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Preparation and antibacterial activity of Ag/SiO_2 thin film on glazed ceramic tiles by sol–gel method

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Abstract

In the present study, silver-doped silica thin films on glazed surface of ceramic tiles were well prepared by sol–gel method to achieve antibacterial activity. Thermal treatment was done in the air at 1100 °C for two hours. The Ag/SiO_2 thin films were investigated through Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD) and wavelength dispersive spectrometry (WDS). Atomic absorption spectroscopy (AAS) was used for the quantitative determination of the silver ion concentration being released from Ag/SiO_2 films over a 24 day period. The antibacterial effects of Ag/SiO_2 thin films against *Escherichia coli* and *Staphylococcus aureus* were also examined. From the analysis results, it was found that high temperature treated coating consists of two phases of SiO_2 and Ag based on the trapping of the Ag phase in the silica matrix. The presence of Ag elements on the surface of the coated tiles, were also observed. Thermal treatment at high temperatures caused sharp XRD peaks and high crystallinity in this system. Ag^+ ions were released constantly and the mean release rate (±SD) was 0.104 ±0.01 μg/ml during 24 days. Coating films exhibited an excellent antibacterial performance against both bacterium.

Keywords: Antibacterial; Sol–gel method; Ag/SiO_2 thin film; Tile

1. Introduction

Microorganisms like bacterium, fungi, protozoas, viruses, etc. commonly infect humans in the living environment. Several natural and inorganic materials such as tea extraction, copper, chitosan, zink and titanium dioxide have been used as antimicrobial agents [1–4]. However, among them silver or silver ions have been long known to have widespread antibacterial activities [5]. Silver atoms bind to thiol groups (–SH), forming steady S–Ag bonds with thiol-containing compounds, causing deactivation of enzymes inside the bacteria [6]. In addition, once silver ions enter the cell, they intercalate between the purine and pyrimidine base pairs, breaking off the hydrogen bond of two anti-parallel DNA molecules [7]. There are also other mechanisms suggested for silver antibacterial activities [8]. Therefore, there have been a broad range of commercial usages of silver or silver ions as antibacterial agents.

Silver-doped ceramics and glasses tend to be chemically durable, releasing silver ions for a long time, thus having a good antibacterial activity [9]. Ceramic tiles which are commonly used in any home or environment do not have antibacterial activity and microorganisms easily grow on their surfaces especially in moist environments. This, in turn, affects people's health. Therefore, preparing antibacterial film on the glazed surface of ceramic tiles and examining its antibacterial activity is of essential importance [10]. A variety of different techniques have been used to incorporate silver into silicate glasses including sputtering [11], ion exchange [12,13], ion implantation [14], and sol–gel [15]. Compared to other methods, sol–gel has been preferably used due to the advantages of providing a practical way of reaching uniform distribution of silver particles in silica matrices [16] and high purity and homogeneity of coatings [17]. This method also easily enables controlling the size and concentration of silver; all of which are critical for technical applications.

Many studies have proved the antibacterial activity of silver-containing silica glass [17,18] or silver-doped organic–inorganic

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hybrid [5,19,20], employing the sol–gel method. Some of them have been done on glass substrate [5,17]; however, as far as the authors are aware, no similar researches have been carried out on tiles. This study aimed to examine the preparation and antibacterial activity of silver-doped silica thin film on glazed tiles by sol–gel method. The formation of Ag-doped silica thin films was investigated by X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The release of silver ions in water over a period of 24 days was evaluated to monitor the elution of silver from the coating. In addition, the antibacterial activity of the silver-doped films was studied against gram-positive *Staphylococcus aureus* and gram-negative *Escherichia coli*.

