramic tiles via sol-gel dip coating method and heat treated at 500°C. The coatings were analyzed using SEM and the phases were characterized using GAXRD. The results show that Degussa P25 content significantly influences the TiO_2 coatings morphology and thickness. Increasing the Degussa P25 content led to a thicker and denser coating with different Degussa P25 content yielded different thickness at specific dipping time. 50 g/L of Degussa P25 was discovered as the maximum amount to be used for achieving good adherence coating on the ceramic tiles. Five dipping of TiO_2 sol containing 50 g/L Degussa P25 was found appropriate to generate coating of continuous layer with average thickness of ~29 μm. The Degussa P25 content, however, shows insignificant effect on coating crystallinity.

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

1.0 INTRODUCTION

The concern on surface contamination and its affiliation with disease transmission have been raised out as early as 1960s [1]. Ceramic tile is commonly used in construction industries for public facilities. However, its lack of antimicrobial feature is a common drawback that continuously tried to be addressed by various studies. Different methods of depositing TiO_2 coating on many categories of ceramic tiles, such as liquid phase deposition (LPD), sol-gel dip coating, and spraying techniques, have shown to enhance its antibacterial activity [2-3]. There are many factors that affect the TiO_2 coating's performances, either from the TiO_2 material synthesis itself or from the substrate properties. The substrate's material and substrate's surface roughness have proven to significantly influence the TiO_2 coating characteristics, such as the coating's microstructure and morphology [4-5]. There are two types of ceramics tiles; the glazed ceramic tiles and the unglazed ceramic tiles. However, most studies of TiO_2 coating on ceramic tiles are concentrated on the glazed type of ceramic tiles [6-8] while the work on unglazed ceramic tile is very limited [9]. Furthermore, the existing works on unglazed ceramic tiles usually employ a combination of TiO_2 material with glaze as the coating material [10-11]. A systematic study on the deposition of TiO_2 coating alone, without the addition of glaze material, on unglazed ceramic tiles is deemed necessary in order to understand the interaction of TiO_2 coating with a pure ceramic substrate. It is aimed that the understanding on how the characteristics of the ceramic substrate in influencing the deposition parameters as well as its effect on the coating properties will further contributed towards deposition of the coating on other types of ceramic substrates, e.g. glaze or vitreous.

The incorporation of Degussa P25 (a commercial TiO_2 nanoparticles) as an additive in the TiO_2 alkoxide sol has allowed for modification of the film morphology, crystallinity, as well as the grain size, leading to a better performance of the films [12-13]. However, studies have also shown that Degussa P25 may produce agglomeration, resulting in bigger grain size that reduces the TiO_2 films photocatalytic activity. The amount of Degussa P25 added to the TiO_2 sol, as well as the nature of the substrate have shown to significantly influence these deposition characteristics [14-15]. Hence, this work was carried out aiming to characterize (microstructure, phases, and coating thickness) the effect of Degussa P25 content on the TiO_2 coating deposited using sol-gel dip-coating technique on the unglazed ceramic tiles. This is a baby step effort with an intention of manufacturing antimicrobial tiles. For an efficient antimicrobial performance, it is intended that the produced coating has a homogeneous morphology with a continuous layer consisting of the TiO_2 crystalline phases (anatase, rutile and brookite). In addition, the coating must also sufficiently covers and adheres well to the entire ceramic substrate without cracks.

