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ORIGINAL ARTICLE

Effect of Silver Content on the Crystalline Phase and Microstructure of TiO_2 Coating Deposited on Unglazed Ceramics Tile

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ABSTRACT – The synthesis of Ag-TiO_2 coating using $AgNO_3$ precursor is expected to give the properties as pure as Ag nanoparticles. Commonly, high concentration of Ag attributed to agglomeration of silver species and reduction to Ag^0 particles on TiO_2 surface. In contrast, at lower concentration, Ag species exist as AgO, Ag_2O and Ag^0. Hence, the exact amount of Ag, which can effectively control the particle growth and agglomeration, surface area, thermal stability and band gap of the TiO2 coating, are still vague and stated differently. In the present study, the effect of Ag content on the phase transformation and surface morphology of Ag-TiO_2 coating were reported. TiO_2 sol were prepared by incorporating Ag at 2.5, 5 and 7.5 mol % and deposited on unglazed ceramic tiles thru five times dip coating. The deposited Ag-TiO_2 coatings were heat treated at 500 °C for 1 hour soaking time. XRD analyses revealed that the deposited Ag-TiO_2 coating consists of anatase, rutile, Ag_2O and metallic Ag. Almost all the coating surfaces illustrated cracks. Increased Ag content lead to presence of tiny particles on the surfaces and EDX spectrum revealed the presence of Ti, O and metallic Ag particles. However, at the addition of 5 mol % Ag, there was no metallic Ag presence and a dense coating with the lowest thickness of ±11.4μm is observed.

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KEYWORDS
Unglazed ceramics tile; TiO_2coating; Ag-TiO_2 coating; $AgNO_3$ precursor; mol %

INTRODUCTION

Titanium dioxide (TiO_2) semiconductor photocatalyst possessed good physical and chemical stability, low toxicity, high catalytic activity, low cost and ease of production [1]. These good properties of TiO_2 used as an additive in biodiesel fuel [2] and one of the famous coating material in industrial technology. The process of photocatalysis takes place upon the photoexcitation of TiO_2 semiconductor. It can degrade organic pollutants and acts as antimicrobial under UV-light irradiation. The limitation of TiO_2 was due to its wide bandgap (3.2 eV) and fast recombination of photogenerated electron-hole pairs [3, 4]. Thus, to enhance the performance of TiO_2, metal-doped such as Pt, Au, Cu and Ag were believed can improve the photocatalytic activity of TiO_2 by shifting the irradiation wavelength from UV to the visible range region [5]. Silver (Ag) is among the particularly interested doping agent within the field of advanced nanotechnology. Ag doping can eliminate the recombination of electron-hole pairs [6] in the catalyst and Ag promote electron excitation by creating a local electric field [7]. Most importantly, Ag can serve as antibacterial efficiency to several kinds of bacterium, including gram-positive and gram-negative bacteria. The multiple functionalities of silver have led researchers to conduct a brought range of silver doped titania coated sanitary wares, medical devices, food preparation surfaces and air conditioning filters. The use of Ag nanoparticles powder form in coating application on different surfaces has been reported abundantly by previous researchers [8-11]. Ag nanoparticles, however, have high market value and sensitive to light exposure which it turns black in color upon light radiation. Thus, this leads researches producing Ag nanoparticles by synthesising using Ag precursor, for examples AgI, AgCl, AgBr and $AgNO_3$.