2. Materials and methods

2.1. Preparation of coating films

Silver-doped coating films were prepared employing the sol–gel method. The starting solution was made from tetraethylorthosilicate (TEOS, Merck, 99%), distilled water (H_2O), nitric acid (HNO_3, Merck, 2 M) ethanol (C_2H_5OH Merck, 99.9%) and silver nitrate (Across, >99%) as a precursor for silver. Molar ratio of ethanol:H_2O:$AgNO_3$:TEOS was 2.2:3.75:0.24:1. In the first step, TEOS, ethanol and distilled water were mixed. Then, HNO_3 was added drop by drop while the PH was controlled using the PH meter (Sartorius Py-P11-PH meter, Germany) at the value of around 1.5. After two hours of vigorous stirring at room temperature, $AgNO_3$ was added and the solution was further stirred for another two hours. A few hours following the preparation of the sol, coating was applied using dip-coating technique. As a coating substrate, ultrasonically cleaned glazed ceramic tiles with 2.5 cm by 2.5 cm surfaces were used. All films were dried at 100 °C for an hour in an Isotemp oven. Thermal treatment was then done in the air at 1100 °C for two hours.

2.2. Characterization

Chemical composition of dried sols being heat-treated at 1100 °C was analyzed using XRD and FTIR analyses. XRD measurements were performed using a diffractometer with Cu anode (Model: SIEMENS, D5000) in a 2θ range of 5–70° at a fixed incident angle of 0.02. FTIR spectrum were determined in transmission mode using a Fourier transform infrared spectrometer (Model: PE1760x) in the range of 4000–400 cm^{-1} with a resolution of 1 cm^{-1} in KBr-diluted medium.

Investigation of coating surface and homogeneity of the coating were performed using SEM (Model: PHILIPS, XL30). The presence and distribution of Ag and Si elements on the surface of the specimens were observed using wavelength dispersive spectrometry (WDS) micrographs (Microspec WDX-3PC analyzer). To measure the coating thickness, SEM pictures from a longitudinal section of the specimen were also obtained. A film of gold was deposited on each specimen before being observed under the microscope to achieve better and sharper pictures.

2.3. Evaluation of silver release rates

Atomic absorption spectroscopy (AAS) was used to determine the silver ion concentration being released from Ag/SiO_2 films. Sterile double distilled water was used as the test fluid. Ceramic pieces coated with Ag/SiO_2 film, 2.5 cm × 2.5 cm in size, were immersed in 100 ml of the test fluid. The liquids were then taken out on a daily basis from the sample and the concentration of Ag^+ was measured by atomic absorption spectrophotometer (AA-6800, Seris, Shimadzu, Japan) for up to 24 days.

2.4. Antibacterial test

The antibacterial activities of silica thin films against *E. coli* (ATCC:25922) and *S. aureus* (ATCC:25923) were investigated. Blanc experiment was carried out using uncoated tiles. *S. aureus* and *E. coli* were chosen as they are among the most prevalent species of gram-positive and gram-negative bacteria causing infection, respectively.

3. Results and discussion

Fig. 1 shows the results of the XRD analysis of the sol treated at 1100 °C after being dried. Peaks of SiO_2 and elemental Ag were seen in the XRD pattern. Four distinct peaks at 2θ values of 21.98°, 28.4°, 31.46°, and 36.03° corresponded to the crystobalite (SiO_2) phase. Shorter peaks at higher 2θ values which are related to the SiO_2 phase could also be found in the XRD pattern (JCPDF card NO. 39-1425). In addition, there were sharp peaks at 2θ values of 38.11°, 44.27° and 64.27° corresponding to (1 1 1), (2 0 0), and (2 2 0) planes of metallic Ag, respectively (JCPDF card NO. 04-0783). It can be concluded that high temperature treated coating consists of two phases; the SiO_2 phase and the Ag phase.

