



Synthesis and effectiveness of Cu-infused TiO_2 - SiO_2 based self-cleaning and antibacterial thin-films coating on ceramic tiles

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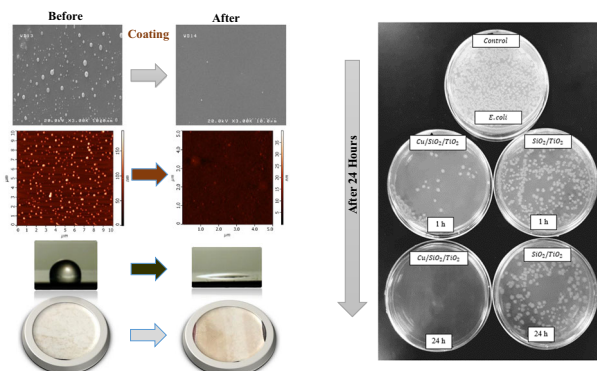
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Abstract

The aim of this research is the study of self-cleaning and antibacterial activity of SiO_2/TiO_2 thinfilm contains copper in it on ordinary ceramic tiles substrates. Four solutions using the sol-gel method with various volume ratio of Si/Ti precursors (i.e., 1/9, 2/8, 3/7, and 4/6) were prepared. Then, they were deposited on the ceramic tiles via the dip-coating technique and heated through thermal treatment at 650° for an hour. The XRD results show anatase and rutile structures are the main phases in the composite films of $Cu/SiO_2/TiO_2$ coatings. The rms roughness obtained by AFM for ceramic tile was initially ~ 20 nm, which reduced to < 2 nm after deposition. The SEM images, depicted a uniform and crack-free thin-film coating with a thickness < 30 nm. Stearic acid coating was applied on the samples as a pollution and was completely removed after being subjected to 24 hrs of UV illumination ($400\text{--}800 \mu W/cm^2$) in an environment with low and variable humidity (21–37 RH). About 76° reduction of water contact angle (WCA) was observed during photocatalytic test for the 1/9 (optimum) sample. In addition, a 33° decrease in WCA was measured in the light-induced hydrophilicity experiment. The 1/9 sample that reacted mostly under UV illumination in both photocatalytic and light-induced hydrophilicity was concluded as the optimum one. To improve the antibacterial property of the coating, copper nitrate trihydrate was added to the 1/9 solution. Moreover, antibacterial test was performed through “viable cell count” method by *E. coli* bacteria. The results of antibacterial test showed a 99% and 99.99% reduction in the number of *E. coli* bacteria during 1 and 24 hrs intervals, respectively. This is, surprisingly, to the best of our knowledge, the same as the results that can be obtained using silver nanoparticles.

Graphical abstract



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Keywords Self-Cleaning · Antibacterial Coating · Copper nitrate trihydrate · TiO_2 - SiO_2 thin films · Photocatalytic activity

Highlights

- Self-cleaning take place before 24 hours under a very weak UV illumination.
- Elimination of 99% and 99.99% of E. coli bacteria within 1 and 24 hours of using Cu instead of Ag.
- Self-clean and antibacterial thin-film coating which is commercially affordable rather than using detergent materials.
- No visible changes have been observed in the design or color of ceramic tiles.
- Applicable to use in different environments with variable climate conditions.

1 Introduction

Today, smart and advanced functional coatings are being extensively used in the areas of marine, automobile manufacture, environmental tools, and building materials. The use of surfaces with special wettability, like self-cleaning and anti-bacterial surfaces, has become more common in both industrial and academic research fields. Since cleaning the different surfaces in a building requires a considerable amount of energy, time, detergents, and financial resources, one is led to find an alternative self-cleaning for eliminating the pollution on these surfaces [1]. Furthermore, there is a big competition among companies to produce highly efficient anti-bacterial surfaces like ceramic tiles. The use of these surfaces is essential, especially for use in schools, restaurants, industrial facilities, public places, playrooms, and particularly hospitals [2–4].

One way to induce the self-cleaning property is to use photocatalyst materials. The production of photocatalytically active building materials that are activated by UV radiation makes it possible to obtain a self-cleaning and self-sterilizing surface that can degrade some organic pollutants in the surrounding. Among the photocatalytic materials, we benefit the optical properties of TiO_2 nanoparticles. TiO_2 is one of the most interesting ones that has been widely used as a target for various microorganisms. It is chemically stable, non-toxic, low cost, and most importantly photo stable [5], high photoactive, broad-spectrum active, and antibacterial, which makes it an ideal photocatalyst. Titanium dioxide has a variety of crystal phases such as anatase, rutile, and brookite. Among these crystal phases, the anatase and rutile phases exhibit a high photocatalytic activity [6, 7].