Kulczyk-Malecka et al.[12] investigated the diffusion of silver in TiO/Ag/TiO_2 stacks deposited onto soda-lime glass by pulsed DC reactive magnetron sputtering. It found that silver diffuse slightly into the titania layer at the higher annealing temperature. Aazam [6] reported on the study of Ag-TiO_2/multi-walled carbon nanotubes nanocomposites for the photocatalytic degradation of thiophene. The prepared nanocomposites were range from 1-4 wt % of Ag. However, the XRD phase analysis shows only TiO_2 phase, which it concluded that Ag is completely united with TiO_2 matrix since there is no Ag peak observed in the XRD pattern. The entire nanotube surface is uniformly covered with Ag-doped TiO_2 nanoparticles, which even the XRD pattern of the MWCNT is unable to be identified. Gomes et al.[13] reported low amount of 0.1 wt % Ag is effective for the degradation mixture of five parabens (methyl, ethyl, propyl, benzyl paraben and butylparaben) using low transferred ozone dose (TOD). Nickel-based metallic filter with Ag-TiO_2 coating by using electrophoretic deposition revealed the presence of anatase, rutile, AgO, Ag_2O and metallic Ag phases in the composite at high per cent Ag concentration (10 wt % and 15 wt %). While, at low Ag concentration (5 wt %) exhibited anatase, rutile and metallic Ag [14]. In addition, increasing the initial silver nitrate concentration leads to an increase in the degree of crystallinity of samples. This has written by Vakhrushev et al. [15], which stated that the transformation of TiO_2 phase into whether anatase or rutile were accompanying by silver nitrate decomposition processes. Ag−TiO_2 with 0.75−3.5 %

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Ag proposed by Mogal Sajid et al. [16] which synthesised by a single-step sol-gel method presented predominantly anatase phase and the mixed anatase-rutile at 3.0 and 3.5 %. In contrast, Ag peak reported at Ag-TiO_2 samples of 2.5 to 3.5 % only. Ag dopant also promotes the transformation of anatase to rutile at lower calcination temperature. As increasing amount of Ag, the lower the calcination temperature for crystallisation of TiO_2 needed.

The mechanism of enhanced antibacterial effect of Ag-TiO_2 coating with different TiO_2 content deposited on titanium substrate prepared using the electroless plating technique studied by Liua et al. [17]. TiO_2 nanoparticles incorporated well into Ag matrix and promoted Ag ion release, which enhanced the antibacterial effect of Ag-TiO_2 coatings. The micrograph of Ag is homogeneously distributed within the TiO_2 structure. Ag particles are spherical, while TiO_2 particles are in rectangular shape [18]. Ag-doped TiO_2 for improved photocatalytic properties of TiO_2 by doping 0.04 Ag/Ti molar ratio, was studied by Lopez Ortiz et. al [18]. It revealed that silver peak overlapping with anatase phase and confirming the presence of metallic silver in the cubic phase. While the morphology by TEM image consists of agglomerates of ellipsoid particles nanometer size. Ag-doped TiO_2 nanotubes fabricated by ion implantation and anodization studied by Xinggang and Dong [19] has proven that Ag ions can improve the resistance of Ti foil to corrosion. After the implantation, a compact tubular structure of Ag-doped nanolayer generated on the surface of Ti foil without Ag nanoparticles found on the surface. Most reported-on SEM micrograph had revealed that low amount of Ag doped TiO_2 coating are homogenous, dense and cover the substrate completely. For example, Cotolan et al. [20] were using the ratio of 0.0037 Ag, and Kaygusuz (Koizhaiganova), et al. [21] used 0.25, 0.5, 0.75, 1, 2 and 5 % of nAg-TiO_2 that formed on leather samples. Halin et al. [22] investigated Ag/TiO_2 thin film deposited on a glass substrate using the sol-gel spin coating method. The surface morphology of the film porosity increased as increasing Ag content (0.5-1.0 g Ag), large flaky size and cracks throughout the coatings.

However, it is undeniable that the microstructure of the Ag-TiO_2 coating depends on the synthesis method, concentration of doping, types of substrate and heat-treated temperature. Even though a number of researchers have reported on the study of silver doping TiO_2, there still an argument on the exact amount of silver doping titania need to use for an effective reaction of silver doped TiO_2 on ceramics material. The excessive or even using less amount of Ag doping sometimes may cause increases defects in the lattice of TiO_2, resulting in a decrease in photocatalytic activity because the defects work as a recombination centre [23]. Continual research is needed to develop Ag-TiO_2 nanomaterials and preparing methods for coating on other substrates, for example, ceramics tiles (instead of glass as a commonly studied sample). In this present paper, we attempt to report on the effect of Ag content on phase transformation and surface morphology of Ag-TiO_2 deposited on unglazed ceramic tile to understand how Ag gave influence on the crystalline phase formation and its microstructure.

