Antibacterial persistence of hydrophobically glazed ceramic tiles

Jinho Kim1 · Ungsoo Kim1 · Kyusung Han1 · Junghoon Choi1

Received: 15 March 2022 / Revised: 8 May 2022 / Accepted: 31 May 2022 / Published online: 1 July 2022
© The Korean Ceramic Society 2022

Abstract
The antibacterial properties and durability of copper-glazed ceramic tiles were systematically investigated in detail in terms of the hydrophobicity change with glaze thickness. The water contact angle of the standard glaze without copper was 25.2° ± 0.2°, whereas the copper glaze showed hydrophobicity which was dependent on the glaze thickness. A maximum contact angle of 109.6° ± 0.4° was measured from the copper-glazed surface with thickness of 150–200 μm. As the contact angle and hydrophobicity of the copper glaze increased, the antibacterial efficiency against Staphylococcus aureus and Escherichia coli also increased. An antibacterial efficiency of 99.9% was demonstrated from the copper-glazed sample with the thickness of 150–200 μm. In addition, it was confirmed that 99.9% of the antibacterial efficiency of the copper-glazed ceramic tiles could be maintained for at least 2 years. In ion dissolution measurements of the standard and copper glazes, Ca, Na, Si, and K ions were observed, and Cu ion dissolution was only observed from the copper glaze. These results suggest that the hydrophobicity and strongly negative surface charge, which were contributed from Cu addition into the glaze composition, could block the access of bacteria to the glaze surface, and bacterial killing via Cu ion dissolution occurs.

Keywords Antibacterial · Copper glaze · Ceramic tile · Hydrophobic · Surface properties

1 Introduction
Ceramic tiles made from natural raw materials such as clay, limestone, and pottery stone are fabricated by means of a firing process at > 1000 °C and are used as construction materials for interiors and exteriors owing to their excellent mechanical strength, chemical resistance, and surface glaze esthetics. Research on functional ceramic tiles, such as tiles with antibacterial, anti-pollution, and heat-insulating properties, is being actively conducted [1–6]. In particular, the recent COVID-19 pandemic is expected to increase the market demand for ceramic tiles that are effective in killing bacteria and viruses. The utilization of ceramic tiles with antibacterial properties as key building materials for private homes and public buildings could become a major means of preventing the spread of disease by inhibiting bacterial infection or colonization.

Ceramic tiles have a glassy surface glaze coating layer, and their commercial value can be increased by realizing esthetic value as well as various functionalities for the surface glaze. There are two ways to realize antibacterial properties for ceramic tiles. The first is to coat the surface glaze with an antibacterial material, and the second is to include the antibacterial material in the surface glaze composition [7–20]. Conventional antibacterial porcelains are prepared by coating the surface glaze with a polymer solution or nano metal oxide (ZnO, CuO) sol that has sterilizing properties. The use of such ceramic tiles, however, is limited due to the additional processing required and their poor antibacterial durability. In addition, the killing of bacteria using an antibiotic has the side effect of contributing to increasing bacterial resistance. Antibacterial ceramics based on photocatalysts have limited applications because they require UV light irradiation. In addition, photocatalysts undergo irreversible phase transitions during firing processes at temperatures over 1000 °C, which degrade their antibacterial properties [13, 14]. Recently, research on improving antibacterial properties by inducing superhydrophobicity on the surface of inorganic materials such as metals and ceramics has gathered momentum [2–4, 21–26]. The antibacterial activities of some superhydrophobic metal and ceramic surfaces may occur via inhibition of bacterial adhesion and prevention of the formation of thick biofilms on the substrate surface.
rather than via the destruction of either the bacteria or the bacterial surface film.

Copper glazes, which contain copper oxide, are traditional porcelain glazes, and it is known that a crystalline phase is formed during surface glazing, depending on the heat treatment conditions, resulting in various color changes [18–20, 27–29]. In particular, Cu and Cu alloys are solid antimicrobial materials registered with the US Environmental Protection Agency and are widely used in the development of antibacterial products. Our group reported that oxidation and reduction heat treatment conditions affect antibacterial properties and hydrophobicity when copper oxide or metallic copper is added to traditional porcelain glazes [18–20, 36]. Reinosa et al. reported that water repellency and antibacterial properties were realized by adding iron oxide and copper powder to the surface glaze of ceramic tiles [30]. However, excellent antibacterial properties are known to exist when superhydrophobic surfaces with contact angles of over 150° are realized for plastics, metals, and ceramics, and mild hydrophobicity does not guarantee high antibacterial efficiency for a substrate. Also, reports on the durability of the copper glaze applied to the ceramic tile surface have not been confirmed so far.

