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RESEARCH PAPER

Synthesis of Self-Assembled Ag-ZrO_2 Plant Shape for an Effective Antibacterial Ceramic Application

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ABSTRACT

Zirconia nano plant shape with silver nanoparticles were synthesized by reverse micro emulsion-mediated Sol-gel method with effective antibacterial property suitable for ceramic industry. ZrCl4 and silver nitrate have been used as the major raw materials. TEM studies show that leaves and arms of the antibacterial dendritic would be trapped by the amorphous phase of the glaze, therefore, it would be established into the ceramic appliance. The particle size distribution of leaves of the dendritic were in the full range of 20–150 nanometer. Antibacterial activities of deposited films against S. aureus, Pseudomonas aeruginosa and E. coli on the ceramic tile heat treated at 700 °C and 900 °C have been compared. It can be seen by preparation and antibacterial studies before and after 200 hours in a weathering chamber, that the Silver/Zirconia nano-dendritic composite after heat treated at 700°C exhibits a much reliable antibacterial activity pigment without UV light irradiation, for ceramic application.

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INTRODUCTION

Ceramic appliances are really attractive, decorative, luxury, and variety with excellent chemical durability and widely used in houses. However, ceramic appliances, household ceramic porcelain, and tile are widely varied, but they have almost a joint point that is “glaze” on their surface. Unfortunately, dangerous microorganisms can quickly breed in every moist place, for example, kitchen, hospital, school, hotel, etc. Therefore, preparation and study of the antibacterial pigment for ceramic or coating on the glazed surface are essential [1, 2].

Silver nanoparticles can present antibacterial and even antivirus properties without needing ultraviolet light. Ag^+ on bacteria reacts with its proteins. There are some previous studies described the antibacterial mechanism and how Ag can inactivate the enzymes of proteins of bacteria [1, 3]. Nanosilver doped or composited materials are chemically durable. It can be released silver ion for an appropriate period [4]. Because of the high thermal stability of zirconium dioxide, if silver nanoparticles can be grown in the structure of the ZrO_2 film on the glazed of a ceramic, it would be possible to have a strong stable antibacterial

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efficiency of its surface without UV illumination [5-10].

Nano silver-based or metal-doped TiO_2 pigments or coatings as the eco-friendly products have been synthesized by several methods such as sol–gel processing, liquid phase deposition (LPD), PVD sputtering, reverse micro-emulsion, and etc. [11-16]. Etiemble et al. had an innovation about Zr-Cu-Ag composite coating deposed by magnetron PVD sputtering with antibacterial function. Nkou Bouala et al. have studied Ag-based bio-ceramic films formed on zirconium by micro-arc oxidation and thermal evaporation [17, 18]. Chung-Hsin Lu et al. have studied on photocatalytic activity of the TiO_2 powders by Microemulsion-mediated hydrothermal [19].

Silver self-assemble ZrO_2 nano-dendritic thin films prepared by the LPD method have not been reported for antibacterial applications, up to now. In this research, reverse microemulsion mediated sol-gel route has been employed to control the shape of in-situ formed Ag– ZrO_2 as nano-dendrites. Then, some tiles have been coated by LPD of the as-received gel and calcined at 700°C and 900°C. The structure of the Ag–ZrO_2 gel before calcination and after coating (after calcination) were studied by TEM, SEM, and antibacterial tests.

MATERIALS AND METHODS

Reverse microemulsion synthesis

Self-assemble ZrO_2 nano-dendritic composited with silver nanoparticles were synthesized by the