EXPERIMENTAL

The materials use for the preparation of TiO_2 sol were titanium (IV) isopropoxide (TTiP, Sigma Aldrich 97% purity), ethanol (C_2H_5OH, Polyscientific 95% Denatured), hydrochloric acid (Merck 37% purity HCL) and deionized water acts as titanium precursor, solvent, catalyst and hydrolysis medium. At first, two types of solution that were sol A and sol B with a ratio of 4:1 were prepared under room temperature condition. Sol A involved a mixture of 8 ml ethanol and 32 ml deionised water stirred homogeneously for 30 minutes. Then, 0.4 ml HCL was added to the solution. While Sol B consists of 2 ml TTiP and 8 ml ethanol mixed together and stirred vigorously for 30 minutes. Both sol A and sol B are then mixed together with stirring is maintained for 1 hour. 2.5 g Degussa P25 (Sigma Aldrich 99.5 % purity) was mixed into the sol to promote the crystalline growth of TiO_2 sol.

For incorporation of Ag ions, silver nitrate ($AgNO_3$ Merck) of 2.5 mol %, 5 mol %, and 7.5 mol % were carefully dissolved into acetonitrile (CH_3CN, Merck) as reducing agent before it was added into TiO_2 sol respectively. The sol was then left 48 hours in the dark for the ageing process. Substrates of unglazed ceramics tile (20 mm × 10 mm × 4 mm) were cleaned by immersing in acetone followed by ethanol and distilled water for 10 minutes in an ultrasonic bath. After that, the entire cleaned substrates were oven-dried at 110 ˚C for 2 hours. The cleaned substrates were dip-coated into Ag-TiO_2 sol by using a mechanical dip coater machine at 30 mm/min dipping speed and 5 s dwell time. The Ag-TiO_2 coated substrates were then allowed room drying for 3 hours before 30 minutes oven dry at 110 ˚C. The coating procedures are repeated for five times to produce homogenous and high coating quality of Ag-TiO_2 coating. The coated substrates were heat-treated at 500 °C for 1 hour, with a heating rate of 2 °C/min. The crystallinity of the coated ceramics tile measured by GAXRD at 2θ range of 10°-80° with grazing angle of 4° using the PANalytical X'PERT PRO MPD Model PW 3060/60 with Cu Kα of 1.54060 Å. Surface morphology was examined by Scanning Electron Microscope (SEM) (JEOL model JSM-6010PLUS/LV).

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of uncoated and Ag-TiO_2 coating deposited on the unglazed ceramics tile substrate. The uncoated ceramics tile substrate consists of crystalline peaks assigned to the ceramics substrate components such as silica oxide (SiO_2), potassium cyanide (KCN), zirconia oxide (ZrO) and aluminium silicate (Al_2SiO_5). The XRD pattern of TiO_2 coating (without Ag) deposited on unglazed ceramics tile shows the presence of anatase phase (JCPD no. 21-1272) with three highest angles of 25.3° (101), 48.08° (200) and 54.9° (105); while rutile phase (JCPD no. 21-1276) was detected at 27.5 (110) and 35.7° (101) angles. In general, an increase in Ag contents leads to the growth of more crystalline phases. The evident shown by the presence of more crystalline peaks of Ti, O, Ag_2O and Ag in the diffraction patterns of

higher Ag contents (5 mol % and 7.5 mol% Ag –TiO_2). Vakhrushev et al. [15] had reported the same relationship between Ag concentration and degree of crystallinity. In their work, an initial increase of $AgNO_3$ concentration shows an increment in the degree of crystallinity in the samples.