2.0 METHODOLOGY

Figure 1 shows the flowchart of the TiO_2 coating preparation on ceramic substrates. TiO_2 coatings were prepared by using titanium (IV) isopropoxide (TTiP) (Sigma Aldrich Co.) as the titanium precursor in the sol. Ethanol (C_2H_5OH), hydrochloric acid (37%, HCl) and deionized water, are used as the solvent, catalyst and hydrolysis medium, respectively. In general, two different solutions (Sol A and Sol B) were initially prepared at room temperature. Ethanol and deionized water (mol ratio of 1:7) was mixed and stirred continuously for 30 minutes. Then, 0.4 ml HCl was added dropwise to the solution (Sol A). Simultaneously, TTiP and ethanol (mol ratio of 1: 39) was mixed in another beaker and stirred vigorously for 30 minutes (Sol B). Next, both Sols were mixed together dropwise and placed under an hour of constant stirring. Subsequently, three different amounts of Degussa P25 (particle size ~21nm) was added bit by bit and slowly to the solution, respectively, yielding 25, 50, and 100 g/L of Degussa P25 concentration in the TiO_2 sol. These solutions were kept under continuous stirring for 48 hours to undergo the ageing process.

Table 1 summarizes the sample code used for the TiO_2 coating deposition. The unglazed ceramic tiles with dimensions of 20 mm × 10 mm × 5 mm were utilized as substrates in this study. Using a portable profilometer, the tiles' surface roughness is measured to be 5.5 ± 0.2 μm, while the porosity is determined at 34.14% (using the ASTM C373 standard). The coating process was performed by using a custom-made mechanical dip coater machine. The dipping speed and dwelling time used are 30 mm/min and 5 s, respectively. After the dipping process, the TiO_2 coated ceramic tiles were dried for 24 hours at ambient temperature and subsequently dried for 30 minutes in an oven set at 110°C.

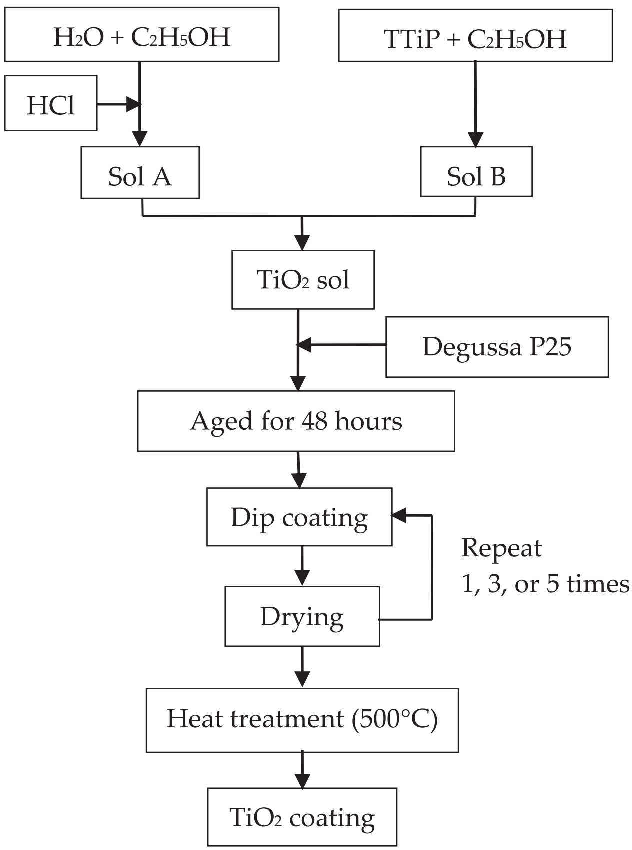

Figure 1: Flowchart of the TiO_2 coating preparation on ceramic substrates

For the purpose of studying the correlations between the coating morphology and the number of dipping times, three different dipping samples were produced. These three samples correspond to one, three and five dipping times, respectively. The annealing process of the samples was carried out at 500°C for an hour, employing 2°C/min of heating rate. For the coating analysis, scanning electron microscope (JEOL model JSM-6010PLUS/LV) was used to examine the coating morphology. PANalytical X'PERT PRO MPD Model PW 3060/60 with Cu Kα of 1.54060A° set at 30 mA and 40 KV, in the 10° – 80° 2θ range, and 4° grazing angle was utilized to acquire the GAXRD diffraction pattern of the coating.