The results of the FTIR analysis of the dried sol followed by heat treatment at 1100 °C are depicted in Fig. 2. Peaks at 491,784 and 1096 cm^{-1} were the most important peaks, related to Si–O–Si bonds. These peaks were related to the bending vibration, symmetric stretching and stretching vibration modes of this bond, respectively. There was also another shoulder peak related to the Si–O–Si bond at about 1200 cm^{-1}. The absence of the nitrate peak at about 1390–1400 cm^{-1} [17], showed that the nitrate groups were burned and removed from the system during thermal treatment.

The mechanism of the formation of Ag/SiO_2 thin films is not so clear, but two different mechanisms have been

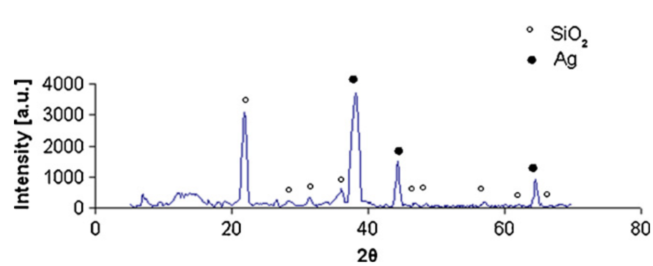

Fig. 1. XRD patterns of Ag/SiO_2 silica gel heat treated at 1100 °C.

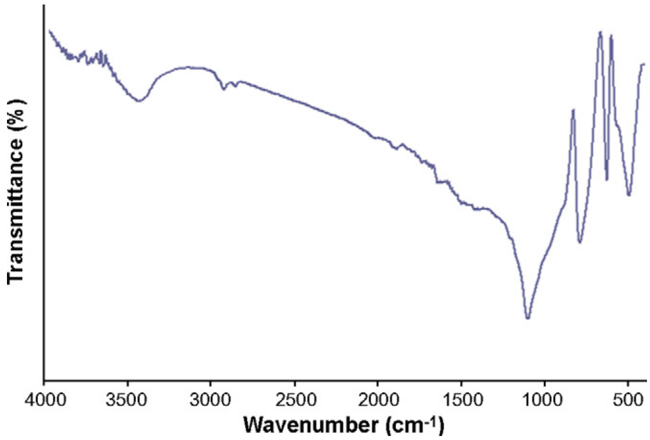

Fig. 2. FT-IR spectra for silver-doped silica gel heat treated at 1100 °C.

introduced [17,20] for the interaction between the Ag and SiO_2 phases:

1. Substitution of some Si elements in the SiO_2 structure by Ag elements.
2. Physical trapping of elemental Ag atoms in the SiO_2 matrix.

From these data, it is hard to confirm the first mechanism, but the transformation of SiO_2 network was observed due to the Ag^+ ions in the FTIR data. If there were any substations of the Si atoms by Ag atoms in the silica structure, a shift in XRD peaks of SiO_2 would appeared due to the differences in atomic radii of these two atoms. Since there was no shift in the XRD pattern of the SiO_2 phase, it seems that the interaction between SiO_2 and Ag phases is based on the physical trapping of the Ag phase in the silica matrix. However, further study is required to find out the interaction of Ag in silica matrix. Thermal treatment at high temperatures caused sharp XRD peaks and high crystallinity in this system. Peaks related to the silanol groups of SiOH which were heat treated at lower temperatures at 570 and 790 cm^{-1} could be seen in similar systems [17]. However, these peaks cannot be seen in the FTIR pattern of Fig. 2. It shows that all the SiOH phase is transformed to the SiO_2 phase. There was a peak at 3436 cm^{-1} which was related to the Si–OH stretching of the surface silanols hydrogen groups [17], naturally present at the surface of SiO_2 particles. In similar systems which are heat treated at lower temperatures, another band related to H–O–H deformation interacting through hydrogen bonds with silanol groups [17] was observed, but