Even though the role of pure titanium dioxide in textiles is now known to everyone, it is suggested to add silicon dioxide to the surface coating formulation in order to improve the efficiency of titanium dioxide photocatalytic property and surface hydrophilicity. Silica plays an important role; increasing the surface area close to titanium dioxide, and acidity of the surface [8]. One strategy to avoid the release of TiO_2 from the surface to the environment is to fix the photocatalyst in a SiO_2 matrix [9, 10]. It is found that

after adding SiO_2 , the just produced water contact angle (WCA) is small, and it is also very hydrophilic in the dark. The $\text{SiO}_2/\text{TiO}_2$ composite film has been found not only to improve hydrophilicity but also photocatalytic activity [11]. These characteristics, i.e., bonding role, acidity, and enhance photocatalytic behavior makes the SiO_2 preferable for our study [8, 12, 13].

It is well known that metal ions such as silver [8, 14, 15], copper [16–20], and zinc have antibacterial property, a phenomenon known as the oligodynamic effect. If these metals are combined with the TiO_2 film on the glazing sanitary ware, it would be possible to develop sanitary ware which has photocatalysts that produce sterilization under ultraviolet light and the metal ions have antibacterial effects even in the dark [21, 22].

Silver nanoparticles either interact with the cell membrane or enter the cell, cause the cell to die. The analogous mechanism for copper nanoparticles is yet unknown, however, it is believed by some to be similar to that of silver [20]. Copper is one of the trace elements, and also vital for living microorganisms. It is a constituent of enzymes that are involved in processes such as electron transport and the redox cycle. The concentration of copper generally found in microorganisms is in the millimolar range; a higher concentration of free ion Cu^{2+} can be toxic for cells, although its toxicity is reduced when combined with organic compounds. Copper disrupts amino acid biosynthesis pathways by producing reactive oxygen species (such as H_2O_2). H_2O_2 disrupts the amino acid biosynthetic pathways by damaging the iron-sulfur enzymes, which happen to be the primary intracellular targets of copper's toxicity, and the DNA by generating free radicals [20]. In this work, we follow an approach to obtain a self-clean and antibacterial coating on ordinary ceramic tiles substrates. To the best of our knowledge, copper has not been shown 99.99% antibacterial property in the self-cleaning coating on ceramic tiles substrates. This value is reported for silver; therefore, the use of copper instead of silver was investigated in this work. Furthermore, removing the contaminations on the surface in weak UV illumination and low humidity conditions, are the other goals.

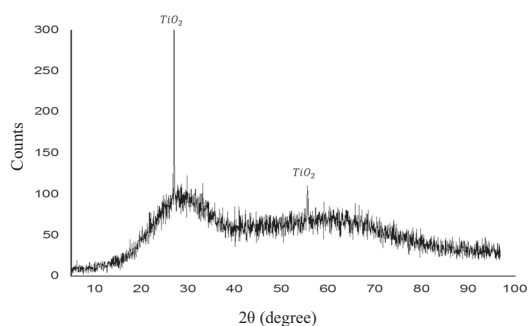


Fig. 1 X-ray diffraction pattern of 1/9 ($\text{SiO}_2/\text{TiO}_2$) thin film sample

2 Experimental details

Ordinary ceramic tiles were chosen as the substrates and were cleaned using water, acetic acid, and ethanol, respectively. The $\text{TiO}_2/\text{SiO}_2$ composite films were made using the sol-gel method. 1 ml of Tetraethylorthosilicate (TEOS) in 6 ml ethanol is hydrolyzed for 1 h containing 0.01 ml HCl, as TEOS precursor solution. Then, 3 ml Titanium Butoxide was dissolved in a 17 ml ethanol solution. Next, after mixing TEOS with varied amounts of Titanium butoxide precursor solution, additional amounts of HCl catalyst were added (Titanium Butoxide/HCl = 1:0.5 in volume ratio). Therefore, four different solutions were obtained with various volume ratio, i.e., 1/9, 2/8, 3/7, and 4/6 [11]. Then, using the dip-coating method, the substrates were coated and heat treated at 650° in a cubic furnace for an hour.

To study morphology, composition, thickness, and crystal phase in the structures, methods such as AFM (NT-MDT AFM), SEM, cross-section SEM (SEM, Hitachi S4460), and XRD (XRD, Philips, X'Pert) were used. To determine hydrophilicity and photocatalytic activity, the WCA of the surfaces were measured. After employing different experiments, optimum solution (i.e., 1/9 sample) was chosen to add the antibacterial material.

To investigate the light-induced hydrophilicity and photocatalytic activity, the samples were placed under a UVA lamp ($400\text{--}800\ \mu\text{W}/\text{cm}^2$, 365 nm wavelength) in a low humid environment ($\sim 21\text{--}37$ RH) for 24 hrs. The WCA was taken three times every 2 h and monitored after 24 hrs illumination. The wettability of a solid surface is measured by the contact angle (CA) between the edge of the distilled water droplet and the surface below it, that is denoted by θ [23, 24].