Table 1: Sample code for TiO_2 coatings prepared on ceramic substrates

Sample	Degussa P25 Content	Dipping times
A	25 g/L	1
B	50 g/L	1
C	100 g/L	1
D	25 g/L	3
E	50 g/L	3
F	100 g/L	3
G	25 g/L	5
H	50 g/L	5
I	100 g/L	5

3.0 RESULTS AND DISCUSSION

3.1 Surface Morphology

Figure 2 exhibits the surface as well as the cross-sectional morphologies of the uncoated unglazed ceramic tile. It is noticeable that the morphology of the tile is very rough, porous and consists a lot of pores. This is consistent with the tile's surface roughness measured earlier.

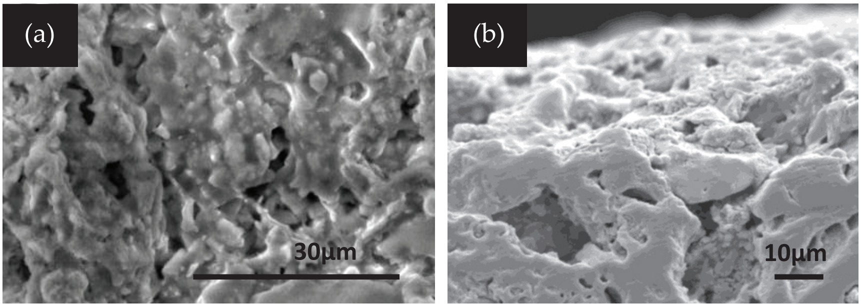

Figure 2: (a) Surface and (b) cross-sectional morphology of the uncoated unglazed ceramic tile

Figure 3 shows the surface morphology of TiO_2 coating with different Degussa P25 content (25, 50, and 100 g/L) deposited on unglazed ceramic tile at one, three, and five dipping times. It can be seen clearly that the TiO_2 coating structure change from agglomerates or patches to continuous layer as the Degussa P25 content increases. For example, TiO_2 coating with 25 g/L of Degussa P25 formed big agglomerates, which further change to smaller agglomerates at 50 g/L, and to a uniform solid surface with micro cracks at 100 g/L; at 1 dipping time (Figure 3 (A, B, C)). Besides, at 3 dipping times (Figure 3 (D, E, F)), the coating morphology change from smaller agglomerates to patches and to a uniform surface as the Degussa P25 content increases from 25 g/L to 50 g/L and 100 g/L, respectively. Similarly, at 5 dipping times, the coatings change from patches to uniform layer and to a uniform surface with macro cracks with the increased of the Degussa P25 content (Figure 3 (G, H, I)).

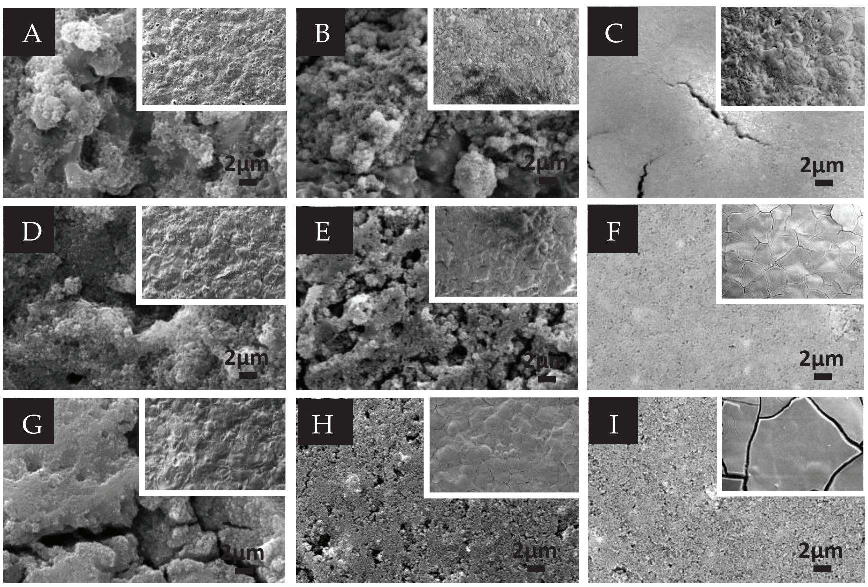

Figure 3**:** Surface morphology of TiO_2 coating with different Degussa P25 content and dipping time (Insets: morphology at lower magnification – 100x magnifications). (Note: The symbol A – I corresponds to the samples as tabulated in Table 1)