In this study, the effects of surface properties and copper ion dissolution on the antibacterial properties of glazes were systematically investigated for ceramic tiles manufactured by industrial processes. The surface properties of the copper glaze including the contact angle, glossiness, roughness, and surface zeta potential were analyzed corresponding to the glaze thickness. Moreover, copper-glazed ceramic tiles were installed in a public bathroom, and antibacterial persistence evaluation was performed for 2 years. Staphylococcus aureus (S. aureus, gram-positive) and Escherichia coli (E. coli, gram-negative), which are commonly found in humid indoor environments, were used to study the antibacterial properties of the copper-glazed ceramic tiles.

2 Materials and methods

Ceramic tile specimens were prepared by spray coating an engobe and a copper glaze to the surface of the ceramic body in turn, and then using a roller hearth kiln to perform a fast-firing process. The tile body is composed of 21 wt% clay, 13 wt% limestone, 40 wt% pottery stone, 13 wt% pyrophyllite, and 13 wt% white clay, and the engobe is a mixture of 60 wt% frit, 23 wt% buyeo feldspar, 15 wt% Edgar Plastic Kaolin (EPK), and 2 wt% zircon. The surface glaze was prepared by mixing frit (92 wt%) and EPK (8 wt%), and then copper powder was added (3 wt%, based on the total weight). Table 1 shows the chemical composition analysis results for the frit and EPK used to prepare the surface glaze. The body of the ceramic tile specimen was prepared by uniaxially pressing granules of the starting materials and using a spray dryer (EYERA SD-1000) with a metal square mold (60 mm × 60 mm) to form the tile shape. The glaze was spray-coated on the surface of the specimen body by mixing the solid content of the starting material with distilled water at a ratio of 65 wt%, and then the coated surface was dried for 3 h. In addition, the thickness of the copper surface glaze was varied in the range of 50–250 μm by controlling the spray coating time. For reference, the thickness of the standard surface glaze was adjusted between 150 and 200 μm. Fast-firing conditions for the production of ceramic tile specimens require a maximum temperature of 1110 °C and a residence time of 48 min.

X-ray fluorescence (XRF, ZSX-Primus, Rigaku) was used to perform a chemical analysis of the starting material, and the particle sizes and crystal structure were determined using particle size analysis (PSA, LA-950V2, Horiba), X-ray diffraction (XRD, D-Max 2500, Rigaku), and field-emission scanning electron microscopy (FE-SEM, JSM-6390, JEOL). Hot-stage microscopy was used to analyze the thermal behavior of standard glazes and copper glazes, and a maximum temperature of 1050 °C and a heating rate of 10 °C/min were used. The contact angle and gloss of the surface glaze were measured using a surface tension meter (DST-60, Surface Electro Optics) and a glossmeter (Rivers Park II 9104, BYK Gardner), respectively. In addition, confocal laser microscopy (OLS40-SU, Olympus) was used for surface roughness measurement and 3D imaging of the surface glaze. The chemical resistance, abrasion resistance, and frost resistance of the ceramic tile specimens were evaluated according to the KS L 1001 (Ceramic tiles) standards. The chemical resistance was evaluated by observing the change in the surface glaze after immersing the ceramic tile specimen in 3% HCl solution or NaOH solution for 8 h. To evaluate the abrasion resistance, after mounting a ceramic tile specimen at an angle of 45° to the test device, 10 kg of standard abrasive powder (SiC) was dropped on the surface over a period of 8 min, then the change in weight was measured, and a final weight change of less than 0.1 g

Table 1 XRF analysis of kaolin and frit used as raw materials

|        | SiO₂ | Al₂O₃ | CaO | K₂O | Na₂O | MgO | ZrO₂ | ZnO | B₂O₃ | Others |
|--------|------|-------|-----|-----|------|-----|------|-----|------|--------|
| Kaolin | 44.46| 37.12 | 2.41| 0.69| 0.73 | 0.43| –    | –   | –    | 14.16  |
| Frit   | 54.41| 6.96  | 9.26| 4.21| 3.20 | 2.70| 6.42 | 5.81| 6.36 | 9.49   |