To study the photocatalytic activity, the obtained coatings were covered by stearic acid using the spin-coating technique, and were kept in the normal lab conditions for 24 hours, so that the stearic acid was fully dried. The CA of the water droplet was measured at two different stages in the sample: before applying the stearic acid and during the UV irradiation. The CA of samples before applying the

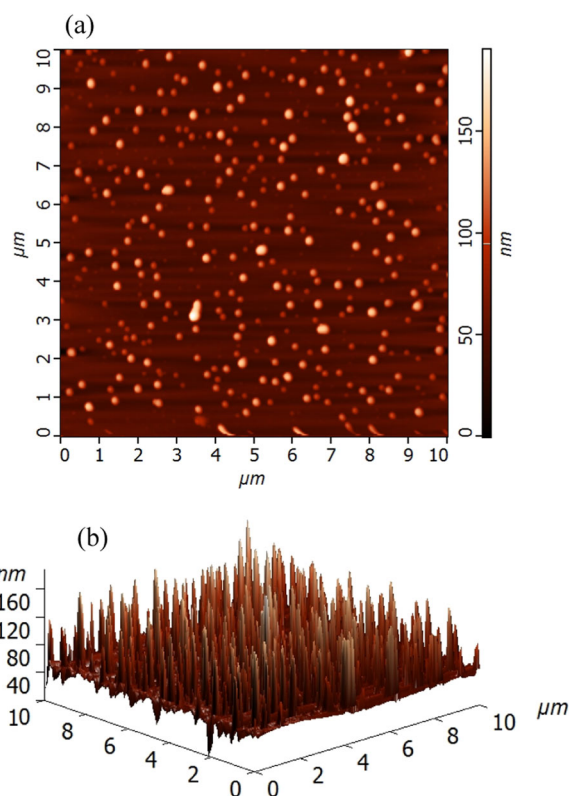


Fig. 2 a 2D and (b) 3D AFM images of control ceramic tile sample

contamination (stearic acid), and after covering with stearic acid are denoted by θ_0 and θ , respectively. Then, the samples were subjected to UV beam and monitored up to 24 hrs.

Finally, the antibacterial activity of the 1/9 ($\text{Cu}/\text{SiO}_2/\text{TiO}_2$) sample was determined by a viable cell count experiment, performed on one pathogen, namely *Escherichia coli*, which represents a gram-negative bacteria. In fact, *E. coli* plays a role in the corruption process, but if found excessively in the human body, it can cause diarrhea and fever [2]. During the test 10^5 CFU/ml of *E. coli* bacteria was applied on the 1/9 ($\text{SiO}_2/\text{TiO}_2$), 1/9 ($\text{Cu}/\text{SiO}_2/\text{TiO}_2$), and also control sample (i.e., a bare ceramic tile). Afterward, bacteria were gathered from the samples and control surface after 1 and 24 hrs. To investigate the adherence of coating to the ceramic tiles' substrate, a common tape test was performed to study the peeling of the coating.

3 Results and discussion

As mentioned in the introduction, one way to obtain self-cleaning surfaces is to benefit from the photocatalytic activity of TiO_2 . Therefore, an X-ray diffraction pattern was obtained to ascertain of existing the main crystal phases of TiO_2 in the coatings. XRD analysis of 1/9 ($\text{SiO}_2/\text{TiO}_2$)

Fig. 3 a 2D and (b) 3D AFM images of various volume ratio of $\text{SiO}_2/\text{TiO}_2$ samples

