

Self-Cleaning Surfaces with Superhydrophobicity of Ag–TiO₂ Nanofilms on the Floor Ceramic Tiles

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Abstract—The goal of this study was the surface modification of industrial floor ceramic tiles by sol-gel dip coating method to improve the antibacterial and hydrophobicity activity of floor tiles. TiO₂ and Ag–TiO₂ nanofilms were prepared on floor tile. Ag–TiO₂ and TiO₂ films with different AgNO₃ and TiO₂ content were characterized by scanning electron microscopy X-ray diffraction, energy-dispersive X-ray spectroscopy and wettability to determine the topologies, microstructures, chemical compositions and cleanability, respectively. The results showed that, the wettability was significantly improved by increasing silver content comparing with pure TiO₂. The antimicrobial effect of the synthesized nanofilm was carried out against Gram-negative and Gram-positive bacteria (*S. aureus* ATCC 6538 and *E. coli* ATCC 25922) respectively. The synthesized Ag–TiO₂ thin film showed enhanced bactericidal activities compared to the neat TiO₂ nano film both under visible light. Antibacterial properties increased with increasing of AgNO₃ from 0.1 to 0.2 wt % and the amount of *S. aureus* ATCC 6538 and *E. coli* ATCC 259 were reduced by 99 and 95%, individually. With comparing of all samples, it could be observed that, the percentage of reduction of *S. aureus* ATCC 6538 was higher than that of *E. coli* ATCC 259.

Keywords: Ag–TiO₂ coating, sol-gel, antibacterial, hydrophilicity

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INTRODUCTION

Titanium dioxide (TiO₂) has attracted the attention of many researchers due to its cheapness, availability, strong oxidizing power, non-toxicity, antibacterial properties and self-cleaning properties [1–3]. TiO₂ can be deposited on the surface of various substrates, such as glass, ceramics, metals, cement, bricks to create a coating with self-sterilization and self-cleaning properties to destroy bacteria and kill them [4–6].

Due to the above properties, TiO₂ is used in food industries, medical, automotive, tile, ceramic, solar cell [7–9]. However, the main problem is that, the lack of visible light prevents its practical application. To overcome this problem, many studies have recently used noble metal doping such as Ag and Cu to increase antibacterial activity in visible light [10–13]. In general, it is believed that, silver ions interact with proteins by reacting with the SH groups present in bacteria, leading to the inactivation of the proteins [14–16]. Moreover, silver ions can interact with DNA of bacteria preventing cell reproduction [17–21]. Both effects lead to the death of the bacterial cells [22]. Page et al [23] reported that preparation of Ag₂O–TiO₂ films on glass substrates by sol gel method and investigated their antimicrobial properties by irradiating UV light at 365 nm. They found that, Ag-doped TiO₂ coatings

were significantly more anti-microbially active than TiO₂ coatings. Yu et al. [24] showed that, TiO₂ composites and silver nanoparticles have antibacterial activity even in the absence of visible light, indicating that, silver nanoparticles are responsible for the anti-microbial effect of coatings in the dark. They also showed that, the higher antibacterial activity of composite films under UV light is due to the synergistic antibacterial effects of the photocatalytic reaction of TiO₂ and Ag coatings. Sun et al. [25] deposited Ag–TiO₂ thin films on glazed tile surface by liquid phase deposition method (LPD). The films were prepared from ammonium hexafluorotitanate(IV) and silver nitrate and annealed at 600°C which showed a high antibacterial activity versus *Staphylococcus aureus* and *Escherichia coli*.

Sol-gel process is a conventional method to prepare composite Ag–TiO₂. In this study, TiO₂ and Ag–TiO₂ thin films deposited on floor tiles were prepared by a template sol-gel technique. Thin films with different contents of AgNO₃ and TiO₂ were deposited on floor tiles by dip coating at room temperature. Different characterization methods were used to analyze the resultant films. The antibacterial effect of the obtained thin films on Gram-negative and positive bacteria was

Table 1. Prepared samples with different weight ratios of TiO₂ and AgNO₃

Sample	TiO ₂ , %	AgNO ₃ , %
S	—	—
S _{0.05T}	0.05	—
S _{0.1T}	0.1	—
S _{0.05T,0.1A}	0.05	0.1
S _{0.1T,0.1A}	0.1	0.1
S _{0.05T,0.2A}	0.05	0.2
S _{0.1T,0.2A}	0.1	0.2

tested. The hydrophilicity effect of films was obtained using water contact angle measurement.