It can also be seen, in Figure 1 that Ag-TiO_2 with 2.5 mol % shows the presence of tetragonal anatase identified at an angle of 25.3° (101) and Ag_2O (JCPD no. 41-1104) at angle 26.6 (110). For the 5 mol % Ag content, anatase presence was identified at three highest peaks of 25.3° (101), 48.08° (200) and 54.9° (105); while rutile peaks were detected at 2θ angle of 27.4° (110) and 69.7° (112) and, Ag_2O ws identified with a peak observed at angle 26.6° (110). A similar peak of anatase, rutile and Ag_2O present in 7.5 mol % Ag-TiO_2 coating. However, at 7.5 mol % Ag-TiO_2 coating, peaks of metallic Ag (JCPD 41-1402) were identified at angle 76.8° (201) and 45.3° (103). It should be noted that the metallic Ag peak was not identified at 2.5 mol % and 5 mol % Ag-TiO_2 coating. This indicates that almost all Ag added has been doped well into anatase lattice at low concentration of Ag addition. A well doped Ag into TiO_2 is an important criterion for a good photocatalytic activity [24]. Similarly, the presence of anatase and rutile were also reported by Noberi et al. [14] in Ag-TiO_2 coating nanocomposite particles. Noberi et al. [14] had also stated that the increasing amount of Ag at 10 wt.% and 15 wt.% in the composite contributed to the formation of AgO and Ag_2O phases. This is also observed in our work where the presence of Ag_2O is observed at 2.5, 5 and 7.5 mol % Ag-TiO_2 coating.

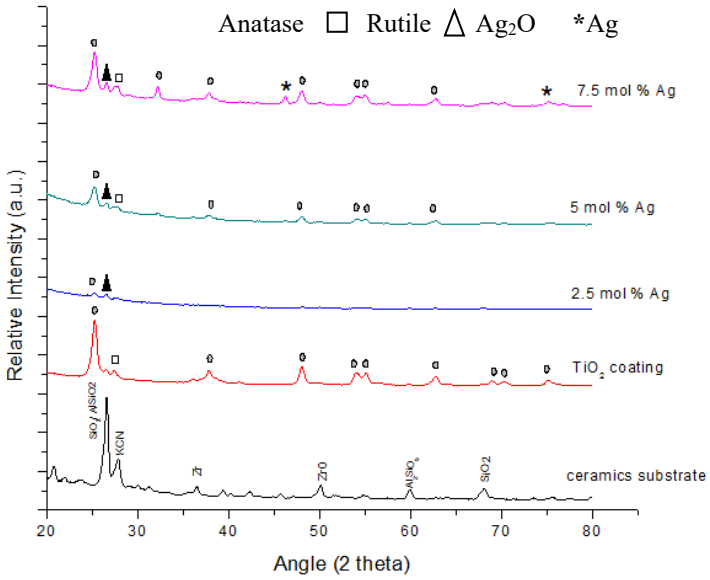


Figure 1: XRD pattern of Ag-TiO2 coated on unglazed ceramic tile substrates.

Table 1 illustrated the surface morphology and cross-section microstructure at different amount of Ag in TiO_2 coating on unglazed ceramic tiles substrate. The surface morphology of Ag-TiO_2 coating shows cracks with dry mud like surfaces. Similar microstructure (a mud-crack shaped/dry like river bed-like layer) was also reported by Demircia et al. [25] in the undoped and Ag-doped TiO2 films on Si substrates by sol-gel method and heat-treated at 500 °C. However, in work reported by Halin et al. [22] a large flaky size cracks of Ag/TiO_2 thin film were observed when the Ag/TiO_2 deposited on a glass substrate via sol-gel spin coating method and heat-treated at 450 ˚C.

It can be seen that, at 2.5 mol % Ag, fewer cracks are observed compared to 5 mol % and 7.5 mol % Ag content. Meanwhile, at the higher Ag content of 5 mol % and 7.5 mol %, the microstructure also revealed the presence of tiny particles (later, identified as Ag particle during EDX mapping), which is randomly distributed on the surfaces. This could be due to the migration of Ag^+ ions into TiO_2 surface during crystallisation, hence contributed to the formation of Ag and/or Ag_2O [25]. It is also observed that at the highest amount of Ag (7.5 mol%), the surface of Ag-TiO_2 coating became more intense with the presence of more and smaller cracks. This could be due to the increasing amount of Ag, which attributed to Ag aggregations in the form of particles. Hence, lead to the formation of many but smaller cracks. The surface cracking may occur due to the excessive water loss in the substrate during the calcination process.