Others: included ignition loss
was considered to be the criterion for passing the test. The frost resistance was evaluated by observing the change in the surface glaze after immersing the ceramic tile specimen in room temperature water for 24 h, then maintaining it in a −20 ± 3 °C freezer for more than 8 h, and finally immersing it in water at room temperature for 6 h. To analyze the dissolution behavior of the glaze, the ceramic tile specimen was immersed in distilled water at 20 °C for 24 h, and then the water was extracted and measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 5300DV, PerkinElmer, USA). The zeta potential of the surface glaze was measured using a zeta potential analyzer (ELSZ, Otsuka Electronics, Japan) after immersing a ceramic tile specimen in a 10 mM NaCl solution injected with monitor particles for 1 h.

The antibacterial properties of the surface glaze were evaluated according to the JIS Z 2081/ISO 22196 standard method. After inoculation of the glazed surface with *S. aureus* ATCC 6538P and *E. coli* ATCC 8739 bacteria, microorganism growth inhibition and the bactericidal properties of the glazed surfaces were evaluated. The antibacterial activity $R$ was obtained as follows:

$$ R = \left[ \log \left( \frac{B}{A} \right) - \log \left( \frac{C}{A} \right) \right], $$

where $R$ is the antimicrobial activity, $A$ is the average number of viable bacterial cells immediately after inoculation of the untreated test specimen, $B$ is the average number of viable bacterial cells on the untreated test specimen after 24 h, and $C$ is the average number of viable bacterial cells on the antimicrobial test specimen after 24 h. The antibacterial efficiency (%) of the ceramic tile against the two bacteria was evaluated as 99.9% if the $R$ value was two or more.

$$ \% = (1 - 10^{(−R)}) \times 100. $$

Antibacterial activity and antibacterial efficiency were measured as average values for the six specimens. In addition, to evaluate the antibacterial persistence of the ceramic tiles, 10 ceramic tile specimens were attached to an aluminum frame and mounted on the wall of a public toilet to simulate the conditions of use for the tiles, and their antibacterial properties were evaluated every 6 months for a total of 2 years.

### 3 Results and discussion

Figure 1 shows the results of the analysis of the copper powder and copper glazes (5 wt% metallic copper) added to the surface of the ceramic tiles. From the FE-SEM images shown in Fig. 1a, it was confirmed that the copper powder consists principally of leaf-like microscopic structures of 15–30 μm in size, with 30–90 nm primary particles also present. It is known that metal particles with sizes of several to tens of nanometers exist in this luster glaze, but in such nanoparticles have a strong tendency toward agglomeration, making it difficult to apply the material as a component of industrial glazes. To ensure the dispersibility of the metal nanoparticles in the glaze, in one study nano-sized copper and zirconia particles were dispersed in sepiolite nanofibers and applied to the surface glaze of ceramic tiles [4, 31]. The copper powder used in the experiment reported here was in the form of combined primary particles with a size of several tens of nanometers, and because the average particle size is 17.39 μm, the powder can be used without pretreatment in the surface glaze. The XRD analysis indicated the absence of any phases in the copper powder used in the experiment of than the copper phase. Figure 1b shows the thermal behavior of the standard and copper glazes (5 wt% metallic copper) as determined via hot-stage microscopy. The difference in the softening points and thermal behaviors of the standard and copper glazes is a cause of the formation of cracks in
the glaze during the sintering process. In Fig. 1b, it can be seen that the softening point and spheroidization point of the standard glaze were 821 and 979 °C, respectively, which are very similar to the results for copper glaze (softening point: 828 °C, spheroidization point: 981 °C). Therefore, it was confirmed that the sintering conditions of standard glazes can be applied to glazes with added copper powder.

Figure 2 shows the XRD results of the standard glaze and the copper glazes with thicknesses in the range of 50–250 μm. For the standard glaze, diopside (CaMgSi2O6) and zircon (ZrSiO4) phases were observed and a broad peak indicating the amorphous phase was measured at 2θ values of 20°–30°. However, in the copper glaze, across the entire thickness range, although an amorphous phase and a zircon phase were still observed, a tenorite (CuO) phase was observed instead of the diopside phase. In this glaze, copper exists in various forms, depending on the firing temperature and atmosphere. In an oxidizing atmosphere, the copper source dissolved in the glaze exists as Cu\(^{2+}\) and is precipitated as CuO, which makes the glaze appear green [18–20, 33]. In the XRD analysis, the ratio of the intensities of the zircon peak, \(I_z\) at 27°, and the CuO peak, \(I_C\) at 35°, \(I_z/I_C\), was measured as a function of the thickness of the copper glaze, and the lowest value, 1.46, was observed at the thickness of 150–200 μm. It is known that the intensity of the CuO peak on the copper glaze surface increases because copper cations with high mobility in the glass matrix move toward the surface as the thickness of the glaze increases, which facilitates oxidation [32].