EXPERIMENTAL

Materials

Propanol (CH₃CH₂CH₂OH, 99% purity, Merck KGaA), titanium dioxide (TiO₂, 99% purity, Sigma-Aldrich), tetraisopropyl orthotitanate (99% purity, Merck KGaA), silver nitrate (AgNO₃, 99% purity, Merck KGaA) and bacteria of *S. aureus* ATCC 6538 and *E. coli* ATCC 25922 (Microbiology Laboratory of Scientific Research Center, University of Tehran) were provided as initial materials. The strains were cultured in Muller Hinton broth and Standard Methods Agar (TSA (trypticase soy agar) using the appropriate times and temperatures of incubation. The substrates used were selected floor tiles from Golchin Co.

Preparation of TiO₂ and Ag–TiO₂ Films on the Floor Tile

The experiments were performed in the ceramic laboratory of Maybod Islamic Azad University. Samples were prepared by following procedures:

Preparation of TiO₂ film on the floor tiles: 2 molar hydrochloric acid was obtained with 16.5 mL of concentrated hydrochloric acid (37% purity) and distilled water into 100-mL flask. To prepare the precursor solution for the production of TiO₂ film, first 85 mL of propanol and 6 mL of titanium isopropoxide (Ti{OCH(CH₃)₂}₄) were stirred at 40°C. Then, 2 molar hydrochloric acid was continuously added as catalyst to the solution until pH 3. The water in the solution caused a gentle hydrolysis of the solution. The solution was stirred at room temperature for 6 h to complete this reaction. In the next step, TiO₂ particles were added to the solution with different weight ratios from 0.05 and 0.1 wt % and mixed for 15 h. The floor tiles were immersed in the solution at ambient temperature for 30 s to complete the immersion deposition process.

Preparation of Ag–TiO₂ film on the floor tiles: For preparing the coating of Ag–TiO₂ on the floor tiles, the steps are repeated as mentioned before. After adding of TiO₂ particles, 0.1 and 0.2 wt % AgNO₃ were added and the solution stirred for 6 h. The floor tiles were immersed in the solution at ambient temperature for 30 s to complete the immersion deposition process. The substrates dimensions of floor tiles were 30 × 15 × 3 mm. The substrates were cleaned in acetone and then an ultrasonic bath was used by ethanol.

Figure 1 shows a schematic of the preparation of nano Ag–TiO₂ film. Primary tile samples were used as a control sample to evaluate the results. The codes of prepared samples with different weight ratios of TiO₂ and AgNO₃ were shown in Table 1. The prepared samples were studied by the following techniques. X-ray diffraction (XRD, Japan Shimadzu, CuK_α 40 kV, 30 mA) through a D8-Advance Bruker instrument equipped with a CuK_α radiation source with $\lambda = 1.5406 \text{ \AA}$, and configured in horizontal 2 θ geometry. The surface morphology and grain size were measured by field-emission scanning electron microscope (FESEM) (Hitachi S-4100 SEM, Hitachi High-Tech, Minato-ku, Tokyo, Japan) with an EDS system (MIRA II, SAMX). For FESEM study, to prevent the charging effect, the samples were coated with a very thin layer of gold. The static contact angle of the distilled water drop with the surface of thin film was measured using a domestic made instrument with a × 1000 magnification lens and a digital camera (model canon-25 megapixel). Ten milliliters of distilled water was slowly released on the thin film surface. The image of the contact angle was analyzed by ImageJ software code and the method of low-bond axisymmetric drop shape analysis (LB-ADSA) [26]. To measure the antimicrobial activity, the killing time test was used.