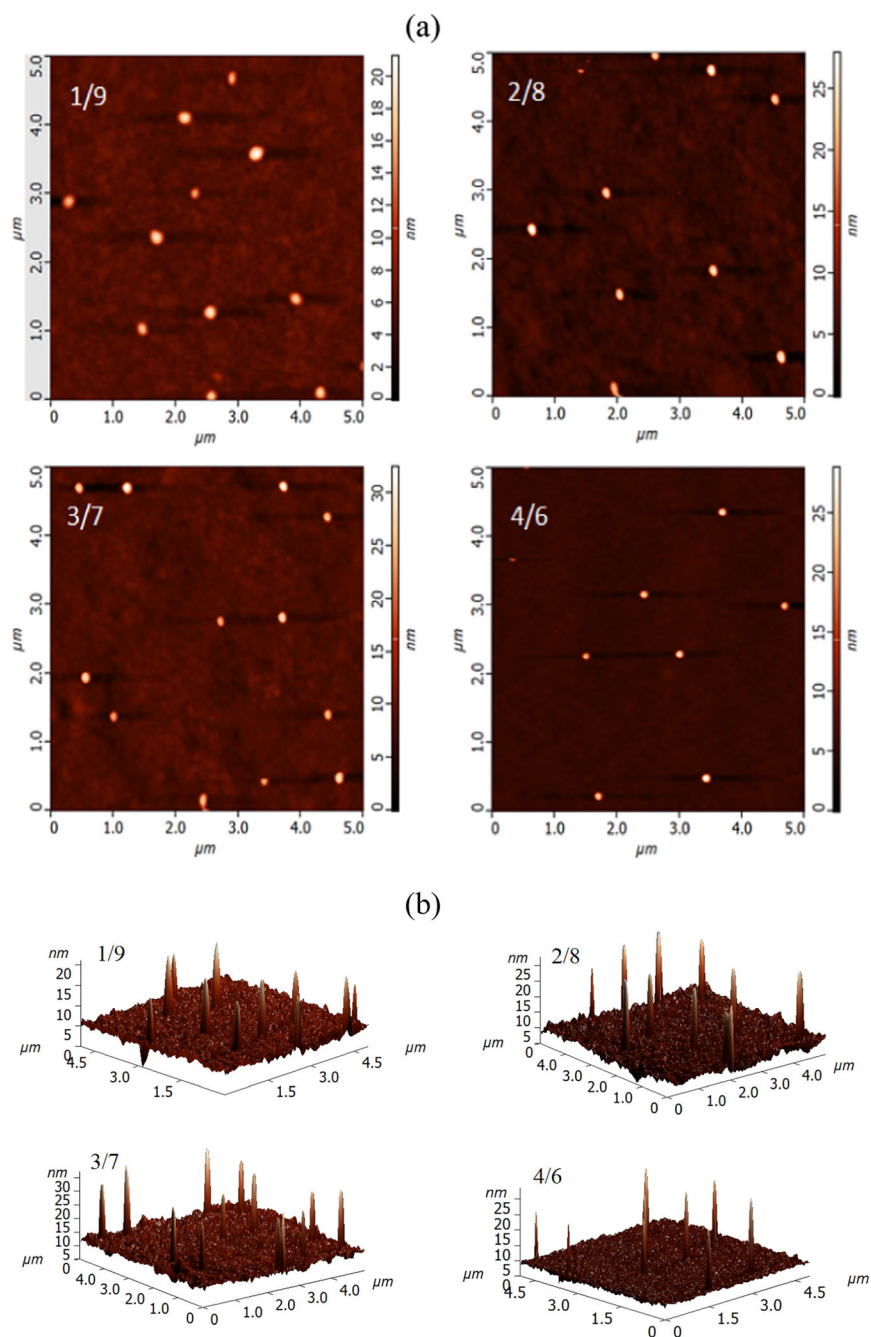


Table 1 The rms roughness of control, four various volume ratio of $\text{SiO}_2/\text{TiO}_2$, and $\text{Cu}/\text{SiO}_2/\text{TiO}_2$ coated samples

Sample	rms roughness (nm)
Control (Uncoated tile)	20
1/9 ($\text{SiO}_2/\text{TiO}_2$)	<2
2/8 ($\text{SiO}_2/\text{TiO}_2$)	<2
3/7 ($\text{SiO}_2/\text{TiO}_2$)	<2
4/6 ($\text{SiO}_2/\text{TiO}_2$)	<2
1/9 ($\text{Cu}/\text{SiO}_2/\text{TiO}_2$)	<2

sample is chosen as a representative, which is depicted in Fig. 1. It shows a big amorphous hump and two other sharp peaks. The amorphous hump indicates the SiO_2 presence as the main material exists in the soil of the ceramic tile. The sharp peaks of TiO_2 signify formation of well-developed crystals in the films that are corresponding to rutile and anatase phases, respectively. Therefore, as the presence of these crystal structures of TiO_2 is verified, photocatalytic activity is expected [6, 7, 25].

The other main item of making a surface easy to clean, is to profit the hydrophilic surface. Therefore, changes of the