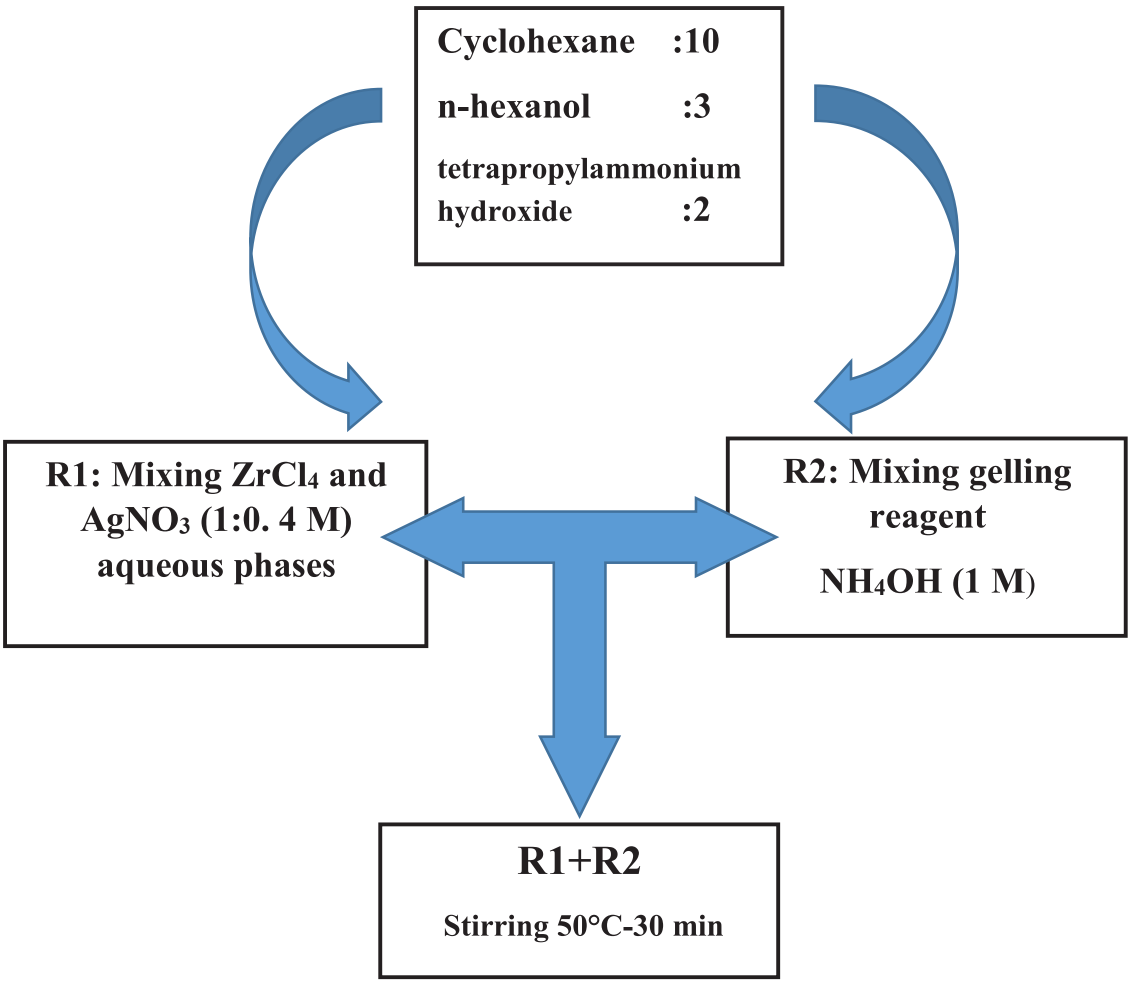

Fig. 1. The synthesis procedure of Ag–ZrO_2

reverse microemulsion-mediated sol-gel method. This method can control the particle size and morphology by reducing the time and temperature of reaction in comparison to the conventional sol-gel process.

The synthesis procedure can be seen in Fig. 1. The precursor of self-assemble ZrO_2 nano-dendritic composited with silver nanoparticles nominated nano-dendritic remained in the down layer of microemulsion that was separated by decanting.

Preparation and characterization of Ag/ZrO_2 films

The nano-dendritic gel was coated on the pieces of 50 × 50 mm^2 of a glazed tile by the LPD method [1] and located in a desiccator for 2 min. In order to compare the antibacterial activity, all the coated tiles were calcined at 700 and 900°C for 60 min.

Microstructures of synthesized gel and the coated tile were studied by several techniques such as: Transmission electron microscopy (TEM, 90KV EM 208 Philips) and scanning electron microscopy (SEM, CM 120 Philips), and Energy-dispersive X-ray spectroscopy (EDS, TESCSN, MIRA3, Czech). The hybridized bonding of the synthesized gel was studied by Fourier transform infrared spectrophotometer (FT-IR, PerkinElmer, USA, 400 cm^{-1} to 4000 cm^{-1}).

Antibacterial property of the coated tiles

The antibacterial properties of the tiles coated by LPD against S. aureus ATCC: 6538, Pseudomonas aeruginosa ATCC: 27853, and E. coli ATCC: 25922 were studied based on international standard ISO 22196-2011 (without UV lamp application) that so-called "Assessment of antibacterial activity. The mentioned bacteria were used at a concentration of 1.6×10^8 CFU/ml.

The 0.5 McFarland of S. aureus ATCC: 6538, Pseudomonas aeruginosa ATCC: 27853 and E. coli ATCC: 25922 were prepared. The microbial suspensions were contacted with each LPD ceramic tiles and control tiles for 24 h. The bacteria were studied after treatment with specific media and incubated at 37°C for 37 h.

The stability of the antibacterial activity of the Ag–ZrO_2 nano-dendritics films on the ceramic tiles after 700°C annealing temperature was tested in a weather chamber (Xeno test Atlas Electric Device Co., Chicago, USA Model beta LM). The simulated solar irradiation was activated at the coated tiles with an intensity of 120 w/m2 at 340 nm.