RESULTS AND DISCUSSION

X-ray Diffraction Studies of TiO₂ and Ag–TiO₂ Films

The XRD analysis of samples with different weight ratios of TiO₂ and AgNO₃ on floor tiles was shown in Fig. 2. Crystal structure of samples was identified by JCPDS card which showed TiO₂ and Ag₂O₃ phases, respectively. Specifications and preferential growth orientation of the created peaks by TiO₂ and Ag₂O₃ phases are given in Table 2. As it was shown in Fig. 2 with addition of TiO₂ and AgNO₃, except TiO₂ and Ag₂O₃ phases, mullite and quartz phases were detected due to the effect of the substrate. In all samples, the main diffraction angle at 2 $\theta \approx 27^\circ$ was related to the rutile phase of TiO₂ in (110) diffraction line. The diffraction lines related to Ag₂O₃ were 2 $\theta = 37.05^\circ$, 42.70°, 60.45° that indicated the good dispersion of nanocrystalline silver particles in the matrix. The XRD pattern of the control sample (S) showed the amorphous structure and the formed peaks in the

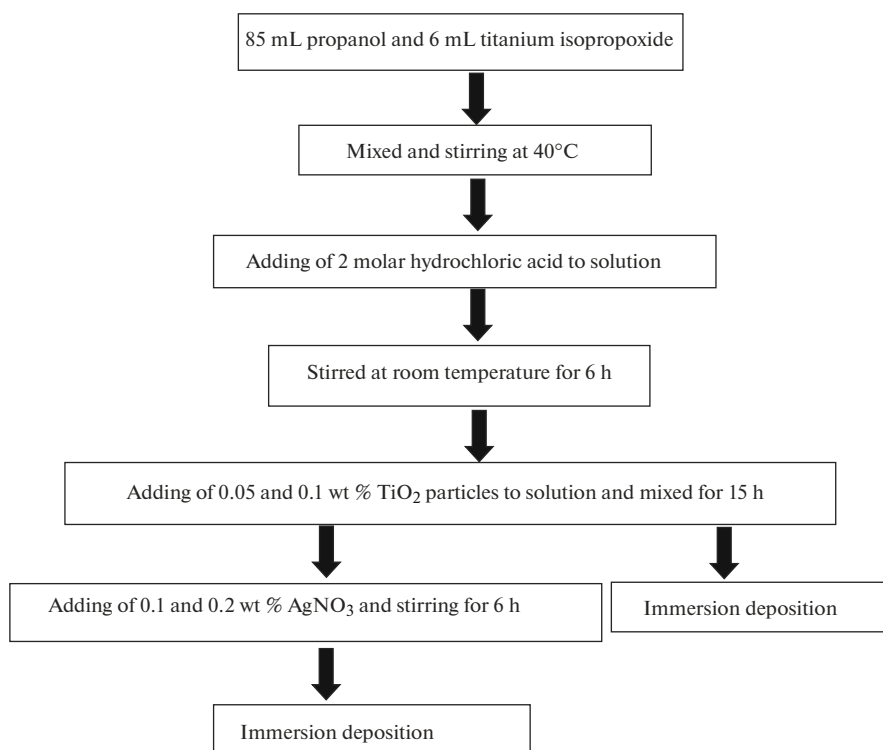


Fig. 1. Schematic of the deposition steps.