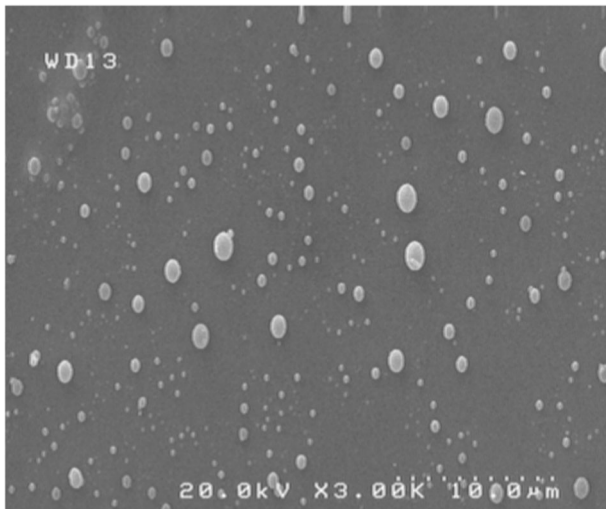


Fig. 4 SEM image of control sample

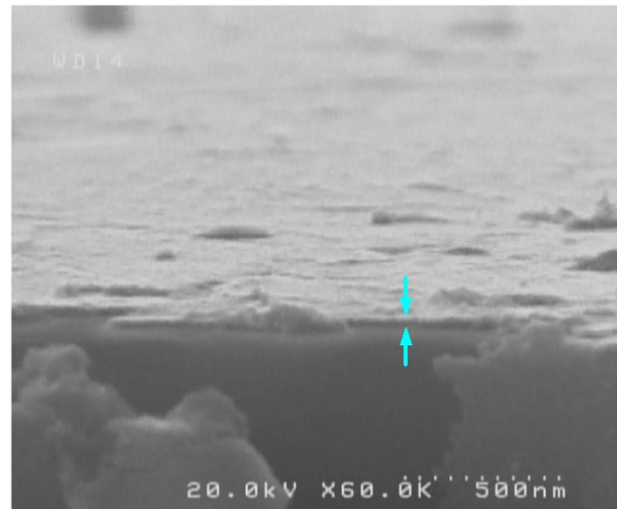


Fig. 6 Cross-section SEM image of 1/9 ($\text{SiO}_2/\text{TiO}_2$) sample

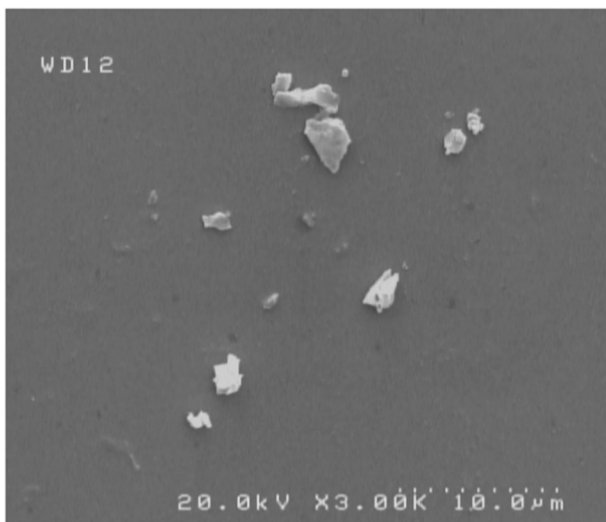


Fig. 5 SEM image of 1/9 ($\text{SiO}_2/\text{TiO}_2$) sample

surface roughness before and after coating on the ceramic tile substrates were monitored. AFM images of the control sample are depicted in both 2D and 3D formats, in Fig. 2. The rms roughness of control sample was found to be about 20 nm. AFM illustrations of four different coatings of $\text{SiO}_2/\text{TiO}_2$ in 1/9, 2/8, 3/7, and 4/6 ratios in 2D and 3D images are shown in Fig. 3. Their rms roughness were measured less than or equal to 2 nm; it indicates that the surface roughness was decreased after deposition (Table 1).

Due to the residue [26, 27] of ceramic tile some spherical particles has been formed during the ceramic production, that has shown in the SEM image of Fig. 4. The SEM image of 1/9 ($\text{SiO}_2/\text{TiO}_2$) sample as evident is shown in Fig. 5. The number of residue (impurities) decreased after coating the control sample with a self-cleaning layer, drastically. The dark color is the obtained thin-film coating and the presence

Table 2 The contact angle reduction in light-induced hydrophilicity test for four various volume ratio of $\text{SiO}_2/\text{TiO}_2$, and $\text{Cu}/\text{SiO}_2/\text{TiO}_2$ coated samples

Sample	$\Delta\theta$ (degree)
1/9 ($\text{SiO}_2/\text{TiO}_2$)	33
2/8 ($\text{SiO}_2/\text{TiO}_2$)	32
3/7 ($\text{SiO}_2/\text{TiO}_2$)	27
4/6 ($\text{SiO}_2/\text{TiO}_2$)	29
1/9 ($\text{Cu}/\text{SiO}_2/\text{TiO}_2$)	29

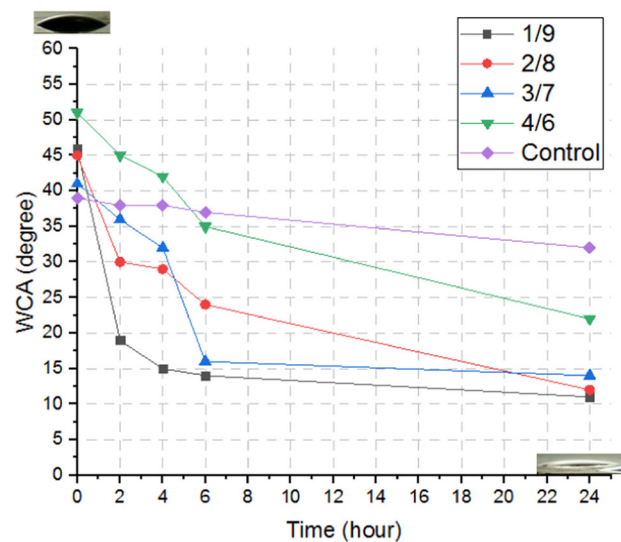


Fig. 7 Water contact angle measurements results for samples with various volume ratio of $\text{SiO}_2/\text{TiO}_2$ and control one in light-induced hydrophilicity

of white points on the surface of 1/9 sample could be agglomerations of Ti particles [2]. According the obtained cross-section SEM image, thickness of the self-clean