The antibacterial study on the tiles was done after 200 hours in the Xeno test weather chamber. The antibacterial activities of the LPD ceramic tiles before and after weathering treatment have been compared.

Temperature effect

As mentioned in the text, one of the main challenges of the present study is to achieve the optimal synthesis temperature. The factores that allow Ag/ZrO_2 nanodentrite to diffuse sufficiently so maintain the optimal temperature.

Diffuse in Glaze

Glazes do not have a specific melting temperature and turn into a thick liquid at different temperatures. Modifier materials in glaze (such as Na_2O, K_2O) reduce the melting point. NaO_2 and K_2O are effective melting aids and play an important role in reduction of the melting temperature. They are also effective in increasing the coefficient of expansion and reducing the surface tension. SiO_2 has a high melting point but in the presence of molten oxides is reducing the melting temperature, so lowering the temperature due to the reducing effect of NaO_2 and K_2O leads to increase the viscosity and reduce the emission.

Antibacterial Properties

Temperature is another critical parameter because depending on the temperature range, the microbes reproduce, become dormant, or die. Hence, it was found that each microorganism has a minimum temperature at which the membrane gels and the transport processes of the microbes are so slow that their growth cannot occur; an intermediate range of temperature at which the enzymatic reactions take place at a maximum rate. A maximum temperature from which the denaturation of the proteins occurs because the membranes of the cells collapse and their lysis process takes place. Denaturation is usually due to the breaking of bonds such as hydrogen bonds in the membranes. It is worthy to mention that these bonds are more easily broken by humid heat (in an atmosphere saturated with water vapor), because water molecules can displace hydrogen bonds. For this reason, moisture is another critical aspect of microorganisms' survival, and the higher the presence of water, the lower the bond-breaking temperature.

RESULTS AND DISCUSSION

TEM studies

Figs. 2a and 2b show TEM images of the sample Ag–ZrO_2 synthesized by reverse microemulsion mediated sol-gel route in different magnifications, it presents self-assembled nano-dendritics, clearly. The specific surface area of ZrO_2 particles was effective on the antibacterial activity of Ag-ZrO_2 nano-dendritic.

As the sol-gel temperature was elevated up to 50°C, the morphology of the ZrO_2 particles changed from a rod-like shape into a polyhedral shape

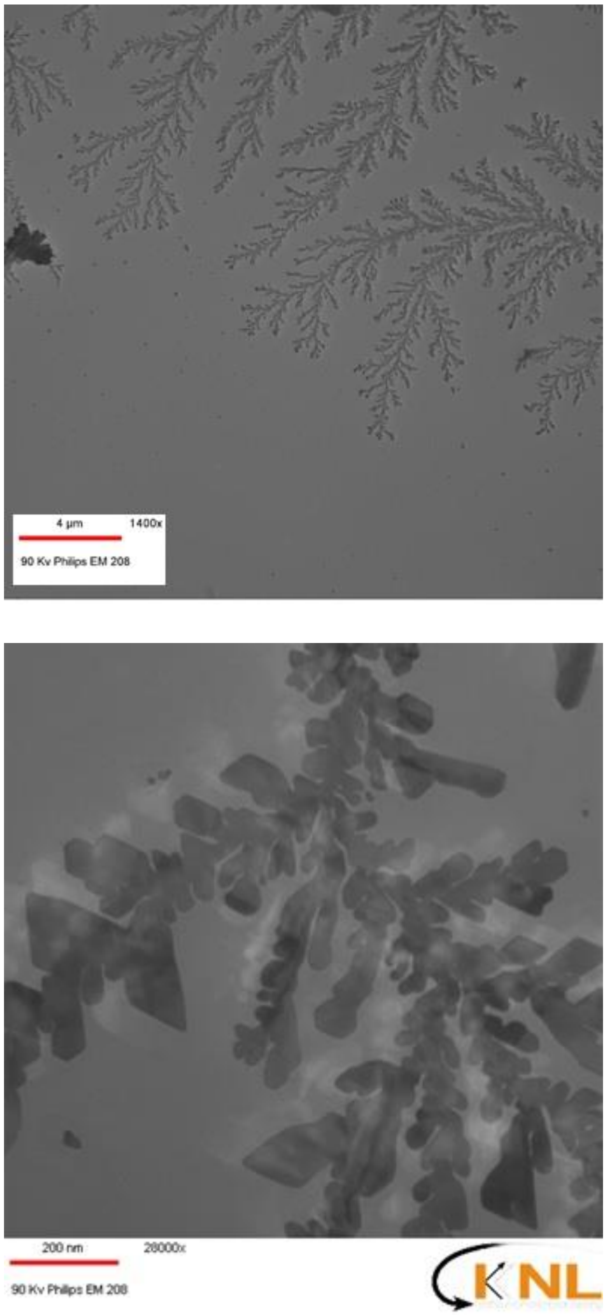

Fig. 2. TEM images in different magnification of the sample Ag–ZrO_2 prepared by reverse microemulsion mediated Sol-gel route.