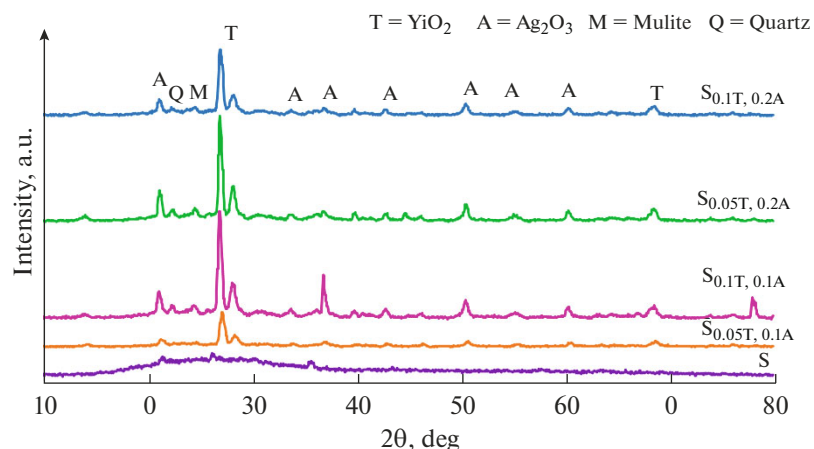


Fig. 2. XRD patterns of films with different weight ratios of TiO_2 and AgNO_3 on floor tiles.

range of $2\theta = 20^\circ\text{--}30^\circ$ were related to quartz and mullite phase with very wide peak. Fluctuations in the spectrum were owing to the amorphous nature of the tile. By increasing the amount of TiO_2 from 0.05 to 0.1 wt % ($S_{0.05T,0.1A}$ and $S_{0.1T,0.1A}$) and fixing the amount of AgNO_3 (0.1 wt %) constant, the peak intensities was increased sharply, especially in $2\theta = 27.9^\circ$ for TiO_2 and $2\theta = 37.05^\circ$ for Ag_2O_3 . While with adding of 0.2 wt % of AgNO_3 and increasing the amount of TiO_2 from 0.05 to 0.1 wt % in $S_{0.05T,0.2A}$ and $S_{0.1T,0.2A}$, the peak

intensity $2\theta = 27.9^\circ$ of TiO_2 was reduced. With comparing the X-ray diffraction pattern of the samples, it was seen that, with increasing of TiO_2 and AgNO_3 , all of peaks were more intense.

Surface Morphology and Chemical Composition of TiO_2 and Ag– TiO_2 Films

Figure 3 shows the surface microstructures of the TiO_2 and Ag– TiO_2 films on the floor tile. The grain

Table 2. Characteristic for coating the tiles with TiO₂ and AgNO₃ from XRD analysis

Sample	S _{0.05T,0.1A}	S _{0.05T,0.2A}	S _{0.1T,0.1A}	S _{0.1T, 0.2A}
TiO ₂ peak, deg	27.44	27.91	27.12	27.91
(hkl)	(110)	(110)	(110)	(110)
JCPDS card	01-073-1782	01-088-1175	01-076-0324	01-088-1175
Ag ₂ O peak, deg	60.45, 37.05	60.45, 37.05	60.45, 37.05	60.45, 37.05
(hkl)	(312), (112)	(312), (112)	(312), (112)	(312), (112)
JCPDS card	01-074-1368	01-074-1368	01-074-1368	01-074-1368

Table 3. Grains size obtained from FESEM analysis

Sample	S _{0.5T,0.1A}	S _{0.1T,0.1A}	S _{0.05T,0.2A}	S _{0.1T,0.2A}	S _{0.05T}	S _{0.1T}	S
Grain size, nm	42.83	45.10	29.35	29.84	22.08	19.87	19.29

size of the FESEM results using Nanoscope software was given in Table 3.

By coating of TiO₂ film on the floor tile, the grain size of S_{0.05T} and S_{0.1T} samples were increased compared to control sample of S. However, with increasing of TiO₂ from 0.05 wt % (S_{0.05T}) to 0.1 wt % (S_{0.1T}), the grain size was decreased. Moreover, by coating of Ag–TiO₂ film on floor tile, the grain size and surface roughness were increased. By increasing of AgNO₃ content from 0.1 wt % (S_{0.05T}) to 0.2 wt % (S_{0.05T}) with 0.05 wt % of TiO₂ particle, the grain size was decreased. Also with adding of 0.1 wt % of TiO₂ particle in all samples the grain sizes (S_{0.1T, 0.1A} and S_{0.1T, 0.2A}) were reduced. According to Table 3, with a constant value of 0.05 wt % of TiO₂ and doping of AgNO₃ from 0.1 to 0.2 wt %, the grain sizes were increased 2 and 1.4 times, respectively. Consistent with Table 3, with comparing of S_{0.1T, 0.1A}, S_{0.1T, 0.2A}, S_{0.1T} it was seen that, with a constant value of 0.1 wt % TiO₂ and doping of AgNO₃ from 0.1 to 0.2 wt % the grain size was increased 2.26 and 1.5 times, respectively. In addition, larger pores were produced by doping of AgNO₃ which was resulted in increasing of porosity and surface roughness.