It should also be noted that the coatings' surface morphology at different Degussa P25 content is also affected by the number of dipping time. For instance, at 50 g/L of Degussa P25, with one dipping time, the coatings' morphology shows an agglomerated surface (Figure 3 (B)). However, the morphology is found as a patches surface at three dipping time (Figure 3 (E)). Later, a homogenous surface with uniform distribution of solid is observed at five dipping times (Figure 3 (H)). On the other hand, when 100 g/L of Degussa P25 is used, a dense coating (but consists of cracks) is formed at one dipping (Figure 3 (C)). The morphology is then observed to contains macro cracks at three dipping times, and later severe cracks are found at five dipping times (inset of Figure 3 (F, I)). The formation of cracks at increased number of dipping could also be associated with the thicker coating formation, the dissimilarities in linear thermal expansion coefficients between the ceramic substrate and the TiO_2 coating, as well as the TiO_2 coating's grain interaction and grain size which produced intrinsic film stresses during drying, crystallization, and densification processes [7,10]. Based on the observation, it is noticeable that a uniform surface morphology of TiO_2 coating had successfully obtained with the utilization of 50g/L Degussa P25 at 5 dipping times. A uniform surface (not an agglomerates or patches) without cracks is needed for an efficient antimicrobial performance.

3.2 Cross-Sectional Morphology

The cross-sectional morphology of TiO_2 coating with different Degussa P25 content (25, 50, and 100 g/L) deposited on unglazed ceramic tile at one, three, and five dipping times are shown in Figure 4. The TiO_2 coating produced is observed as a denser layer in contrast to the ceramic substrate that is consisting of pores. Figure 4 shows that the increase in Degussa P25 content produced denser coatings. For example, at five dipping times (Figure 4(G, H, I)), the coating produced with 25 g/L Degussa P25 content looks more brittle and less dense with compared to the coating with 50g/L. Moreover, coating produced with 100 g/L Degussa P25 content looks firmer and denser.

Besides, the increase of Degussa P25 content also affect the continuity of the TiO_2 layer deposition, therefore, influencing the average thickness of the TiO_2 coating formed. TiO_2 coatings with lower Degussa P25 contents (25 g/L and 50g/L) fail to exhibit uniform coating layers. For 25 g/L Degussa P25 content, no continuous coating was produced even after five dipping times (Figure 4 (A, D, G)).

These samples of TiO_2 coatings produced TiO_2 patches, where a continuous coating layer is not evident. Hence, it is unable to determine the average thickness of the coatings for these samples. For 50 g/L Degussa P25 content, a continuous layer of coating with an average thickness of ~29 µm was only observed at five dipping times (Figure 4 (H)). Furthermore, for a higher Degussa P25 content (100g/L), ceramic tile which was dip-coated once exhibits an average coating thickness of ~12 µm. This value is higher than the surface roughness of the unglazed ceramic tiles (~5.5 µm). Hence, by using 100g/L Degussa P25, dipping the tile once into the TiO_2 Sol is enough to obtain continuous coating covering the whole tile's surface. However, the obtained continuous layer is not adhering well to the ceramic substrate where thin voids at the interlayer of the ceramic substrate and the TiO_2 coating are observed.