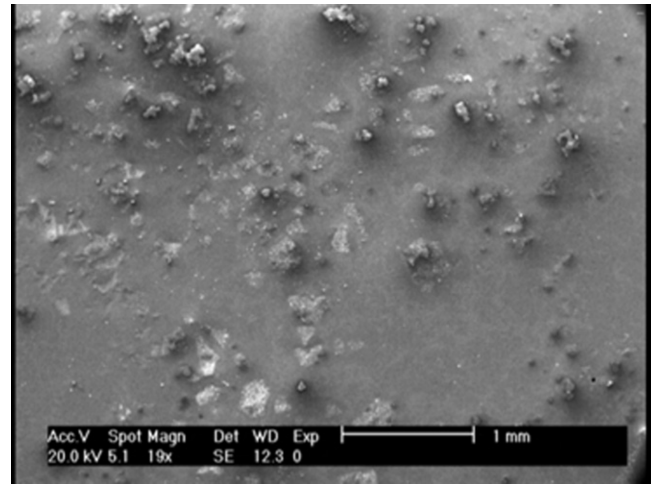

Fig. 3. SEM picture of the surface morphology of the Ag/SiO_2 thin film on glazed ceramic at 1100 °C.

in the FTIR of Fig. 2, this peak was disappeared. This means that all of the SiOH phase is converted to the SiO_2 phase. Jeon et al. demonstrated the FT-IR spectra of comparison between pure silica and silver doped silica [17]. It was shown that 2 peaks at 620 and 2900–3000 cm^{-1} will appear in the FTIR of silica due to the Ag doping. In the FTIR of Fig. 2, these 2 peaks can also be seen with higher intensity which is the result of thermal treatment of the film at higher temperatures.

SEM images were taken after deposition of a continuous thin film silica matrix at the surface of the glazed tiles. Fig. 3 illustrates the SEM micrograph of the surface of heat treated coating. It was found that the surface of the sample was homogeneously covered with the Ag/SiO_2 film. WDS results of the film showed the homogeneous distribution of Si elements and the presence of Ag elements on the surface of the coated tiles (Fig. 4(a)–(c)). A cross-sectional morphology of the coating film with a thickness of about 278 μm is also shown in Fig. 5. Good adhesion of the coating to the substrate could be noticed in this figure. In relation to the surface morphology of the films and the annealing temperature, in this system high temperature treatment led to a circle-like morphology of the Ag/SiO_2 clusters as can be seen in Fig. 6. WDS results showed that the aggregates around these circles are Ag-rich areas. It seems that these circle-like pores are created due to the exhaust of the gases resulting from nitrate decomposition from the surface of the coating, leading to the formation of Ag-rich clusters around these pores.

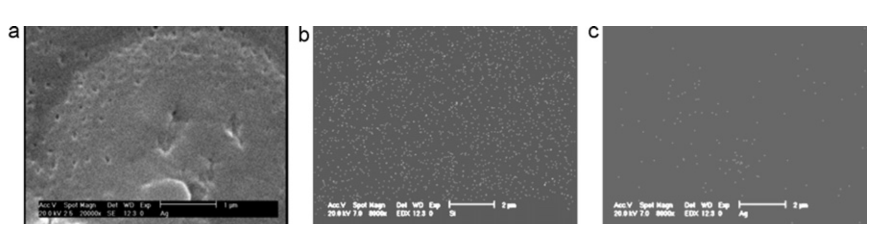

Fig. 4. The results of the surface morphology of the Ag/SiO_2 thin film: (a) SEM picture of the surface; (b)WDS taken from Si distribution labeled (a); and (c) WDS taken from Ag distribution labeled (a).

