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Antibacterial Activity of ZnO Nanoparticles Coated on Ceramic Tiles Prepared by Sol-Gel Method

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Abstract

Zinc oxide nanoparticles on silica matrix thin films were prepared by the sol-gel method and dip coating on ceramic tiles. In this study, EC (ethyl cellulose) and TP (alpha-terpineol) used as a binder and a solvent in sol-gel method, respectively, were studied on the characteristics of thin films. The thin films were dried and calcined at the temperature of 500°C and 600°C soaking 30 min with the heating rate of 1°C/min. The result of glancing X-ray diffraction showed that thin films were ZnO phase on the amorphous phase of silica matrix. Scanning electron microscope showed the ZnO nanoparticles dispersed on thin films and depended on the concentration of EC and TP. The antibacterial activity test on Gram positive (*Escherichia coli*) and Gram negative (*Staphylococcus aureus*) bacteria were evaluated that films have good photocatalytic under UV irradation, and also exhibited high antibacterial activity under repeating for 3 times. As mentioned above, ZnO nanoparticles on thin film can be applied on ceramic tiles for antibacterial activity by using photocatalytic process for eco-friendly, low cost and easy for preparation.

Keywords: ZnO thin film; ZnO nanoparticle; Antibacterial activity; Photocatalytic process; Sol-gel method

Introduction

Zinc oxide exhibits many properties such as semiconducting, antibacterial, antifugal and UV filtering properties[1-4,10]. The antibacterial activity of ZnO thin film has been studied in many researches. The antibacterial properties is given to bactericidal and bacteriostatic mechanisms with focus on generation of reactive oxygen species (ROS)[5]. ROS has been a major factor for several mechanisms including cell wall damage due to ZnO-localized interaction, enhancing membrane permeability, internalization of nanoparticle due to loss of proton motive force and uptake of toxic dissolved zinc ions. These can lead to mitochondria weakness, intracellular outflow, and release in gene expression of oxidative stress, which caused eventual cell growth inhibition and cell death. Ceramic tiles are construction products, which is close to human life. ZnO thin film on ceramic tiles may be a good choice to increase value with antibacterial activity[6].

In the present study, Zinc oxide nanoparticles on silica matrix thin films were prepared by sol-gel method and coating on ceramic tiles. The effect of EC (Ethyl cellulose) and TP (Alpha-terpineol) contents for sol-gel coating, the annealing temperature from 500-600°C were determined on morphology, chemical structure and their antibacterial activity in water.

Materials and Experimental Procedures

Materials

Chemical precursors were synthesized from alpha-terpineol (TP, $C_{10}H_{18}O$, Acros, 97%, ethyl cellulose (EC, CH_2CH_3, Acros, 48%), tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, Acros, 98%, absolute ethanol (C_2H_5OH, Carlo Erba, 99%) as

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starting agents of silica sol-gel. Zinc oxide nano powders, (ZnO, Nanoscience Technology Co., Ltd, 95.5%) used as photocatalytic materials on thin films.

Thin film preparation and testing

The TP and EC concentrations in the sol-gel preparation were varied as shown in Table 1. The concentration of TEOS was prepared by dissolving 5 mL TEOS into 1.5 mL of absolute ethanol. All precursors were mixed all together and stirred at 60°C for 30 min. Then, 0.5 wt% of zinc oxide nano powders were dispersed in solution under stirring at 60°C for 1 h and then aging at room temperature for 24 h to obtain the coating sol. ZnO dispersion gel was deposited on the cleaned ceramic tiles of 1 × 1 in^2 by dip-coating method for 5 s. After coating, the films were dried at 60°C for 24 h and annealed at 500°C and 600°C for 30 min in air.

Table 1. The variations of sol-gel compositions.