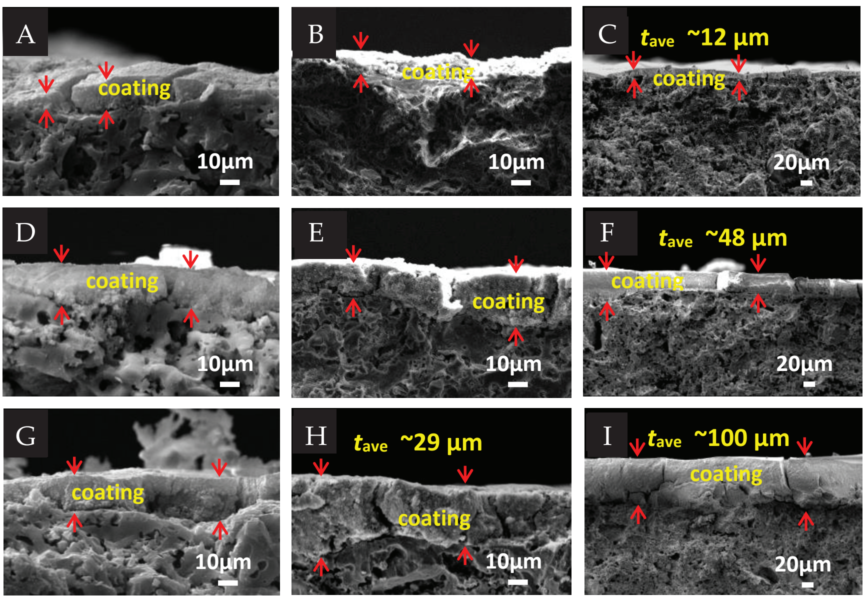

Figure 4: Cross-sectional morphology and average thickness (t_{ave}) of TiO_2 coatings with different Degussa P25 content and dipping time (Note: The symbol A – I corresponds to the samples as tabulated in Table 1)

Figure 4 also exhibits that the thickness of the coating increases in parallel with the dipping time. For the 100g/L Degussa P25 content, as the dipping time increases from one to three and five, the thickness of the coating was shown to increase from ~12 µm to ~48 µm and ~100 μm, respectively. The coating thickness increment on the unglazed ceramic tiles is perhaps due to the change in the substrate's surface roughness which alters the amount of TiO_2 sol that retained on the substrates after each dipping process [16]. Basically, the TiO_2 sol retained on the surface after the first dipping diffuses into the substrate due to the high porosity and surface roughness of the tile. This leads to a thinner coating formation. However, the amount of TiO_2 sol retained on the tile for the following dipping times increases as a result of less porosity, resulting in a thicker coating layer per dipping.

3.3 Phase Analysis

Figure 5 displays the GAXRD diffraction patterns of the uncoated unglazed ceramic tile together with the TiO_2 coated ceramic tile; with three different Degussa P25 content (25, 50, and 100 g/L) at one, three, and five dipping times (marked as 1L, 3L, 5L), correspondingly. The uncoated unglazed ceramic tile comprises of numerous peaks ascribed to the ceramic elements, such as anorthite, diopside, akermanite, and gehlenite. The three highest ceramics peaks are labeled as C in Figure 5. It is apparent in Figure 5 that the TiO_2 crystal phases are present despite the difference in Degussa P25 content and dipping time. Anatase and rutile diffractions are labelled as A and R, respectively. The peaks spotted at 2θ of 25.3° (101), 38°, and 48° are the characteristic peaks of anatase (JCPDS No. 01-070-7348), while the peaks at 27.5° (110), 36°, and 41° corresponds to rutile (JCPDS No. 01-072-4813).