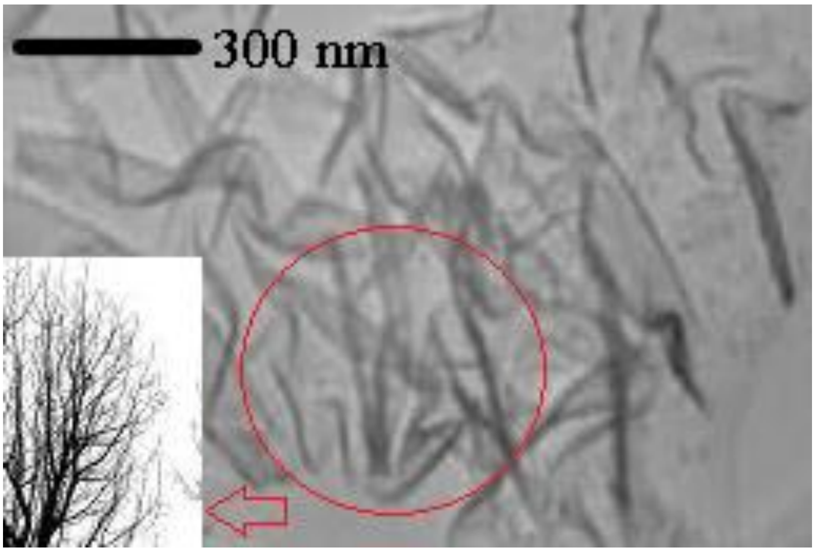

Fig. 3. TEM images of the some rubbed particles from surface of deposited glaze of ceramic tile heat treated at 700 °C

similar to a plant. The particle size distribution of leaf sectors is observed in the range of 20–150 nm.

Fig. 3 illustrates a microstructure of some rubbed particles from the surface of a deposited glaze of ceramic tile heat-treated at 700 °C. As seen, there are some convoluted arms in the glaze matrix related to the successful diffusion of self-assembled nano-dendritic Ag– ZrO_2, but these arms were tending to dissolve in the glaze matrix at the higher temperature 900 °C (Fig. 4). It will be considered that dissolving of the Ag–ZrO_2 nano-dendritic is effective on the antibacterial activity of the ceramic tiles in the next section.

SEM images

SEM images just can show the surface of the

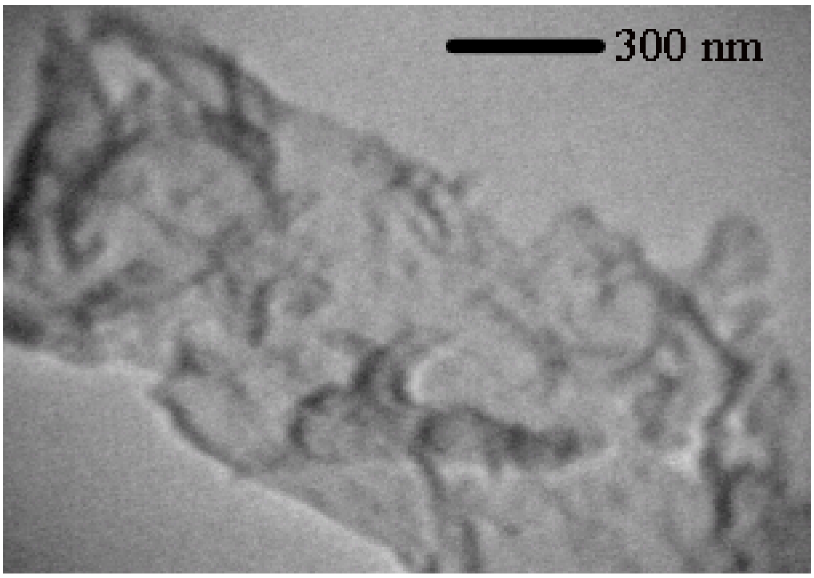

Fig. 4. TEM images of the some rubbed particles from surface of deposited glaze of ceramic tile heat treated at 900 °C