Figure 4 is shown the EDS spectra of the TiO₂ and Ag–TiO₂ films on the floor tile. The presented energy of each of the peaks in the spectra was assigned to a specific atom. Higher peaks were indicated the higher concentrations of the element in the sample. The EDS analysis was employed to verify the chemical composition of the film. In all samples in Fig. 3, it was seen that, the Si and Al elements were related to the substrate and the oxygen form the metal oxide had the highest percentage. In the samples of S_{0.05T, 0.1A}, S_{0.1T, 0.1A}, S_{0.05T, 0.2A}, S_{0.1T, 0.2A}, the peaks created by Ti and Ag element were very small and in the S_{0.05T} and S_{0.1T}

samples, the Ti and O element peaks were increased significantly.

Wettability Behaviors of TiO₂ and Ag–TiO₂ Films

TiO₂ as a semiconductor has various applications that are inherently hydrophilic. The contact angle of a water drop on the solid surface is an important parameter in determining the hydrophobicity or hydrophobicity of the material.

The effect of doping of TiO₂ and AgNO₃ on wettability has been investigated using the contact angle analysis of deionized water droplets of 10 mg on surfaces.

The average contact angle of 5 droplets of water on the surface of the film is measured using ImageJ software to obtain data uncertainty (by precision of two digits). When the contact angle is greater than 90°, the surface is hydrophobic. However, when the contact angle changes is between 30° to 90°, the surface is hydrophilic and if the contact angle is less than 30°, the surface is super-hydrophilic. The wettability behavior of hydrophilic surfaces depends on the chemical composition and structure of the material surface.

Figure 5 shows the images of static contact angle of water drop on produced films on floor tiles. As it was shown in Fig. 4, the surface of the control sample (S) had a hydrophobic behavior with a contact angle of 98°. By adding TiO₂ content, the contact angle of S_{0.05T} and S_{0.1T} samples was reduced and the hydrophobicity turned into hydrophilicity. As the TiO₂ content increased from 0.05 to 0.1 wt %, the contact angle decreased from 88° to 78°. Also, by doping AgNO₃ with TiO₂ content, the contact angle was reduced. The static contact angle of the distilled water drop on sur-