The SEM cross-section of Ag-TiO_2 coating shows that the thickness of the deposited coating varied respectively. Ag-TiO_2 coating thickness of 2.5 mol %, 5 mol % and 7.5 mol % were ±16.5µm, ±11.4µm and ±15.3µm respectively. The difference in thickness could be ascribed to the different amount of colloidal TiO_2 retained on the substrate before calcination [26]. However, the 5 mol % Ag-TiO2 coating exhibited the lowest thickness indicating that the amount of Ag was incorporated well within the TiO_2 compared to 2.5 mol % and 7.5 mol %. The 5 mol % amount of Ag incorporated well with TiO_2 coating. This suggests that the Ag had initially diffused into the TiO_2 coating later excessive Ag lead to the formation of Ag_2O revealed in XRD pattern analyses.

SEM/EDX mapping of Ag-TiO_2 coating presented in Table 2 illustrated the presence of Ti, O and Ag on the coating surfaces. The EDX spectra revealed the presence of Ti, O and Ag signals at 4.508, 0.525 and 2.983 keV similar reported by Tijani et al. [27]. The presence of Ag was seen, overlapping with Ti and O spots. Hence, this can be deduced that the presence Ag could be in the form of AgO, Ag_2O or Ag as identified in XRD results. That is due to the migration of Ag^+ ions from the volume of TiO_2 grains to their surfaces and further reaching the TiO_2 film surface. The presence of AgO,

Ag_2O and Ag could due to the larger radius of Ag^+ (ca.126 pm) compared to Ti^{4+}(ca.68 pm) thus, restricted more diffusion of Ag into the lattice of anatase phase [28]. Increased Ag content in the range of 2.5 mol% to 7.5 mol % had revealed by an increased in weight % and atomic % of EDX spectrum respectively. The order of increasing atomic percentage of metallic Ag is 2.5 < 5 < 7.5 mol % (0.44% <0.88 % < 1.15%).

Table 1: Scanning electron microscopy and cross-section images of Ag-TiO_2 coating on unglazed ceramic tiles.