Figure 5 also exhibits that the ceramic substrate component's peaks are still observed in the diffraction spectra of one, three, and five dipping times of 25 g/L Degussa P25. Similarly, 1 and 3 dipping of 50 g/L Degussa P25 also contain traces of the same ceramic peaks. However, no ceramic peaks are observed at five dipping times of 50 g/L content as well as one, three and five dipping of 100 g/L Degussa P25. Moreover, it can be seen that the peaks of both anatase (101) and rutile (110) at five dipping times, are clearly identified with increasing Degussa P25 content, indicating the presence of these phases. This suggests that by increasing the Degussa P25 content in the TiO_2 solutions, lower number of dipping is needed to continuously cover the entire surface of the substrate. Thus, by using 100 g/L of Degussa P25, 1 dip is already sufficient for producing continuous coating (though with cracks observed on the surface) on the unglazed ceramic surface, while five dipping is necessary if 50 g/L of Degussa P25 is used (with no cracks observed on the surface). This XRD result is in agreement with surface morphology analyses carried out by the SEM.

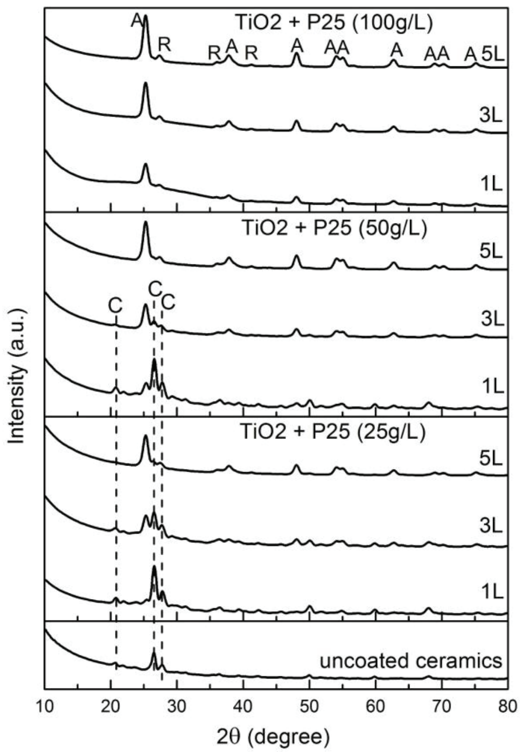

Figure 5: GAXRD diffractogram of TiO_2 coating with different Degussa P25 content (25, 50, and 100 g/L) coated at one, three, and five dipping times on unglazed ceramic tile

4.0 CONCLUSION

Using the sol-gel process, TiO_2 has been successfully dip-coated with different Degussa P25 content (25, 50, and 100 g/L) on the unglazed ceramic tiles. This study demonstrated that the amount of Degussa P25 content has significant effect on the morphology of the TiO_2 coating, but not the crystalline phase. SEM results on surface and cross section show that lower Degussa P25 content produces TiO_2 patches, and as the Degussa P25 content increases, uniform and continuous layer of coatings can be observed. Using 25 g/L of Degussa P25 in TiO_2 solution, no continuous coating was produced on the ceramics tiles even after five dipping time, while coating with 100 g/L of Degussa P25 is suffer with cracks, making it unsuitable for further applications. The coating thickness, which increases with the dipping time, is also correlated to the Degussa P25 content. This work also exhibited that five dipping of 50 g/L Degussa P25 is needed to form uniform and continuous layer of TiO_2 coating covering the tiles, yielding ~29 μm average thickness of coating. The XRD analysis confirms the presence of anatase and rutile in the coatings regardless of Degussa P25 content. It is therefore proposed that further works on evaluating the TiO_2 antimicrobial performance on ceramic tiles will be utilizing 50 g/L of Degussa P25 content deposited at 5 dipping time.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support received from the Ministry of Higher Education Malaysia and Universiti Teknikal Malaysia Melaka through Grant FRGS/1/2014/TK04/FKP/02/F00215. Special thank is also addressed to the members of SM4GT group for the encouragement offered all these while.

REFERENCES

[1] L.W.R. Sanborn, "The relation of surface contaminant to the transmission of disease", *American Journal of Public Health*, vol. 58, no. 8, pp. 1278-1283, 1963.

[2] S.D. Niederhãusern, M. Bondi and F. Bondioli, "Self-cleaning and antibacteric ceramic tile surface", *International Journal of Applied Ceramic Technology*, vol. 10, no. 6, pp. 949-956, 2013.