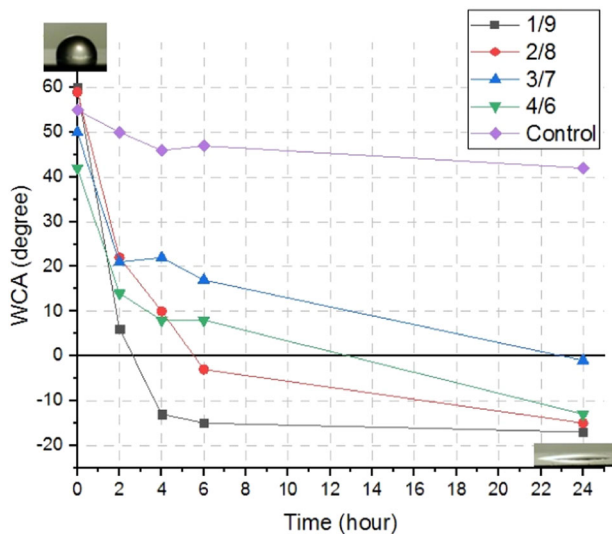


Fig. 8 Water contact angle measurements results for samples with various volume ratio of $\text{SiO}_2/\text{TiO}_2$ and control one in photocatalytic activity

Table 3 The contact angle reduction in photocatalytic activity for four various volume ratio of $\text{SiO}_2/\text{TiO}_2$, and $\text{Cu}/\text{SiO}_2/\text{TiO}_2$ coated samples

Sample	$\Delta\theta$ (degree)
1/9 ($\text{SiO}_2/\text{TiO}_2$)	76
2/8 ($\text{SiO}_2/\text{TiO}_2$)	74
3/7 ($\text{SiO}_2/\text{TiO}_2$)	51
4/6 ($\text{SiO}_2/\text{TiO}_2$)	55
1/9 ($\text{Cu}/\text{SiO}_2/\text{TiO}_2$)	71

coating for all samples were measured smaller than 30 nm (Fig. 6).

In agreement with the self-cleaning of the surface, light-induced hydrophilicity experiment was performed. The WCA of the control sample was measured 39° , while immediately after applying the self-cleaning coating, it became smaller than 10° (a surface with $\text{CA} < 90^\circ$ is considered as hydrophilic, and has a strong adhesion to water droplet, which spreads and wets a large surface area, if the droplet lies almost flat and the CA is less than about 20 degrees, the surface is recognized as superhydrophilic. While the one with $\text{CA} > 90^\circ$ is termed hydrophobic that is highly water-repellent [23, 28–30]). Then, WCA was increased to near $\sim 40\text{--}50^\circ$ after 2 days of remaining in lab. conditions and without any sort of protection. WCA of 1/9 ($\text{SiO}_2/\text{TiO}_2$) sample reduced regularly from $\sim 46^\circ$ at the beginning of the experiment to $\sim 13^\circ$ after 24 hrs UV light irradiation. The obtained values for all other samples are reported in Table 2 and Fig. 7. Obviously, reduction of WCA corresponding to 1/9 ($\text{SiO}_2/\text{TiO}_2$) sample is the most one in comparison with the other samples. This reduction of angle to $< 15^\circ$ is a sign of hydrophilicity or almost superhydrophilicity of the surface. As the roughness of the

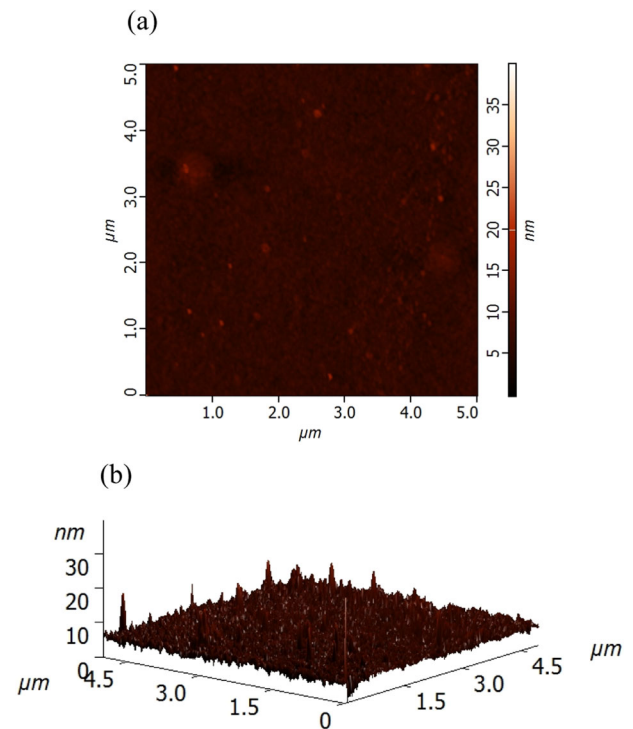


Fig. 9 a 2D and (b) 3D AFM images of the 1/9 ($\text{Cu}/\text{SiO}_2/\text{TiO}_2$) sample

surface dropped, the surface's hydrophilicity increased, and the surface became self-cleaning by sheeting water droplet, reducing the CAs to very low values under irradiation, and then dirt will be washed away.