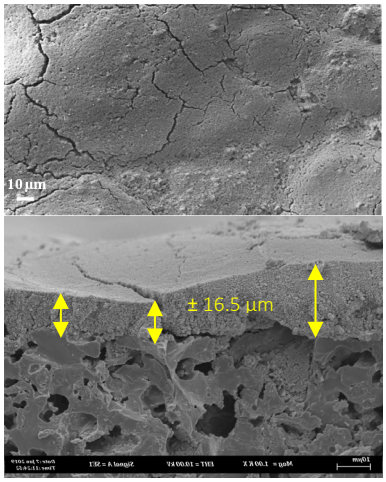
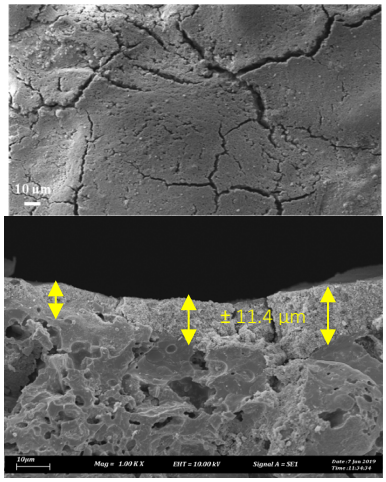
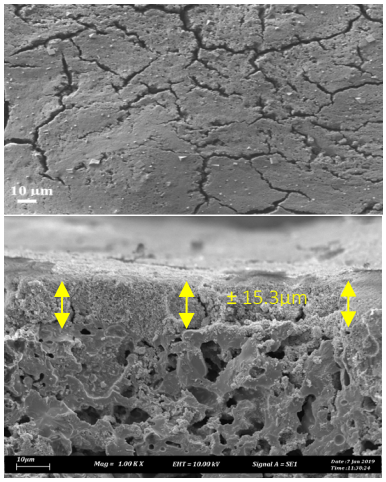
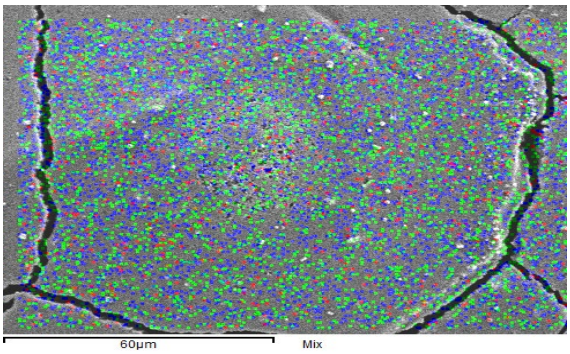
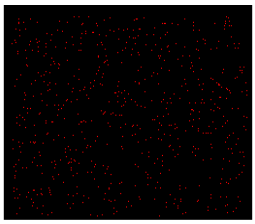
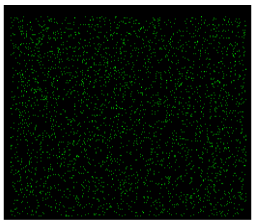
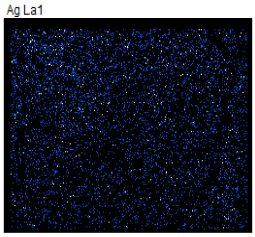
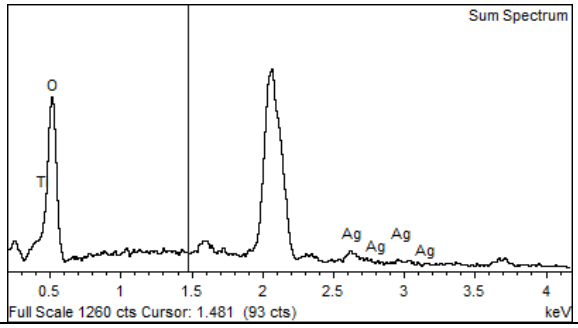
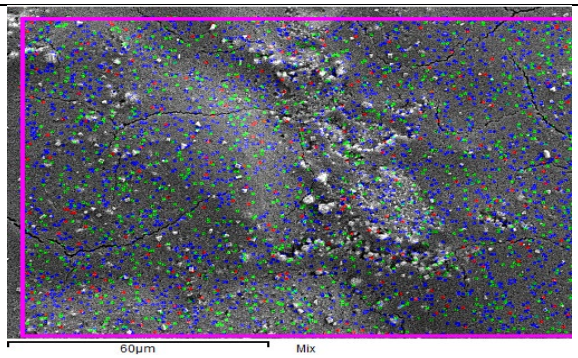
Amount of Ag %		
2.5 mol %	5 mol %	7.5 mol %
		

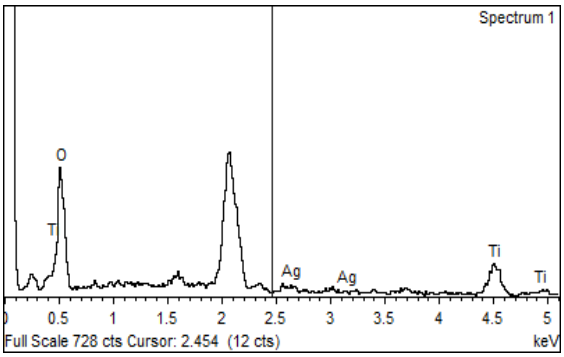
Table 2: SEM/EDX spectra of Ag-TiO_2 coating deposited on unglazed ceramics tiles.

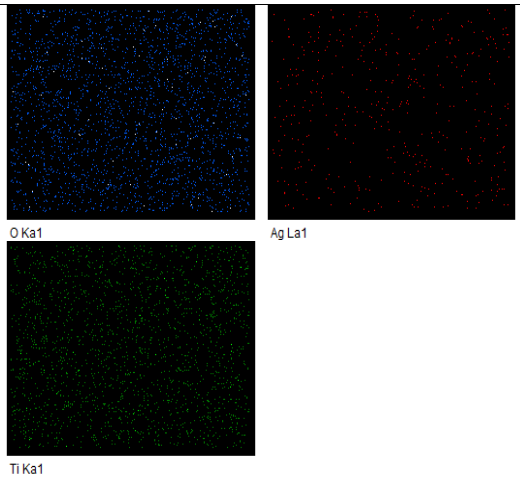
SEM/EDX spectra	Mapping
 (a)	  
	