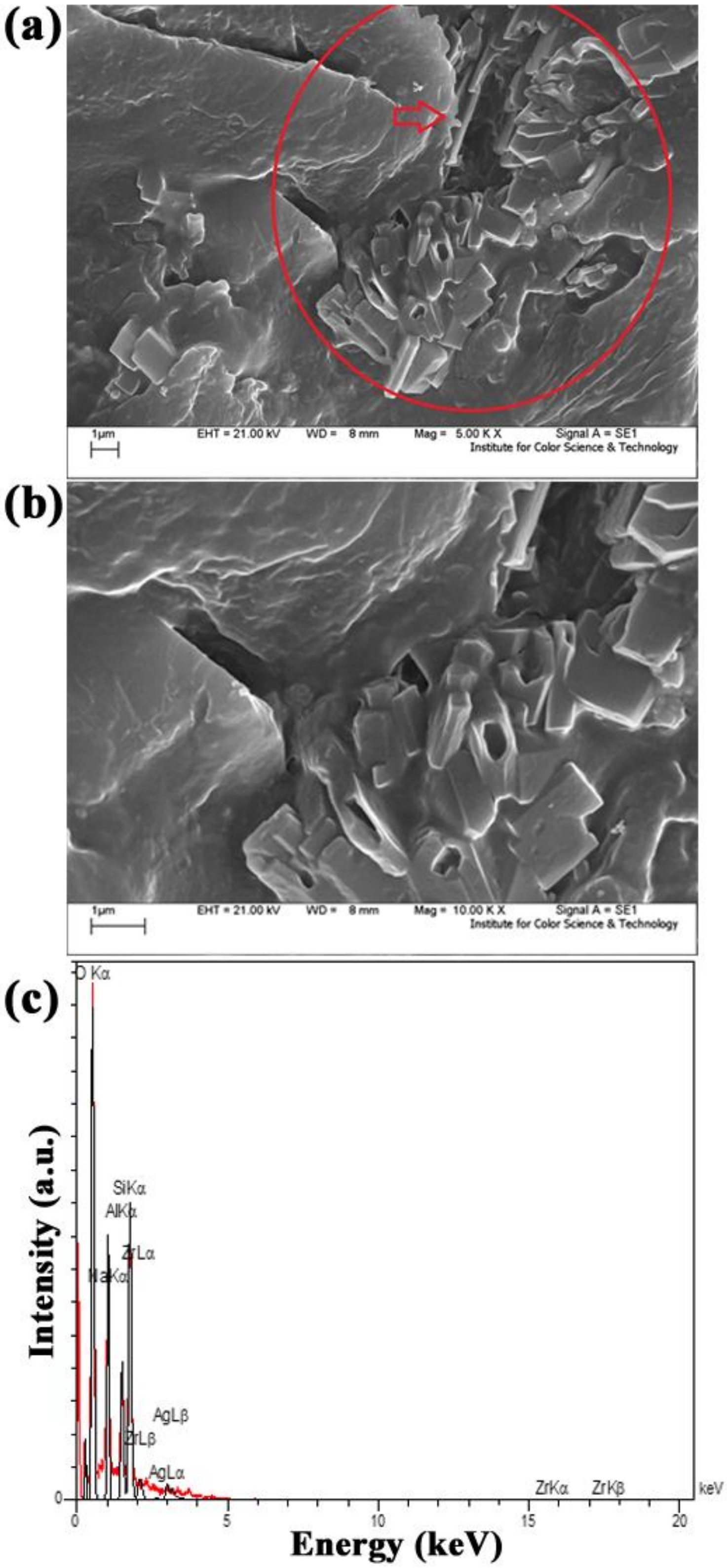

Fig. 5. a, b) SEM images of the surface of deposited glaze of ceramic tile heat treated at 700 °C, and c) EDS point of the leaf center into the glaze.