Code	Ethyl cellulose (wt%.)	Alpha-terpineol (wt%.)	Annealing Temp. (°C)
EC1-TP3-T500	1	37.5	500
EC1-TP3-T600			600
EC2-TP3-T500	2		500
EC2-TP3-T600			600
EC3-TP3-T500	3		500
EC3-TP3-T600			600
EC1-TP5-T500	1	56.2	500
EC1-TP5-T600			600
EC2-TP5-T500	2		500
EC2-TP5-T600			600
EC3-TP5-T500	3		500
EC3-TP5-T600			600

The structural identification of the thin films was carried out using a Glancing X-ray diffractometer (XRD, BRUKER, D8) with Cu Kα radiation at a wavelength of 1.5406 Å[7]. The morphology of the thin films surface was determined by a scanning electron microscope (SEM, Zeiss AURIGA). Bacterial gram positive (*Staphylococcus aureus)* and gram negative (*Escherichia coli*) were streaked onto nutrient broth (NB) and incubated overnight at 37°C. Bacterial of 2.9×10^8 CFU/mL were pipetted in 100 mL water. The ZnO coated tiles were put into the water under UV light. After irradiating every 15 min (15, 30, 45 and 60 min)., 1 mL of water was collected and diluted to spread on the NB agar plate[8]. Plates were incubated at 35°C for 24 h. The result was compared to the control without any thin films. The survival bacterial colonies were counted and the antibacterial activity was calculated by equation 1[9].

$$\textit{Antibacterial activity} = (N/N_o) \times 100 \qquad (1)$$

Where N and N_o are the number of survival bacteria and the number of the bacteria before irradiations.

Results and Discussion

Viscosity of the silica gels

The viscosity of the silica gels was determined by using Brookfield method (Brookfield AMETEK, LV spindle set) as shown in Figure 1. The gel of EC3TP3 and EC3TP5 showed the high viscosity as compared to the others. The viscosity was controlled by the EC concentration. However, the gel viscosity could be adjusted by increasing of the TP concentration for diluting the solution of the sol-gel method.

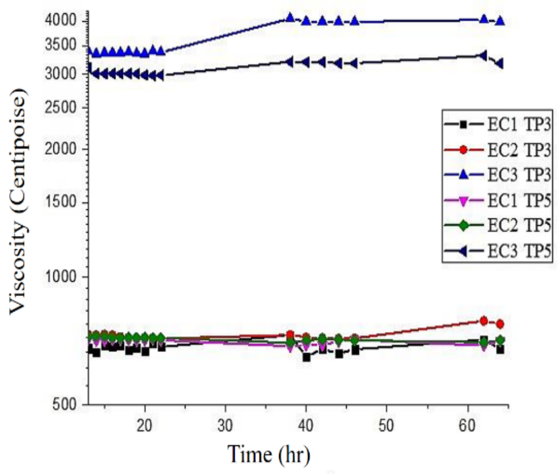

Figure 1. The relationship between the viscosity of the different gels during the aging time.

Structure and morphology

Figure 2. Shows XRD patterns of the ZnO nanoparticles on silica thin films with different concentrations of EC and TP as well as annealing temperatures.

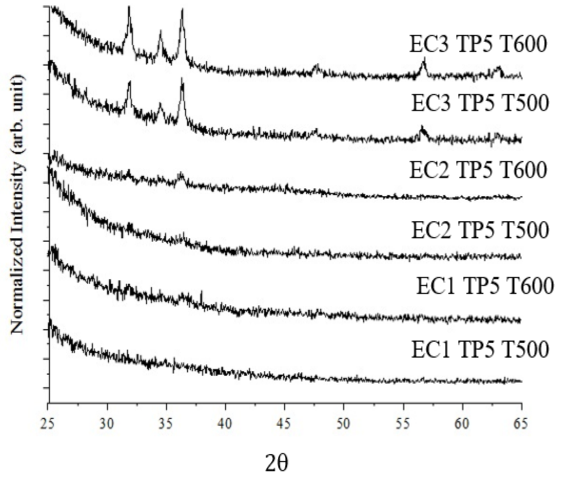

Figure 2. XRD patterns of the ZnO nanoparticles on silica thin film with different EC and TP concentrations annealed at 500 and 600°C.