Element	wt. %	atomic %
O K	56.39	79.91
Ti K	41.5	19.64
Ag L	2.11	0.44

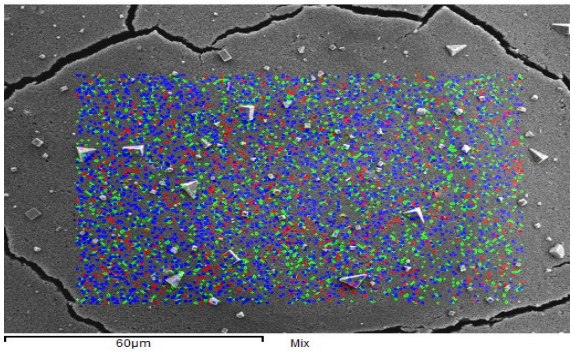


(b)

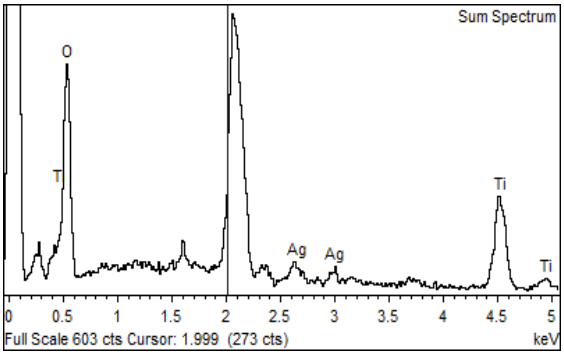


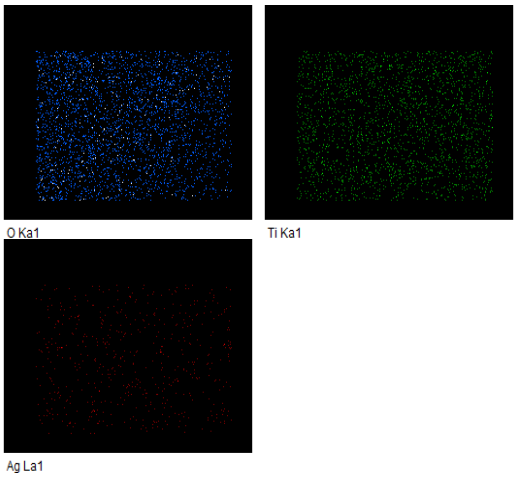


Element	wt. %	atomic %
O K	59.39	82.31
Ti K	36.31	16.81
Ag L	4.3	0.88



(c)





Element	wt %	atomic %
O K	51.32	77.03
Ti K	43.53	21.82
Ag L	5.15	1.15

CONCLUSION

In this work, the effect of silver content on the crystalline phase and microstructure of TiO_2 coating deposited on unglazed ceramics tiles was studied by sol-gel dip-coating technique. The Ag-TiO_2 coating consists of anatase, rutile and Ag_2O phase revealed by XRD analysis and only at 7.5 mol % Ag content in TiO_2 exhibited metallic Ag. As the mol % Ag increased, the crystallinity of the Ag-TiO_2 coated unglazed tiles also increased. Surface morphology of the coated ceramics tile illustrated dry mud like surfaces. Increasing Ag content contributed to the formation of many small cracks. The microstructure of higher Ag per cent of 5 mol % and 7.5 mol %, illustrated tiny particles on the surfaces. The 5 mol% Ag coating had a smoother surface with cracks compared to 2.5 mol % and 7.5 mol % Ag. In addition, the cross-section surfaces of 5 mol % Ag-TiO_2 coating had the lowest thickness compared to 2.5 mol % and 7.5 mol %. SEM/EDX mapping

had revealed the presence of Ti, O, and Ag distributed randomly on the surfaces and Ag overlapped with Ti and O spots. The SEM/EDX atomic % and wt. % of Ag also increased with increased Ag mol % respectively. Further study will involve photocatalytic performances and evaluation of antimicrobial test.

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