Figure 3 and Table 2 illustrate the effects of the change in the thickness of the copper glaze on the surface properties. The standard glaze has a thickness of 100 μm, similar to that of commercial ceramic tiles, and the copper glaze was spray coated at various thicknesses from 50 to 250 μm and fast-fired at 1050 °C. In Fig. 3a, the standard glaze appears milky-white in color and is highly glossy. Indeed, the whiteness and gloss were measured to be 86.2 ± 0.2 and 63.1 ± 0.1 GU, respectively. The copper glaze appears green for the
specimens of each thickness, and there is a significant difference in gloss depending on the glaze thickness. In general, it is known that metallic copper added to a glaze is present in the form of Cu$_2$O or as Cu nanoclusters under reducing-atmosphere firing conditions, and it appears red, whereas under oxidative-atmosphere firing conditions, it is present in the glaze as CuO crystals and appears green [18–20, 33–35]. As the copper glaze thickness increased, the gloss increased, and at a thickness of 150–200 μm, the gloss was 64.3 ± 0.2 GU, which is similar to that of the standard glaze. However, for the 200–250 μm thick copper glaze, gray areas were observed on the surface, and elemental analysis confirmed that copper did not exist in the glaze and was precipitated onto the surface. Confocal laser microscopy analysis (Fig. 3b) revealed that the surface roughness of the copper glaze was greatly affected by the change in glaze thickness, with a similar trend being observed as was seen for the gloss. The surface roughness of the copper glaze was found to be lowest (0.145 ± 0.0015 μm) at the 150–200 μm thickness, for which the best gloss properties were observed; the roughness value is very similar to that measured for the standard glaze (0.143 ± 0.0012 μm). Figure 3c shows 2D images of the surface topology in which the height of the surface glaze is expressed in terms of brightness. As the thickness of the copper glaze increases, cellular structures begin to appear in these images, and it can be confirmed that the most distinct cellular structure is observed for the 150–200 μm thickness glazes. The development of cellular structures on the surface of copper glaze may induce a situation in which the Cassie–Baxter model can be considered appropriate, and the Lotus effect may also occur, which could explain the origin of the superhydrophobicity of the surface [37]. It has been reported that the change in the copper-glazed surface microstructure with glaze thickness is the result of local reflux due to the sudden temperature difference between the surface and the inside of the glaze during cooling step of the fast-firing process [4, 38, 39]. In Table 2, the contact angle of the standard glaze is 25.2° ± 0.2° at the 50–100 μm thickness, for which the best gloss properties were observed; the roughness value is very similar to that measured for the standard glaze (0.143 ± 0.0012 μm). Figure 3c shows 2D images of the surface topology in which the height of the surface glaze is expressed in terms of brightness. As the thickness of the copper glaze increases, cellular structures begin to appear in these images, and it can be confirmed that the most distinct cellular structure is observed for the 150–200 μm thickness glazes. The development of cellular structures on the surface of copper glaze may induce a situation in which the Cassie–Baxter model can be considered appropriate, and the Lotus effect may also occur, which could explain the origin of the superhydrophobicity of the surface [37]. It has been reported that the change in the copper-glazed surface microstructure with glaze thickness is the result of local reflux due to the sudden temperature difference between the surface and the inside of the glaze during cooling step of the fast-firing process [4, 38, 39]. In Table 2, the contact angle of the standard glaze is 25.2° ± 0.2°, which indicates that the silica-based glaze is hydrophilic. As the copper glaze thickness increased, peaking at 109.6° ± 0.4° at 150–200 μm thickness. However, for the 200–250 μm thick copper glaze, the contact angle decreased to 66.3° ± 1.2°, and no lotus microstructure was observed.