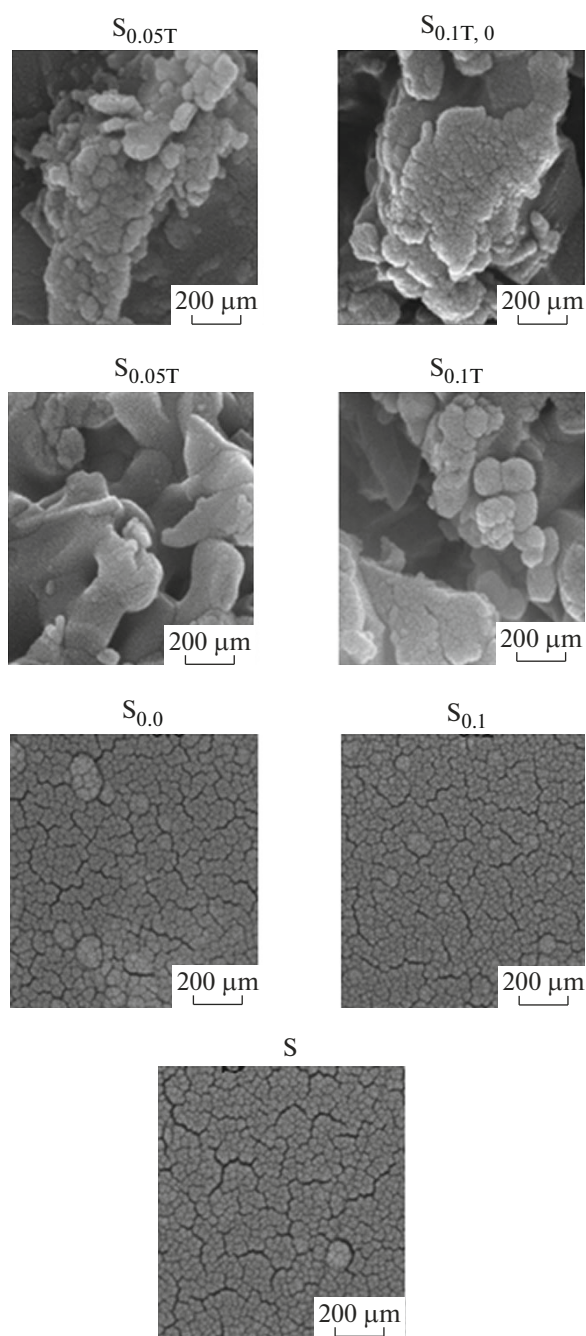


Fig. 3. Surface FESEM images of films with different weight ratios of TiO_2 and AgNO_3 on floor tiles.

faces of $S_{0.05T, 0.1A}$ and $S_{0.1T, 0.1A}$ samples were measured as 77° and 61° , respectively. The contact angle decreased with increasing of AgNO_3 content from 0.1 to 0.2 wt %. $S_{0.05T, 0.2A}$ and $S_{0.1T, 0.2A}$ samples with contact angles of 65° and 20° were hydrophilic and superhydrophilic, respectively. Silver nanoparticles reduced the contact angle and changed the behavior of the samples from hydrophilicity to superhydrophilicity.

In fact, silver had an important effect on wettability properties [27].

Antibacterial Activity Evaluation

The time-kill method was used to evaluate the antibacterial activity. The time-kill method is one of the best methods to obtain information about the dynamic relationship between antibacterial and bacterial species, which depends on the time and effective concentration of antibacterial substances. In this method, the percentage of dead cells relative to living cells in terms of CFU/mL is obtained using agar count and then compared with the growth control tube.

Bacterial testing was performed on two types of Gram-positive bacteria *S. aureus* ATCC 6538 and Gram-negative bacteria *E. coli* ATCC 25922 with an initial concentration of 1×10^5 CFU/mL.

Table 4 presented the experimental results for the qualitative evaluation. The results show that, all samples could prevent the growth of bacteria. This result was expected because of the driving force of silver ion diffusion on the surface which was larger for coatings with higher silver content. Figure 6 shows the reduction ratio of bacteria for different samples by two gram-positive bacteria, *S. aureus* ATCC 6538, and the Gram-negative bacterium *E. coli* ATCC 25922 under visible light. Covering the floor tile with TiO_2 film increased the antibacterial properties. With the increase of TiO_2 content from 0.05 to 0.1 wt % ($S_{0.05T}$ and $S_{0.1T}$) the destruction of bacteria for both bacterial species has increased so that, the percentage of reduction of *Staphylococcus aureus* ATCC 6538 was higher than *Escherichia coli* ATCC 259. However, in tiles coated with AgNO_3 and TiO_2 content ($S_{0.05T, 0.1A}$ and $S_{0.1T, 0.1A}$) caused to kill more bacteria. Although antibacterial properties in composite samples depend on the diffusion of silver ions, therefore the composite with higher silver content had a greater antibacterial effect. Antibacterial properties increased with increasing of silver nitrate from 0.1 to 0.2 wt % ($S_{0.05T, 0.2A}$, $S_{0.1T, 0.2A}$, $S_{0.1T, 0.2A}$) and the amount of *S. aureus* ATCC 6538 and *E. coli* ATCC 259 were reduced by 99 and 95%, respectively. With comparing all the coated samples according to Table 4 and Fig. 5, it could be expected that, the percentage of reduction of *S. aureus* ATCC 6538 was higher than that of *E. coli* ATCC 259.