Antibacterial activity

It indicated that the thin films were amorphous silica and the characteristic diffraction peaks ZnO with hexagonal wurtzite phase (JCPDS No. 36-1451)[(1)] appeared in EC3TP5 annealed at 500°C and 600°C. SEM images in Figure 3 shows that surface coating with variation of EC and TP concentrations. It can be seen clearly that ZnO nanoparticles dispersed on surface of EC3TP5 coating. The ZnO nanoparticles appeared on the coating with increasing the EC concentration as a binder enhancing the adhesive while ZnO nanoparticles disappeared with increasing of TC concentration as a solvent encouraging the dispersion of ZnO nanoparticles. Moreover, the adhesive of ZnO nanoparticles could be improved with the higher annealing temperature from 500°C to 600°C. Therefore, the dispersion of ZnO nanoparticles on thin film depended on EC and TP concentration ratio and annealing temperature.

EC3TP5 thin film was selected for the antibacterial activity testing because of appearance of ZnO nanoparticles on surface. The percentage of *S.aureus* and *E.coli* survival in the water with EC3TP5 thin film at different annealing temperatures were demonstrated in Figures 4-5. It indicated that the percentage of bacterial survival decreased continuously with the irradiation time. The annealing temperature of the thin film at 600°C showed the higher effective of antibacterial activity than that of 500°C for both gram-positive and gram-negative bacterial.

Figure 6 shows the antibacterial activity of EC3 TP5 annealed at 600°C against Gram-negative (*Escherichia coli)* and Gram-positive *(Staphylococcus aureus)* bacteria after repeated testing until 3 times. The results also demonstrated that the bacterial inhibition trended to decrease when repeated testing to 3 times.

The antibacterial activity of EC3TP5 annealed at 600°C showed higher effective against gram-positive bacteria than gram-negative. Moreover, the durability of EC3TP5 annealed at 600°C showed better than that of annealed at 500°C due to the strong adhesive of ZnO nanoparticles.

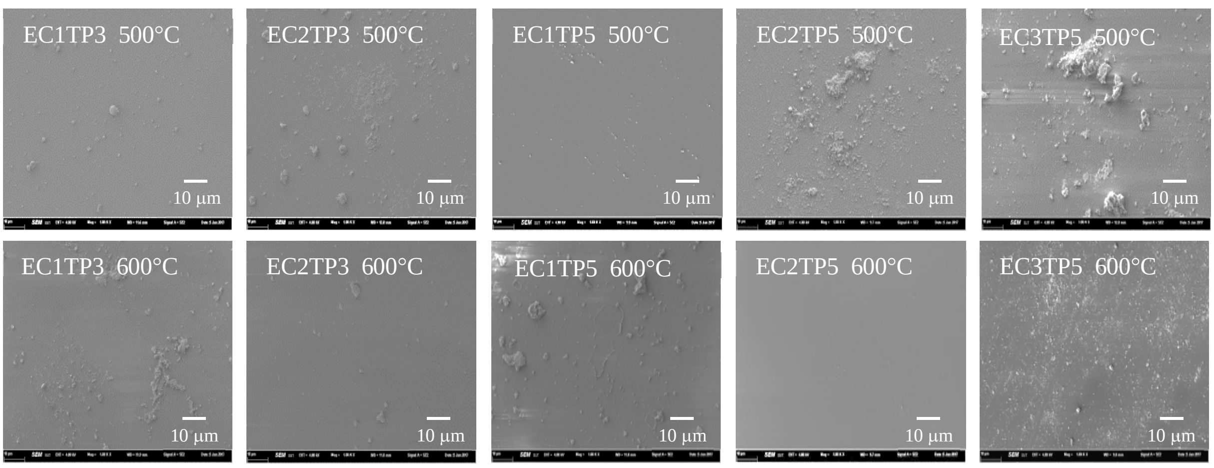

Figure 3. SEM images of the thin films prepared from the different EC and TP concentrations (×1000).