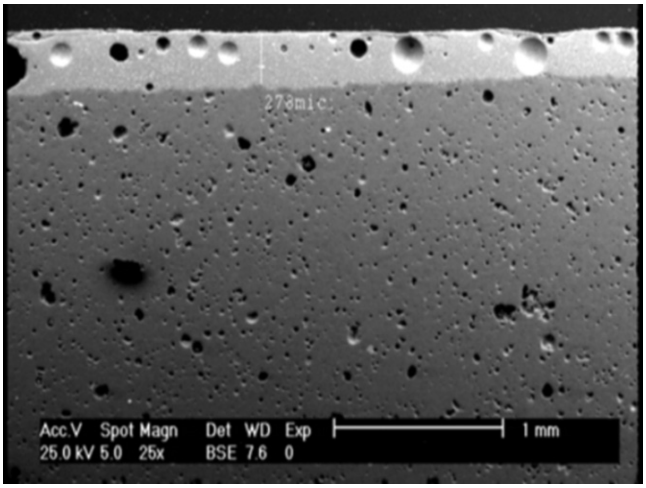

Fig. 5. Cross-sectional picture of the Ag/$Si0_2$ thin film at 1100 °C.

AAS was used for the quantitative determination of the silver ion concentration releasing from Ag/SiO_2 films in water. Fig. 7 shows the release rate of silver ions as a function of soaking time at 37 °C in double distilled water for up to 24 days. It was detected that the release of the Ag^+ ions was fairly constant and the mean release rate(±SD) was 0.104 ± 0.01 μg/ml during 24 days. This indicates that silver ions are released from the surface of Ag/SiO_2 thin films and these ions could kill microorganisms.

Bactericidity of silica thin films was examined by immersing coated tiles into a solution containing concentration of bacteria about 1.5×10^8 CFU/ml for 48 h. Coated tiles were then placed in to sterilized Mueller Hinton Agar (MHA) for a few hours followed by incubation at 37 °C for 72 h. Concentration of the survived bacteria was determined after this time. Uncoated tiles were used as control. The results are shown in Table 1 and Figs. 8 and 9. It could be noticed that the coating exhibited 100% bactericidity against *E. coli* and about 90% against *S. aureus*. This decreased susceptibility can simply be explained by the fact that the cell wall of gram-positive bacteria is thicker than that of gram-negative one, resulting in trapping more silver by peptidoglycan molecules in the cell wall.

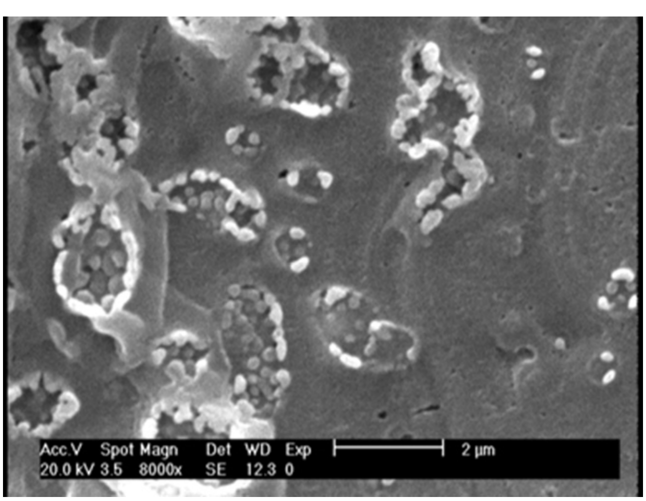

Fig. 6. SEM pictures of circle-like Ag/SiO_2 clusters in the surface of thin film at 1100 °C.

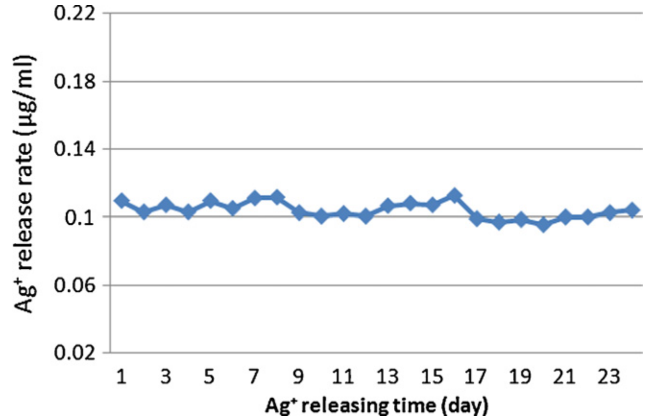

Fig. 7. Atomic absorption spectroscopy of silver ion releasing rate from Ag/SiO_2 thin film as a function of soaking day.