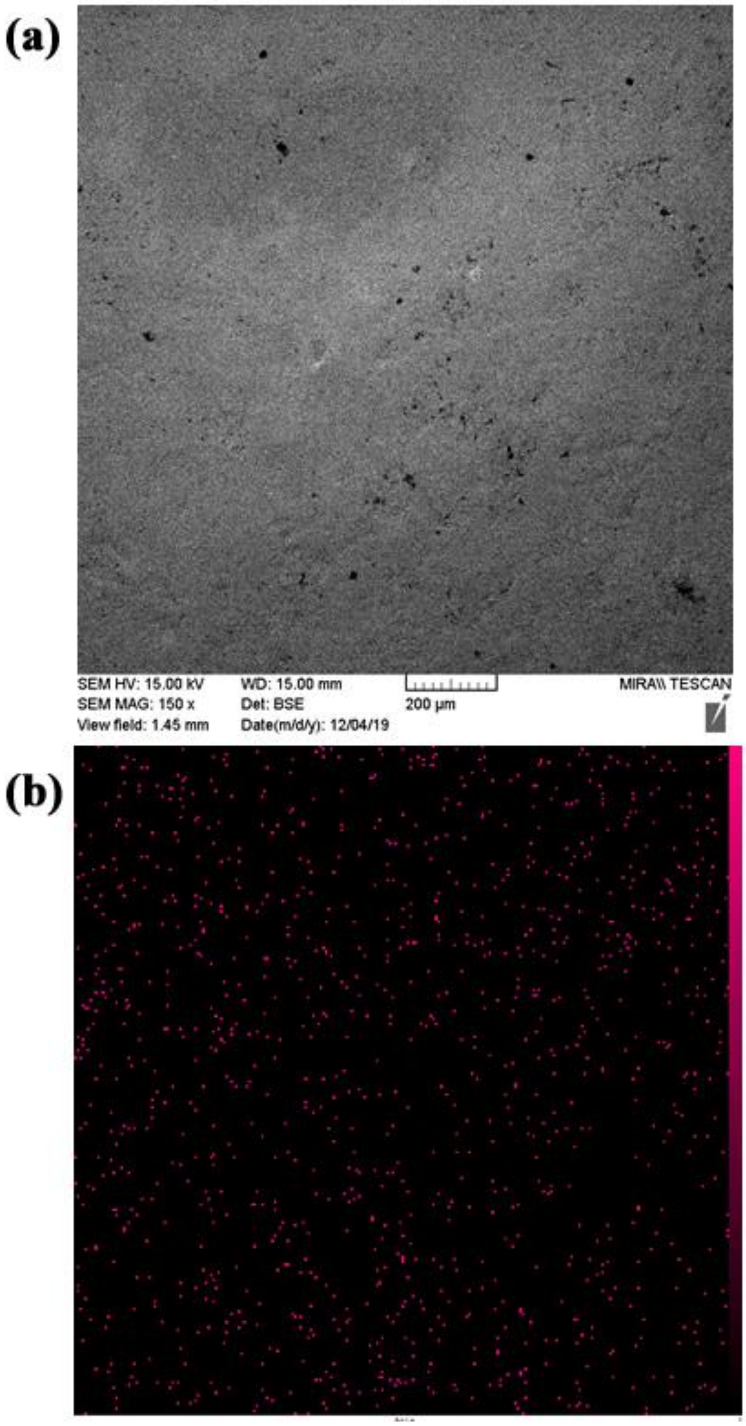

Fig. 6. FESEM of the surface of deposited glaze of ceramic tile heat treated at 700 °C a) Image, b) Ag map

glaze, and there was some difficulty to identify the location of antibacterial nano-dendrites in the matrix of glazed tiles because they would be covered by glaze, therefore by SEM, it cannot see well images. By the way, it can be seen in Fig. 5a and b (related to microstructures of the surface

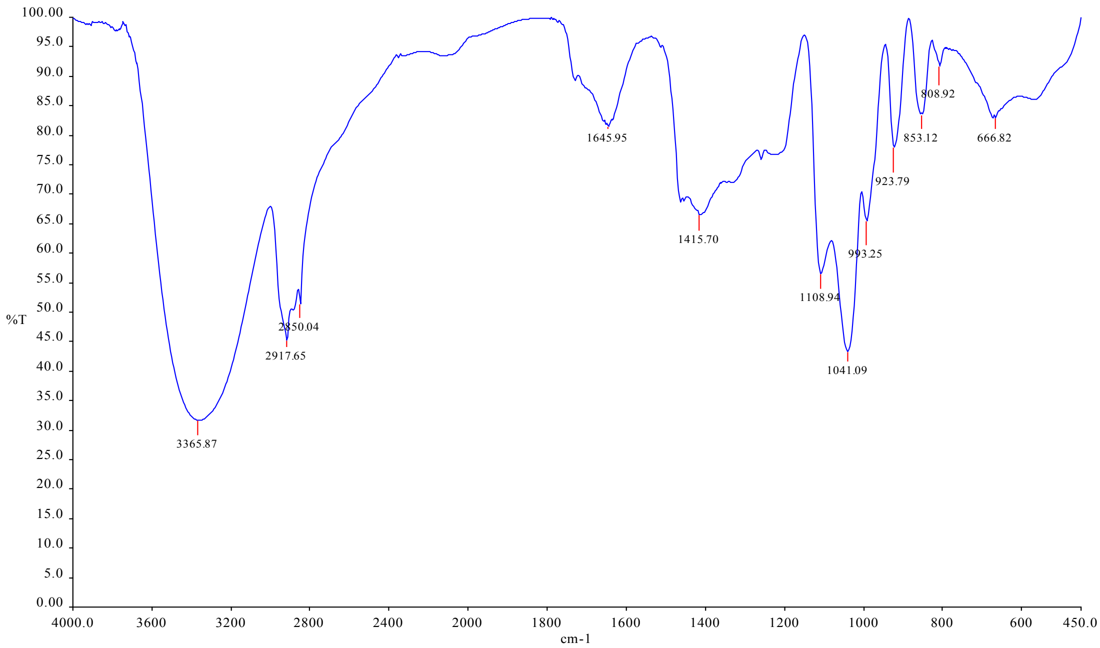

Fig. 7. IR spectra of the gel without heat treated.