[3] S.Q. Sun, B. Sun, W. Zhang and D. Wang, "Preparation and antibacterial activity of Ag-TiO_2 composite by liquid phase deposition (LPD) method", *Bulletin of Materials Science*, vol. 31, no. 1, pp. 61-66, 2008.

[4] M. Yao, J. Chen, C. Zhao and Y. Chen, "Photocatalytic activities of ion doped TiO_2 thin films when prepared on different substrates", *Thin Solid Films*, vol. 517, no. 21, pp. 5994-5999, 2009.

[5] Z.M. Rosli, A.R. Nurhamizah and J.M. Juoi, "The effect of ceramic substrates surface roughness on the deposition of $AgTiO_2$ coating", *Applied Mechanics and Materials*, vol. 699, pp. 9-14 , 2014.

[6] A. Shakeri, D. Yip, M. Badv, S.M. Imani, M. Sanjari and T.F. Didar, "Self-cleaning ceramic tiles produced via stable coating of TiO_2 nanoparticles", *Materials*, vol. 11, no. 6, pp. 1003-1018, 2018.

[7] A.L. da Silva, M. Dondi and D. Hodza, "Self-cleaning ceramic tiles coated with nb_2O_5-doped-TiO_2 nanoparticles ", *Ceramics International*, vol. 43, no. 15, pp. 11986-11991, 2017.

[8] S. Ke, X. Cheng, Q. Wang, Y. Wang and Z. Pan, "Preparation of a photocatalytic $TiO_2/ZnTiO_3$ coating on glazed ceramic tiles", *Ceramics International*, vol. 40, no. 6, pp. 8891-8895, 2014.

[9] P. Sooksaen, N. Saowaros, K. Ngamkaruhasereethorn and A. Pringkasemchai, "Photocatalytic degradation study of titania sol-gel coated on commercial unglazed ceramic tiles", *Key Engineering Materials*, vol. 751, pp. 819-824, 2017.

[10] M. Hasmaliza, H.S. Foo and K. Mohd, "Anatase as antibacterial material in ceramic tiles", *Procedia Chemistry*, vol. 19, pp. 828-834, 2016.

[11] F. Bondioli, R. Taurino and A. M. Ferrari, "Functionalization of ceramic tile surface by sol-gel technique", *Journal of Colloid and Interface Science*, vol. 334, no. 2, pp. 195-201, 2009**.**

[12] T. Sreethawong, S. Ngamsinlapasathian and S. Yoshikawa, "Positive role of incorporating P-25 TiO_2 to mesoporous-assembled tio_2 thin films for improving photocatalytic dye degradation efficiency", *Journal of Colloid and Interface Science*, vol. 430, pp. 184-192, 2014.

[13] J. Kim, A. Sotto, J. Chang, D. Nam, A. Boromand and B.V. Bruggen, "Embedding TiO_2 nanoparticles versus surface coating by layer-by-layer deposition on nanoporous polymeric films", *Microporous and Mesoporous Materials*, vol. 173, pp. 121-128, 2013.

[14] Y. Chen and D.D. Dionysiou, "TiO_2 photocatalytic films on stainless steel: the role of degussa P-25 in modified sol-gel methods", *Applied Catalysis B: Environmental*, vol. 62, no. 3-4, pp. 255-264, 2006.

[15] G. Balasubramanian, D.D. Dionysiou, M.T. Suidan, I. Baudin and J.-M. Laine, "Evaluating the activities of immobilized TiO_2 powder films for the photocatalytic degradation of organic contaminants in water", *Applied Catalysis B: Environmental*, vol. 47, no. 2, pp. 73-84, 2004.

[16] L. Lopez, W.A. Daoud, D. Dutta, B.C. Panther and T.W. Turney, "Effect of substrate on surface morphology and photocatalysis of large-scale TiO_2 films", *Applied Surface Science*, vol. 265, pp. 162-168, 2013.