Figure 4 reports the evaluation of the antibacterial properties of the standard and copper glazes. As shown in
been reported in many previous studies, and much research has been conducted on the effects of surface properties such as surface roughness and the hydrophobicity of metal and ceramic substrates on antibacterial properties [12, 21–23]. In Fig. 4a, it can be seen that the antibacterial efficiency of the copper glaze increases as the surface contact angle increases, despite the fact that the Cu content does not change. Oxide glazes with ionic bonding structures are typically hydrophilic because oxygen ions exist on the surface, and water molecules adsorbed on the surface are easily decomposed to form OH groups [22]. In contrast, copper glazes are able to exhibit antibacterial properties because the cellular structure of the glaze surface increases the contact angle. Figure 4b shows the results of antibacterial persistence for 2 years for ceramic tiles coated with a copper glaze with a thickness of 150–200 μm. In general, organic antibacterial agents have excellent antibacterial properties and can be applied to various products but are known to have low antibacterial persistence. In this study, to evaluate the antibacterial persistence of the copper glaze with a thickness of 150–200 μm in an environment similar to that for which the use of the tile is envisaged, 10 specimens of ceramic tiles (5 × 5 cm) were attached to an aluminum frame and mounted on the wall of a public toilet, and the antibacterial properties of their copper glaze were evaluated every 6 months for 2 years. It was confirmed (Fig. 4b) that the antibacterial efficiency of the copper glaze was maintained at 99.9% against both S. aureus and E. coli bacteria, even after 2 years. In addition, after 2 years, the contact angle, surface roughness, and gloss of the copper glaze were measured to be 108.7° ± 0.2°, 0.146 ± 0.021 μm, and 62.9 ± 0.3 GU, respectively, indicating that there was almost no change in these properties over the course of 2 years. Therefore, it was concluded that the copper glaze surface properties, such as contact angle, roughness, and gloss, have excellent durability, and the antibacterial persistence of the glaze is also excellent.

Figure 5 and Table 3 show the results of ion dissolution and surface zeta potential analyses of the standard glaze and the copper glazes of various thicknesses. In Fig. 5a, it is apparent that Ca, Na, Si, and K ions were observed in the ion dissolution results for all the glazes, and Cu ions were observed only for the copper glaze. In particular, the Ca ion yield was greatest, and the other ion yields decreased in the order Na > K ≅ Si. The total ion dissolution amounts for the standard and copper glazes were measured to be 0.25–0.32 ppm, and the dissolution of copper ions did not appear to have a significant effect on the total amount of ion dissolution. In the evaluation of antibacterial properties (Fig. 4), it can be seen that the standard glaze without copper ion dissolution has an antibacterial efficiency of 0%, so the dissolution of ions other than Cu ions did not affect the antibacterial activity toward S. aureus and E. coli bacteria. Additionally, it can be seen that the content of all dissolved ions including Cu ion was hardly affected by the glazed thickness. This is because most of the ions measured through ion dissolution test (immersion in distilled water for 24 h) are dissolved from the surface of the glaze. The surface zeta potentials of the standard and copper glazes were measured to be −7.2 mV and −12.4 to −17.4 mV, respectively (Fig. 5b), and no correlation was seen between the copper glaze thickness change and the zeta potential. Both S. aureus and E. coli bacteria have negative zeta potentials, and it is known that gram-negative bacteria (E. coli) have more negative charges than gram-positive bacteria (S. aureus) [40, 41]. The antibacterial copper glaze exhibits a surface zeta potential with a negative value of < −12 mV, so electrostatic repulsion occurs between the copper glaze and bacteria. Therefore, the hydrophobicity and surface zeta potential of the copper glaze both inhibit the formation of S. aureus and E. coli bacterial colonies on the glaze surface, conferring antibacterial activity. In general, inorganic substrates that are
superhydrophobic and have a surface contact angle of 150° or more are known to show excellent antibacterial properties, whereas our copper glaze exhibits an excellent antibacterial efficiency of 99.9% despite the surface being only mildly hydrophobic (contact angle, ~100°). The excellent antibacterial properties of this mildly hydrophobic copper glaze are attributed not only to its surface properties, which block bacterial access, but also to the dissolution of Cu ions, which kill bacteria adsorbed on the surface of the glaze.