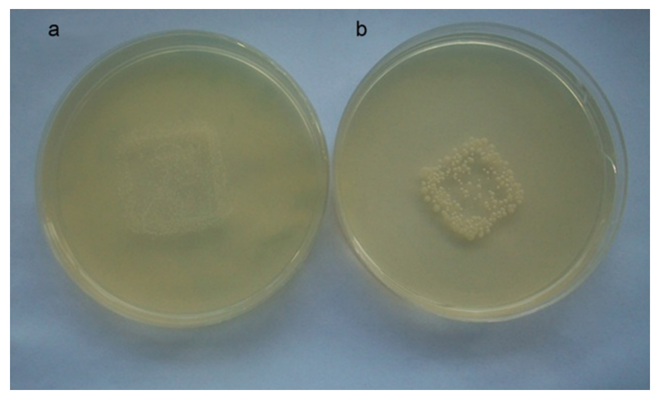

Fig. 8. Test results on *S. aureus* after 72 h: (a) incubated without Ag/SiO_2 coatings and (b) incubated with Ag/SiO_2 coating.

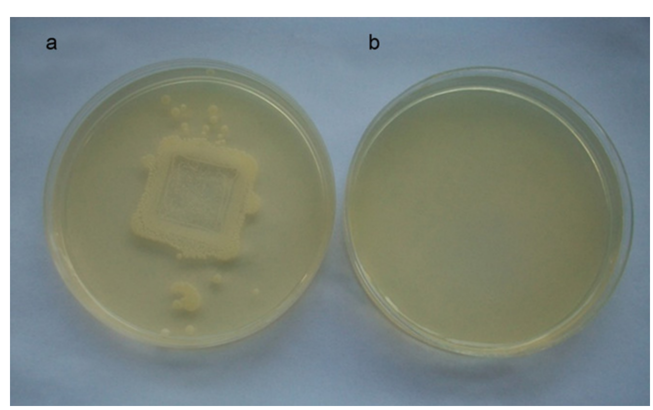

Fig. 9. Test results on *E. coli* after 72 h (a) incubated without Ag/SiO_2 coatings and (b) incubated with Ag/SiO_2 coating.

Table 1
Antibacterial test result on *S. aureus* and *E. coli*.

Bacteria	Case	Start	After 72 h	Reduction of bacteria (100%)
E. coli	Blank	1.5×10^8	1.5×10^4	–
	Ag/SiO2	1.5×10^8	0	100
S. aureus	Blank	1.5×10^8	1.5×10^6	–
	Ag/SiO2	1.5×10^8	10^2	90

4. Conclusion

In the present study, sol–gel method was used to synthesize silver-doped silica thin films. It was applied on the surface of glazed ceramic tiles by dip coating followed by thermal treatment at 1100 °C. According to previous researches, high-temperature processing of silver-doped tetraethoxysilane (TEOS) films (>300 °C) results in the diffusion of Ag^+ ions from the surface into the bulk [21] and silver valence might also be affected by thermal treatment at high temperature to reduce the antibacterial effect [22]. However, in our study the presence of Ag elements on the surface of the glazed tiles was proved by WDS. Silver ions following the applied high temperature treatment(1100 °C) released constantly with the mean rate (±SD) of 0.104 ± 0.01 μg/ml from the surface of the Ag/SiO_2 film as was proved by ASS data and these ions concentration are probably enough to inhibit the development of *E. coli* and *S. aureus*. It could be concluded that as-prepared coated glazed tiles have the antibacterial potential to decrease air pollution and improve hygiene.

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