CONCLUSIONS

TiO_2 and Ag-TiO_2 films were prepared by the sol-gel dip coating method on floor tiles. X-ray diffraction patterns for all samples with different percentages of TiO_2 and AgNO_3 on the floor tile substrates showed that all of the samples had crystal structure. With increasing the weight percentage of TiO_2 from 0.05 to 0.1, the intensity of the peaks, especially related to TiO_2 phase was increased, while with increasing the

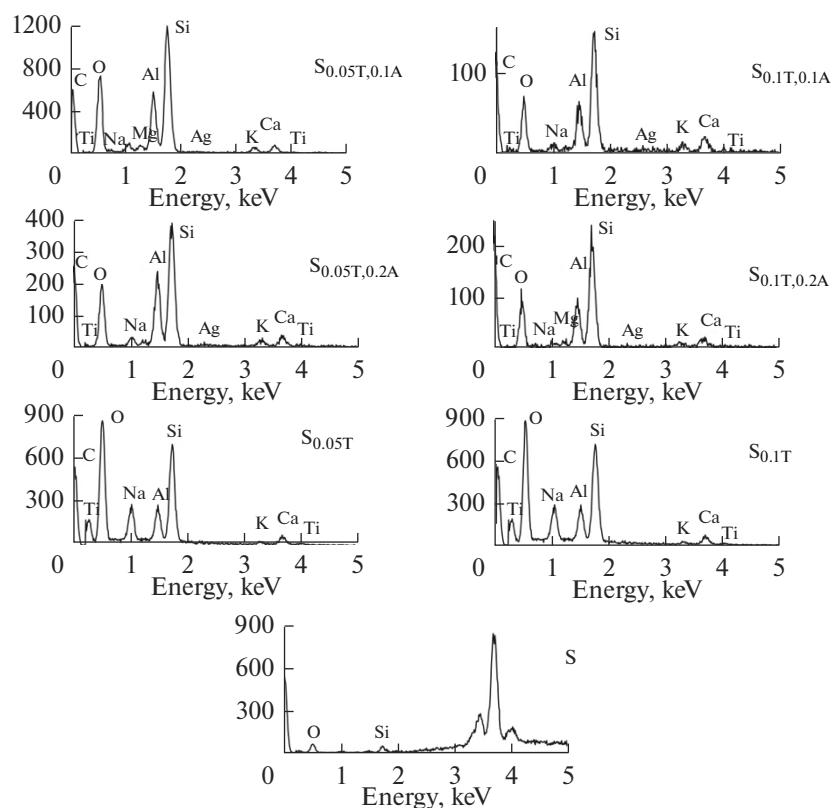


Fig. 4. EDS spectra of films with different weight ratios of TiO_2 and Ag-TiO_2 on floor tiles.