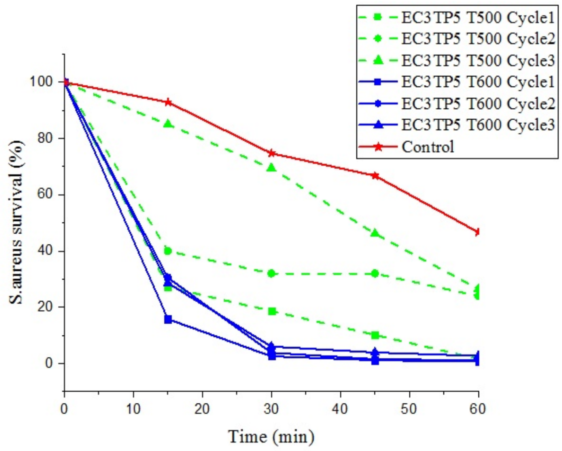

Figure 4. Gram-positive (*Staphylococcus aureus*) bacteria survival for EC3TP5 film annealed at 500°C and 600°C under repeated testing.

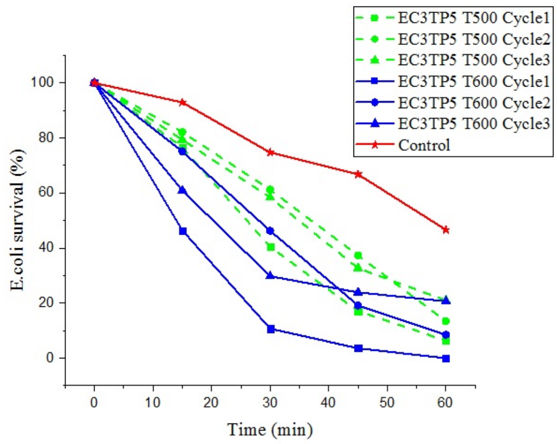

Figure 5. Gram-negative (*Escherichia coli*) bacteria survival for EC3TP5 film annealed at 500°C and 600°C under repeated testing.

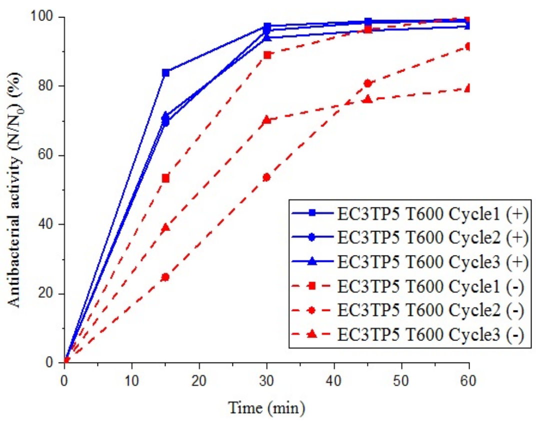

Figure 6. The antibacterial activity test on Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) bacteria under repeated testing.

Conclusions

In this study, 0.5 wt% ZnO nanoparticle dispersed on silica thin films were prepared by the sol-gel dip coating method. EC (Ethyl cellulose) and TP (Alpha-terpineol) were used as a binder and a solvent in sol-gel method. The increasing of EC concentration in the silica gel was related to high viscosity and good adhesive on substrate surface. On the other hand, the high TP concentration decreased the viscosity and improve dispersion of ZnO nanoparticles on surface coating. ZnO nanoparticles on silica thin film showed the antibacterial activity against both on Gram negative (*Escherichia coli*) and Gram positive (*Staphylococcus aureus*) bacteria. Therefore, the antibacterial activity is related to the amount of ZnO nanoparticles adhered on the film surface. ZnO nanoparticle dispersed on thin film prepared by sol-gel method can be coated on ceramic tiles and annealed at 600°C presented the effective antibacterial activity and durability.

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