In Table 4, the chemical, abrasion, and frost resistances of ceramic tiles with the standard glaze and copper glaze (150–200 μm) were conducted in accordance with KS L 1001 (Ceramic tile) standards, and it was confirmed that the physical properties of all the specimens met the standards. In conclusion, ceramic tiles with copper glazes manufactured via industrial processes have excellent antibacterial efficiency and persistence for at least 2 years, as well as excellent mechanical properties, and can be used as materials for building interiors.

### 4 Conclusion

A copper-glazed ceramic tile with 5 wt% metallic copper was manufactured by an industrial process, and the effects of the thickness of the copper glaze on the surface properties and antibacterial properties were investigated. The copper powder used in this experiment was in the form of combined primary particles with sizes of several tens of nanometers, and because the average particle size was 17.39 μm, the copper can be applied without pretreatment as an ingredient of the surface glaze. Copper glazes with thicknesses of 50–250 μm appear green after fast-firing, and XRD analysis results show that the glaze thickness affects the diffraction intensity of the tenorite (CuO) phase. The thickness of the copper glaze influences its surface properties; as the thickness increases, the surface becomes hydrophobic owing to the development of cellular structure, and the highest contact angle of 109.6 ± 0.4° is exhibited for the thickness of 150–200 μm. For the antibacterial evaluation of the copper glaze, *S. aureus* (gram-positive) and *E. coli* (gram-negative) bacteria, which are commonly found in humid environments, were used, and the antibacterial efficiency of the standard glaze without copper was measured to be 0%. However, the copper glaze exhibited antibacterial properties for all the tile specimens, and the antibacterial efficiency increased with the glaze thickness. The copper glaze with a thickness of 50–100 μm had antibacterial efficiencies against *S. aureus* and *E. coli* of 74.8% and 61.2%, respectively. Further, at 150–200 μm, the antibacterial efficiency was measured to be 99.9% against the two types of bacteria. In addition, it was confirmed that copper-glazed ceramic tiles have excellent antibacterial persistence, with the 99.9% antibacterial efficiency being retained after 2 years of installation in a realistic environment. During ion dissolution testing, Ca, Na, Si, and K ion dissolution was detected for both the standard glaze and the copper glaze, and Cu ion dissolution was observed only for the copper glaze, confirming that Cu ions contribute to antibacterial activity. The antibacterial copper glaze exhibits a zeta potential with a negative value of < −12 mV, and hence electrostatic repulsion occurs between the copper glaze and bacteria. Therefore, the hydrophobicity and surface zeta potential (< −12 mV) of the copper glaze together inhibit the formation of colonies of *S. aureus* and *E. coli* bacteria on the glaze surface, and this is one of the origins of the observed antibacterial activity. In addition, a high antibacterial efficiency of 99.9% was measured for the copper glaze, because copper ion dissolution kills bacteria adsorbed on the surface. Copper-glazed ceramic tiles have excellent chemical resistance, abrasion resistance, and
frost resistance values that satisfy the KS L 1001 (ceramic tile) standards. In conclusion, copper-glazed ceramic tiles manufactured using industrial processes have excellent antibacterial efficiency and persistence for 2 years, as well as excellent mechanical properties, and they can be used as materials for building interiors.

Acknowledgements This research was carried out as a ceramic strategy technology development project (KPP19002) supported Korea Institute of Ceramic Engineering and Technology (KICET). Also, this work was supported by the Technology Innovation Program (20010483, Key technology development of porcelain ceramic with high energy efficiency) funded by the Ministry of Trade, Industry and Energy.