Hydrophilic coatings have a feature when exposed to light they are able to break down dirt, a process known as 'photocatalysis,' though it is the coating, not the incident light; that functions as a catalyst and cause the surface to be clean by eliminating the dirt. To study the photocatalytic activity of samples, CA of distilled water droplet before and after stearic acid coating were measured. According to Fig. 8, when TiO_2 is activated by UV light can decompose the stearic acid in 5 h. According the diagram, at the end of experiment, the WCA of samples had a remarkable reduction compared to the beginning. This reduction indicates the elimination of the surface pollution (here, stearic acid) during the first 5 h of a weak UV illumination (Table 3). Moreover, after 5 h the decrease in the WCA is a sign of light-induced hydrophilicity. A negative value of the WCA means that the measured value at the end of the test (i.e., after the stearic acid elimination) is less than the initial one. It was predicted that after 5 h, the light-induced hydrophilicity should progress.

Four solutions with various volume ratio of Si/Ti, were prepared to study the effect of silicon on hydrophilicity and photocatalytic activity [11]. As mentioned previously, the reduction in the rms roughness was the same for the samples; they all showed a favorable performance in both

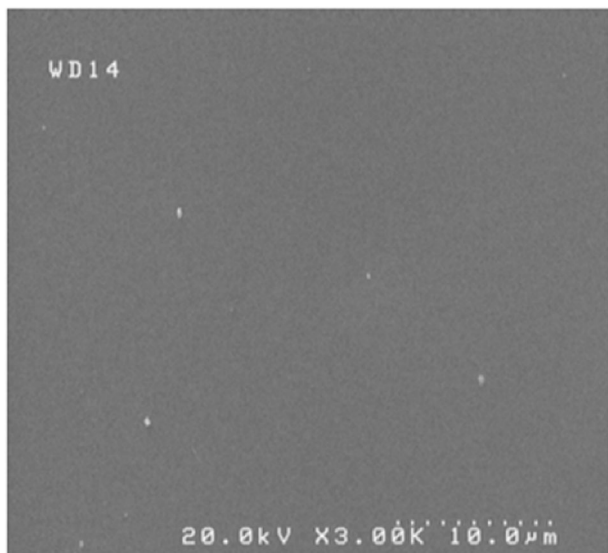


Fig. 10 SEM image of the 1/9 ($\text{Cu/SiO}_2/\text{TiO}_2$) sample

photocatalytic activity and hydrophilicity tests. However, the best efficiency was acquired for the 1/9 ($\text{SiO}_2/\text{TiO}_2$) sample (Tables 2 and 3). Therefore, it was chosen for adding the antibacterial property to this solution and the other solutions were discarded.

Copper nitrate trihydrate was added to the solution, then, the previously mentioned analyses were repeated. As pointed out by some researches [31–33], the presence of copper oxide leads to super-hydrophobicity. However, one has to ensure that adding copper nitrate trihydrate does not change the functionality of the surface. So, after adding copper nitrate trihydrate to the 1/9 ($\text{SiO}_2/\text{TiO}_2$) solution, the existence of crystalline structures of anatase and rutile TiO_2 was evaluated again. It confirms phase search match analyses of XRD, exactly as it was for 1/9 solution without copper. According the AFM images, the rms roughness has not been changed compared to the self-clean coatings that were already obtained; it was measured <2 nm (Table 1 and Fig. 9). Moreover, one observes a crack-free, uniform, and homogeneous surface in the SEM pictures (Fig. 10), which means that the presence of copper does not have a visible effect on the surface morphology.

Photocatalytic activity and light-induced hydrophilicity of 1/9 ($\text{Cu/SiO}_2/\text{TiO}_2$) sample, with CA reduction to smaller than 15° was verified. Afterward, the viable cell count was applied on the samples. According the results of the viable cell count test shown in Table 4, the sample is capable of removing the *E. coli* bacteria. It was determined through viable cell count that the coating containing 0.1wt. % ($\text{Cu}(\text{NO}_3)_3$) (i.e., in $\text{Cu/SiO}_2/\text{TiO}_2$ sample) can eliminate 99% of *E. coli* bacteria in 1 h, and 99.99% after 24 hrs. On the contrary, for a sample devoid of copper 1/9 ($\text{SiO}_2/\text{TiO}_2$), the reduction percentage is 10% in 1 h, and 50% during 24 hrs (Fig. 11). It should be noted that this measurement was