of a deposited glaze of ceramic tile heat-treated at 700 °C) some locations similar to arms of a plant. Fig. 5c is related to the EDS point of the leaf center and confirmed the presence of nanosilver occluded by hybrid zirconia rods. It is obvious that Si, Al and Na elements have been detected because of the glaze.

In order to verify of the homogenous presence of antibacterial agent (nanosilver) in the surface of the antibacterial tile, EDS mapping on the surface of the deposited glaze of ceramic tile heat treated at 700 °C was done (Fig. 6).

FT-IR analyses

Fig. 7 shows the IR spectra of the gels prepared in the range of 400–4000 cm^{-1} without heat-treatment. It can be seen the strong band at 1630 cm^{-1} and some weak bands at 1460 cm^{-1} due to residual organic surfactants. 2,928 cm^{-1} bands are related to C-H stretching.

The broad absorption peak appearing near 3400 cm^{-1} is observed because of a stretching vibration of the O–H group. The high intensity of O–H peak is related to water existing in the obtained gel [20-24]. A strong bond at 1079 cm^{-1} is related to the Zr-OH group, and the weak peaks about 800 cm^{-1} to 471 cm^{-1} may be related to Zr-O and or Ag bonding.

XRD pattern

Fig. 8 shows the X-Ray diffraction of the gels prepared after drying at 100 °C for 5 hours. Because wet gel without drying process presents an amorphous form and after heat-treating appears a weak monoclinic structure of ZrO_2 in crystal form of Baddeleyite. Baddeleyite is a rare zirconium oxide (ZrO_2 or zirconia). It is transparent to translucent, has high indices of refraction, and ranges from colorless to yellow. It is obvious that the Ag weight present is lower than XRD detection.

Antibacterial activities

The antibacterial activities of the deposited films containing Ag–ZrO_2 self-assembled nano-dendritic on the ceramic tile heat-treated at 700 °C (sample Tile1) and 900 °C (sample Tile2) were presented in Tables 1 and 2, respectively. To confirm, it was studied several Gram-positive bacteria and Gram-negative bacteria more than the committal standard (aureus ATCC: 6538, Pseudomonas aeruginosa ATCC: 27853, and E. coli ATCC: 25922) on the ceramic tile heat-treated at 700 °C (sample Tile1 was given in Table 1). 0.5 McFarland (1.6 × 108 CFU/mL) of microorganisms

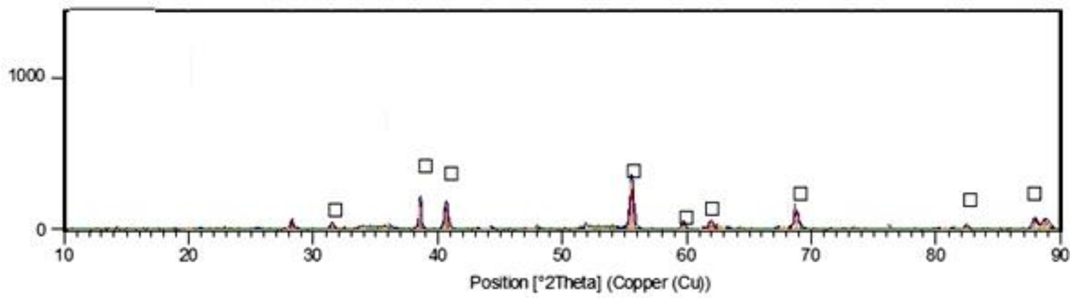

Fig. 8. X-Ray diffraction of the gels prepared after drying at 100 °C for 5 h.

was prepared. Then, the microbial suspension was in contact with the surface of samples for 24 h, and it was next, after culturing on specific media and incubating at 37 °C for 72 h. The results of antibacterial activities were studied.

According to the antibacterial results, tiles 1 and 2 have antibacterial activity against both Gram-negative and Gram-positive bacteria. However, inhibition of Gram-positive bacteria is more complicated than Gram-negative bacteria, but this product represented that can inhibit the Gram-negative and Gram-positive bacteria growth. It

Table 1. Antibacterial activities of deposited films (Ag–ZrO_2 Self-assembled nano-dendritic) on the ceramic tile heat treated at 700 °C (sample Tile1).