References

1. M.P. Seabra, L. Grave, C. Oliveira, A. Alves, A. Correia, J.A. Labrincha, Porcelain stoneware tiles with antimicrobial action. Ceram. Int. 40(4), 6603–6670 (2014)
2. S. Ozcan, G. Acikbas, N.C. Acikbas, Induced superhydrophobic and antimicrobial character of zinc metal modified ceramic wall tile surface. Appl. Surf. Sci. 348(30), 136–146 (2018)
3. J.J. Reinoso, M.M. Rojo, A. Campo, M. Martin-Gonzalez, J.F. Fernandez, Highly efficient antimicrobial ceramics based on electrically charged interfaces. ACS Appl. Mater. Interfaces 11(42), 39254–39262 (2019)
4. J.J. Reinoso, J.J. Romero, P. Jaquotot, J.F. Fernandez, Copper based hydrophobic ceramic nanocoating. J. Eur. Ceram. Soc. 32(2), 277–282 (2012)
5. C.C. Sun, Z.J. Hu, T.Q. Li, H.B. Zhang, Z.J. Sun, Z.G. Zhang, Preparation and properties of ceramic tiles for heat insulation. Mater. Sci. Forum 546–549, 2157–2162 (2007)
6. M. Marangoni, B. Nait-Ali, D.S. Smith, M. Binhussain, P. Colombo, E. Bernardo, White sintered glass-ceramic tiles with improved thermal insulation properties for building applications. J. Eur. Ceram. Soc. 37(3), 1117–1125 (2017)
7. S. Niederhausern, M. Bondi, Self-cleaning and antibacterial ceramic tile surface. Appl. Ceram. Technol. 10(6), 949–956 (2013)
8. N. Baheiraei, F. Moztarzadeh, M. Hedayati, Preparation and antibacterial activity of Ag2SiO3 thin film on glassed ceramic tiles by sol–gel method. Ceram. Int. 38(4), 2921–2925 (2012)
9. A.L. Silva, M. Dondi, M. Raimondo, D. Hotza, Photocatalytic ceramic tiles: challenges and technological solutions. J. Eur. Ceram. Soc. 38(4), 1002–1017 (2018)
10. K. Tongsuriwong, P. Amornpitoksu, S. Suwanboon, Structure, morphology, photocatalytic and antibacterial activities of ZnO thin films prepared by sol–gel dip-coating method. Adv. Powder. Technol. 24(1), 275–280 (2013)
11. O. Akhavan, E. Ghaderia, Cu and CuO nanoparticles immobilized by silica thin films as antibacterial materials and photocatalysts. Surf. Coat. Technol. 205(1), 219–223 (2020)
12. G. Acikbas, N.C. Acikbas, Copper oxide- and copper-modified antibacterial ceramic surfaces. J. Am. Ceram. Soc. 105, 873–887 (2022)
13. I. Krivtsov, M. Ilkaeva, V. Aydin, Z. Amghouz, S.A. Khainkiv, J.R. Carcia, E. Diaz, S. Ordonez, Exceptional thermal stability of undoped anatase TiO2 photocatalysts prepared by a solvent-exchange method. RSC Adv. 5(46), 36634–36641 (2015)
14. R. Fagan, D.E. McCormack, S.J. Hinder, S.C. Pillai, Improved high temperature stability of anatase TiO2 photocatalysts by N, F, P doping. Mater. Des. 96(15), 44–53 (2016)
15. Y. Kato, N. Isu, S. Yamazaki, A. Nakahira, C. Numako, N. Saito, O. Takai, X-ray absorption fine structure analysis of Ag and Zn in the glaze of antibacterial ceramics. Mater. Res. Soc. Jpn. 33(4), 60–65 (2008)
16. H. Yoshida, H. Abe, T. Taguri, F. Ohashi, S. Fujino, T. Kajiwara, Antimicrobial effect of porcelain glaze with silver-clay antimicrobial agent. J. Ceram. Soc. Jpn 118(1379), 571–574 (2010)
17. T.M. Gross, J. Lahiri, A. Golas, J. Luo, F. Verrier, J.L. Kurzewski, D.E. Baker, J. Wang, P.F. Novak, M.J. Snyder, Copper-containing glass ceramic with high antimicrobial efficacy. Nat. Commun. 3(1), 15–21 (2012)
18. H.G. No, U.S. Kim, K.T. Hwang, Evaluation of antimicrobial activity of red copper glaze. J. Korean Soc. Color Stud. 33(1), 15–21 (2019)
19. U.S. Kim, J.H. Choi, H.G. No, K.S. Han, J.H. Kim, K.T. Hwang, Antibacterial properties of traditional ceramic glazes containing copper Oxide. J. Korean Cryst. Growth Cryst. Technol. 29(6), 372–378 (2019)
20. J.H. Choi, J.H. Kim, K.S. Han, U.S. Kim, Antibacterial behavior of copper glazes: effect of copper(II) oxide concentrations and sintering atmospheres. J. Korean Ceram. Soc. 58(3), 287–296 (2021)