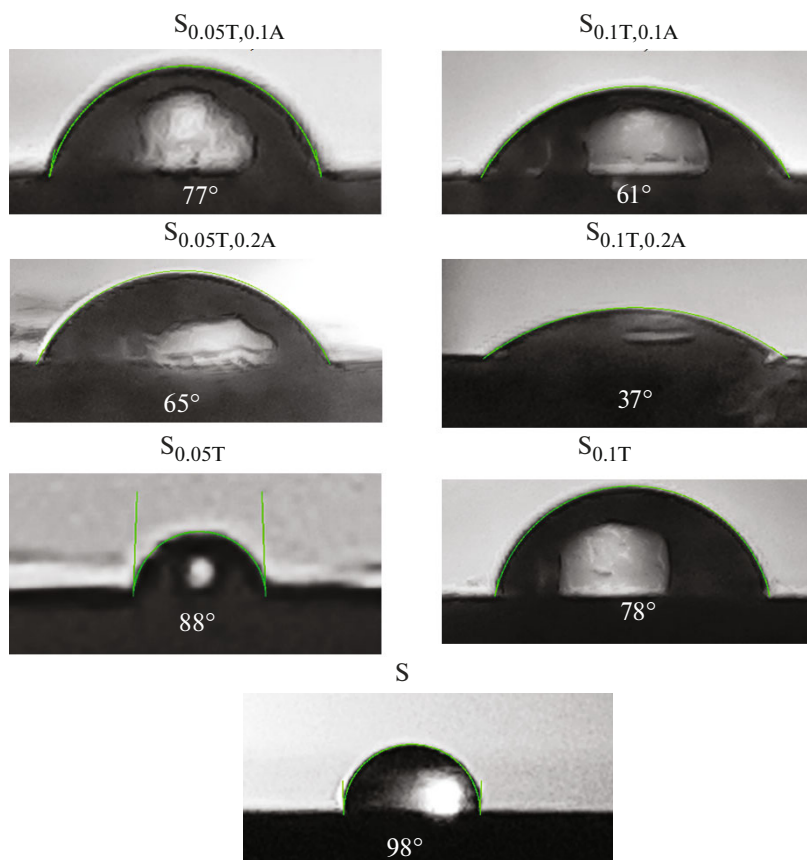
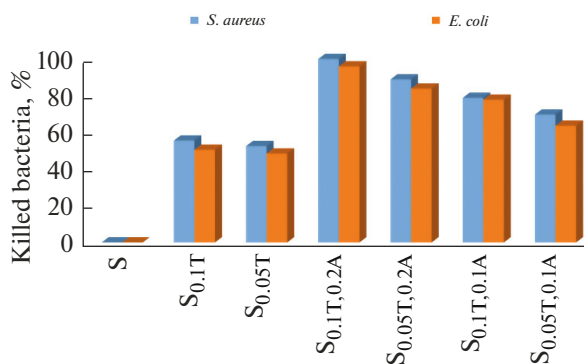


Fig. 5. The static contact angle of water drop with films with different weight ratios of TiO_2 and AgNO_3 on floor tiles.

Table 4. Percentage of bacterial reduction of different samples on the floor tile by two different bacteria

Sample	S _{0.05T,0.1A}	S _{0.1T,0.1A}	S _{0.05T,0.2A}	S _{0.1T,0.2A}	S _{0.05T}	S _{0.1T}	S
<i>S. aureus</i> ATCC 6538							
%	69	78	88	99	52	55	0
<i>E. coli</i> ATCC 259							
%	63	77	83	95	48	50	0

**Fig. 6.** Killing ratio two species of bacteria on the surfaces of films with different weight ratios of TiO₂ and AgNO₃.

weight percentage of AgNO₃, the X-ray diffraction pattern did not change clearly. The results of FESEM showed that, the grain size was decreased with increasing of TiO₂ content. Also, by adding of AgNO₃ content, the grain size and surface roughness were increased. Prototype surfaces with floor tile substrate had a hydrophobic behavior with a contact angle of 98°. Adding of TiO₂ content reduced the contact angle and turned the hydrophobic behavior into hydrophilicity. As the percentage of TiO₂ content was increased from 0.05 to 0.1, the contact angle was decreased from 88° to 78°. Also, silver nanoparticles reduced the contact angle and changed the behavior of the samples from hydrophilicity to super-hydrophilicity.

The inactivation of Gram-negative and positive bacteria (*S. aureus* ATCC 6538 and *E. coli* ATCC 25922) under visible illumination of all films was compared and the films showed the antibacterial activity and better wettability effect with increasing of the silver content. Antibacterial properties increased with increasing of AgNO₃ content from 0.1 to 0.2 wt %. In S_{0.1T,0.2A} sample, the amount of *S. aureus* ATCC 6538 and *E. coli* ATCC 259 were reduced by 99 and 95%, respectively. With comparing all the coated samples, it was observed that, the percentage reduction of *S. aureus* ATCC 6538 was higher than that of *E. coli* ATCC 259.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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