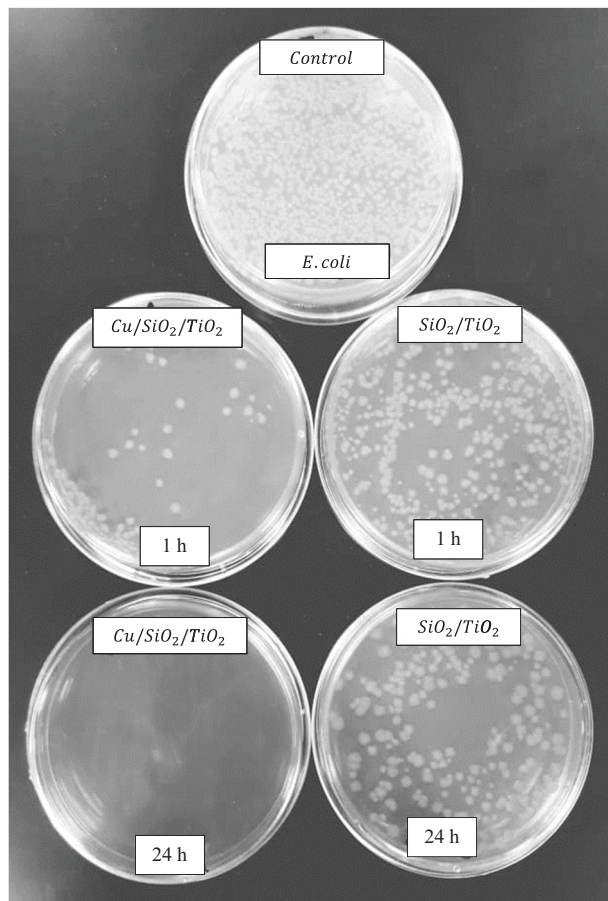


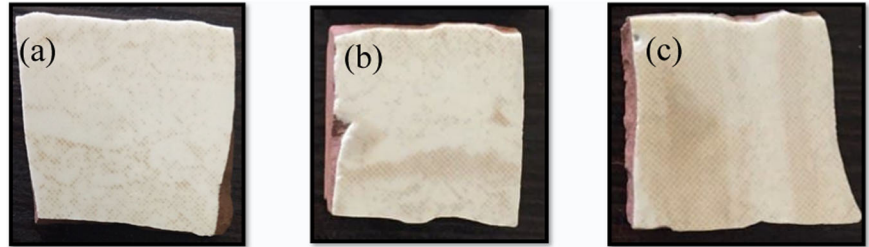
Fig. 11 Antibacterial activity of $\text{Cu/SiO}_2/\text{TiO}_2$ (left), $\text{SiO}_2/\text{TiO}_2$ (right), and control (top) sample

performed on a control sample with no self-cleaning and antibacterial property (see Table 4). The elimination of bacteria in the sample containing only $\text{SiO}_2/\text{TiO}_2$ is due to the presence of TiO_2 in the coating. Bianchi et al. [34], have applied the method of the present work for silver and obtained a 99.99% reduction of *E. coli* after 24 hrs, which is the same as our results using the copper and what TOTO Ltd. obtained for its product using silver [22]. Hirai et al. [35] have obtained the same value of antibacterial effect, however, without using TiO_2 . It is worth mentioning that while the antibacterial property of silver has been known for many years, obtaining such a high reduction using copper is unprecedented. As shown in this study, copper, when combined with $\text{SiO}_2/\text{TiO}_2$, has an antibacterial property similar to that of silver [11, 12, 16].

In the adherence experiment, after detaching the tape, no visible peeling could be observed by naked eyes, the coating was not removed and had sustained its property. Such an adhesion makes these surfaces a viable candidate for walls, interior, and exterior surfaces. In addition, the original design of the ceramic tiles remained intact as in Fig. 12. It shows that the substrate after and before the coating had

Table 4 The viable cell count results of self-cleaning and antibacterial properties of coated ceramic tiles

Measured item	Time (h)	Viable count (CFU/ml)	Reduction percentage (%)	Logarithmic reduction (\log_{10})
Control (Uncoated tile)	–	10^5	–	–
SiO_2/TiO_2	1	9×10^4	10	0.046
SiO_2/TiO_2	24	5×10^4	50	0.301
$Cu/SiO_2/TiO_2$	1	1×10^3	99	2
$Cu/SiO_2/TiO_2$	24	<10	99.99	<4
Photocatalytic tiles +Ag [1]	24	–	99.99	4.72

Fig. 12 Intact design of (a): the control, (b): 1/9 (SiO_2/TiO_2), and (c): 1/9 ($Cu/SiO_2/TiO_2$) samples

not a considerable change in color, which it is important for commercialization.

4 Conclusions

To summarize, using the sol-gel method, we prepared a SiO_2/TiO_2 solution with various volume ratio of Si/Ti. Solutions were applied on the ceramic tile substrates via the dip-coating technique. The crystal structures of anatase and rutile phases were observed in the layers' structures, and roughness of the substrate surface decreased drastically by ~18 nm after applying the self-cleaning coating. After deposition, an almost uniform hydrophilic layer was formed; its WCA was reduced to about 13° after 24 hrs of weak intensity ($400\text{--}800 \mu W/cm^2$) UV lamp illumination. Furthermore, the coating demonstrated the photocatalytic activity and the ability to decompose the contamination in <24 hrs in low humidity (21–37 RH). Then, the 1/9 (SiO_2/TiO_2) solution was chosen as the optimum one and copper nitrate trihydrate was added to the solution to obtain a self-clean and antibacterial thin-film coating on ceramic tiles. The primary objective of this study was to obtain a self-clean and antibacterial coating on ordinary ceramic tiles that can be used in various conditions (i.e., independent of weather conditions or light intensity). Therefore, the self-cleaning function of TiO_2 through hydrophilicity and photocatalysis has been confirmed, especially in the presence of ultraviolet rays. When no UV light is available, or there is a very low-intensity illumination, the copper can remove 99% of *E. coli* bacteria in 1 h, and 99.99% in 24 hrs.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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