Name of Test Bacteria	Concentration of Bacteria(CFU/ml)	The Number of Bacteria Recovered From		
		Groups	Contact Time at (0 hours)	Contact Time at (48 hours)
Gram-positive bacteria				
Bacillus cereus	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1
Corynebacterium pseudodiphteriticum	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	10
Enterbacter faecalis (VRE)	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1
Staphylococcus aureus	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1.6×10^3
Staphylococcus epidermis (MRSA)	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1.6×10^3
Gram-negative bacteria				
Escherichia coli (E. Coli)	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1
Acinetobacter baumannii	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1
Klebsiella pneumoniae	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1.6×10^2
Pseudomonas aeruginosa	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1
Salmonella choleraesuis (Salmonella)	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1

Table 2. Antibacterial activities of deposited films (Ag–ZrO_2 Self-assembled nano-dendritic) on the ceramic tile heat treated at 900 °C (sample Tile2).

Name of Test Bacteria	Concentration of Bacteria(CFU/ml)	The Number of Bacteria Recovered From		
		Groups	Contact Time at (0 hours)	Contact Time at (48 hours)
Gram-positive bacteria				
Staphylococcus aureus	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	3.2×10^7
Gram-negative bacteria				
Escherichia coli (E. Coli)	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	3.2×10^8
Pseudomonas aeruginosa	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	3.2×10^8

Table 3. Antibacterial activities of deposited films (Ag–ZrO_2 Self-assembled nano-dendritic) on the ceramic tile heat treated at 700 °C (sample Tile1) after Xeno test weathering.

Name of Test Bacteria	Concentration of Bacteria(CFU/ml)	The Number of Bacteria Recovered From		
		Groups	Contact Time at (0 hours)	Contact Time at (48 hours)
Gram-positive bacteria				
Staphylococcus aureus	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1.6×10^4
Gram-negative bacteria				
Escherichia coli (E. Coli)	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1.5×10^2
Pseudomonas aeruginosa	1.6×10^8	Control	1.6×10^8	3.2×10^8
		Sample	1.6×10^8	1.5×10^2

is obvious that the antibacterial activity of an antibacterial agent is more than their activity as a film on the glaze surface (and based on previous research) [2, 26-29]. As shown, the annealing temperature is important for antibacterial activities, and in section 3.1, antibacterial agents tend almost to dissolve in the ceramic glaze at a higher temperature, and therefore these phenomena are expected. On the other hand, high annealing temperature caused variation in microstructures decreased the specific surface area of the Ag–ZrO_2, and lowered the antibacterial activity.

Weather chamber (Xeno test) for study on antibacterial stability

In order to produce an antibacterial ceramic with high stable antibacterial property, it is essential to know that is not coefficient just the synthesis and preparation of an antibacterial pigment, but also two other important terms have to be considered too:

1-The antibacterial pigment, agent, or film with high or sufficient thermal stability have to diffuse into the glaze surface of the antibacterial ceramic [6, 10, 25, 26].

2- Identification of the best temperature: because a lower temperature is not coefficient for diffusing into the glaze and making a strong film interface. An upper temperature will be destructive for antibacterial activity [2, 12, 23].

Five samples of the tile 1 (Ag–ZrO_2 nano-dendritic films ceramic tile after 700°C annealing temperature) were tested in a weather chamber (Xeno test Atlas Electric Device Co., Chicago, USA Model beta LM). During the test, a water spray was activated. The simulated solar irradiation was directed at the film surface with an intensity of

120 w/m² at 340 nm. After 200 h, then the samples were dried and subjected to an antibacterial test. The antibacterial activity of the film after weathering as shown in Table 3. It can be realized that the antibacterial activity of tile 1 is a little reduced but acceptable.

CONCLUSION

A reverse microemulsion-mediated route was employed to synthesize a dendritic shape zirconium dioxide (ZrO_2)-nanosilver composite pigment with excellent antibacterial activity. ZrO_2 sol-gel derived precursors were followed by the deposition of silver nanoparticles on the surface of the in-situ synthesized leaves of plant shaped zirconia. Morphology of the ZrO_2 particles changed from a rod-like shape into a polyhedral shape. The particle size distribution of leaves of the plant was approximately in the wide range of 20–150 nm. TEM studies showed that leaves and arms of the antibacterial plant can be diffused into the ceramic glaze of tiles at a high temperature. Antibacterial activities of deposited films (Ag–ZrO_2 self-assembled nano-dendritic) on the ceramic tile heat-treated at 700 °C (sample Tile1) after Xeno test weathering are durable. In the present study, the optimum temperature for the antibacterial properties of ceramic glaze was 700 °C. It can be concluded that the Ag/ZrO_2 nano-dendritic composites have useful permanent antibacterial activity pigment without needing of UV light irradiation, for ceramic application.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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