21. B. Li, B.E. Logan, Bacterial adhesion to glass and metal-oxide surfaces. Colloids Surf. B. 36(2), 81–90 (2004)
22. T. Matsumoto, K. Sunada, T. Nagai, T. Isole, S. Matushita, H. Ishiguro, A. Nakajima, Preparation of hydrophobic La2Mo3O9 ceramics with antibacterial and antiviral properties. J. Hazard. Mater. 378(15), 120610 (2019)
23. X. Zhang, L. Wang, E. Levanen, Superhydrophobic surfaces for the reduction of bacterial adhesion. RSC Adv. 3(30), 12003–12020 (2013)
24. A. Berendjchi, R. Khajavi, M.E. Yazdanshenas, Fabrication of superhydrophobic and antibacterial surface on cotton fabric by doped silica-based sols with nanoparticles of copper. Nanoscale Res. Lett. 6(594), 339–360 (2011)
25. B.J. Privett, J. Youn, S.A. Hong, J. Lee, J. Han, J.H. Shin, M.H. Schoenfisch, Antibacterial fluorinated silica colloid superhydrophobic surfaces. Langmuir 27(15), 9597–9601 (2011)
26. C.R. Crick, S. Ismail, J. Pratt, R. Pavan, An investigation into bacterial attachment to an elastomeric superhydrophobic surface prepared via aerosol assisted deposition. Thin Solid Films 519(11), 3722–3727 (2011)
27. D.A. Stocks, Derivation of ancient Egyptian faience core and glaze materials. Antiquity 71(271), 179–182 (1997)
28. J. Molera, C. Bayes, P. Roura, D. Crespo, T. Pradell, Key parameters in the production of medieval luster colors and shines. J. Am. Ceram. Soc. 90(7), 2245–2254 (2007)
29. P. Colomban, H.D. Schreiber, Raman signature modification induced by copper nanoparticles in silicate glass. J. Raman Spectrosc. 36(9), 884–890 (2005)
30. J.J. Reinosan, J.J. Romero, M.A. Rubia, A. Campo, J.F. Fernandez, Inorganic hydrophobic coatings: surfaces mimicking the nature. Ceram. Int. 39(3), 2489–2495 (2013)
31. M. Ambrosi, S. Santoni, R. Giorgi, E. Fratini, N. Toccafondi, P. Baglioni, High-performance and anti-stain coating for porcelain stoneware tiles based on nanostructured zirconium compounds. J. Colloid Interface Sci. 432(15), 117–127 (2014)
32. J.L. Barton, M. Bilby, Diffusion and oxidation of Cu+ in glass. J. Non Cryst. Solids 30–39(2), 523–526 (1980)
33. M. Wakamastu, N. Takeuchi, H. Nagai, S. Ishida, Chemical state of copper and tin in copper glazes fired under various atmosphere. J. Am. Ceram. Soc. 72(1), 16–19 (2005)
34. E.A. Goldstein, R.E. Mitchell, Chemical kinetics of copper oxide reduction with carbon monoxide. Proc. Combust. Inst. 33(2), 2803–2810 (2011)
35. S.F. Brown, F.H. Norton, Constitution of copper-red glazes. J. Am. Ceram. Soc. 42(11), 499–503 (1959)
36. C.S. Choi, K.S. Han, K.T. Hwang, J.H. Kim, Hydrophobic property of surface glaze of ceramic tiles by copper powder addition. J. Korean Cryst. Growth Cryst. Technol. 29(5), 215–221 (2019)
37. S.S. Latthe, C. Terashima, K. Nakata, A. Fujishima, Superhydrophobic surfaces developed by mimicking hierarchical surface morphology of lotus leaf. Molecules 19(4), 4256–4283 (2014)
38. T.N. Dinh, Y.Z. Yang, J.P. Tu, R.R. Nourgaliev, T.G. Theofanous, Rayleigh-Benard natural convection heat transfer: pattern formation, complexity and predictability. Proceedings of ICAPP’04, 4, 1241 (2004)
39. J.H.E. Cartwright, O. Piro, A.I. Villacampa, Pattern formation in solutal convection: vermiculated rolls and isolated cells. Physica A 314(1–4), 291–298 (2002)
40. E. Klodzinska, M. Szumski, E. Dziubakiewicz, K. Hryniewicz, E. Skwarek, W. Janusz, B. Buszewski, Effect of zeta potential value on bacterial behavior during electrophoretic separation. Electrophoresis 31(9), 1590–1596 (2010)
41. M. Arakha, M. Saleem, B.C. Mallick, S. Jha, The effects of interfacial potential on antimicrobial propensity of ZnO nanoparticle. Sci. Rep. 5, 1–10 (2015)