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Novel route to prepare TiO_2-coated ceramic and its photocatalytic function

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Since it was found that irradiation of TiO_2 with UV-light induced active electron-hole pairs, TiO_2 photo-catalysis has been successfully used to purify water, air [1], to degrade the organic pollutants [2], and to kill bacteria [3]. The application based on use of powder form of TiO_2, however, is limited, because it is not convenient to separate powders from the appliance. The TiO_2 coating materials are now being extensively studied; they are expected to play roles in deodorizing, antibacterial, and self-cleaning etc. in live environments [4, 5].

Presently, the most common method to prepare TiO_2-coated materials is the sol-gel process. The process consists of a hydrolysis of the titanium alkoxide such as tetrabutoxide in a mixture of water/ethanol; a stable sol solution can be obtained by careful control of the experimental parameters. The substrate was then coated TiO_2 via dip-coating technique and heat-treatment [6, 7]. The TiO_2 film obtained by sol-gel method was very thin; it needs to repeat the cycle from dipping to heat treatment more than 10 times to obtain 1 μm thickness film [8]. In this paper, a novel method to prepare TiO_2-coated ceramic plates is reported. The photocatalysis test showed that the TiO_2-coated ceramic plate so formed, can sterilize the Escherichia coli (E. coli) under either irradiation of mercury lamp, or the room daylight.

The nanometer TiO_2 was prepared by hydrolysis with $TiO_2{\cdot}(H_2O)_n$, a low-cost raw material, the details of the processing has been reported elsewhere [9]. The nanometer TiO_2 powders were first dispersed in polyvinyl alcohol aqueous solution via supersonic method. The TiO_2 concentration of the suspension solution thus formed was 2%. The commercial ceramic plates (dishes, tiles) were cleaned and dried. Coating the ceramic plate by dip-coating it in this solution one time at an ambient atmosphere, the withdrawal speed was 3 mm^{-1}, drying the plate in air to form TiO_2 film on the surface, then the coated ceramic plates were placed in a furnace and heat-treated at 700–800 °C for different time durations.

The crystalline structure of TiO_2 in the glaze layer was characterized by X-ray diffraction (XRD, *D*/max-ray) with a Cu K_α radiation under an applied voltage of 40 kV and a current of 50 mA. The particle size of the TiO_2 powder was measured by transmission electron microscope (TEM, Hitachi H-8100). The morphology of TiO_2 in the glaze layer and the thickness of the TiO_2 film were studied by scanning electron microscope (SEM, Hitachi X-650). The light source used in this research is a high-pressure mercury lamp (125 W). The light intensity was measured by a UV irradiance meter (model UV-A), peak wavelength is 365 nm.

The photocatalytic activity of the TiO_2-coated ceramic plates was tested through sterilization of E. coli. The experiment details were as follows: The TiO_2-coated ceramic plates were sterilized in an oven at 120 °C for 60 min to prevent E. coli contamination. 1 mL of E. coli (DH5α) suspension solution [4] approximately 2×10^{10} colony forming units (CFU)/mL was diluted with the TYN solution (1% tryptone, 0.5% yeast extract, 1% NaCl). E. coli cell concentration was adjusted to the required final concentration approximately 10^4 cells/mL 0.1 ml cell suspension solution and 1 ml TYN solution were pipetted onto ceramic plates (TiO_2-coated and blank), spread out to give a liquid film of approximately 10 cm^2, it was then illuminated, or placed in dark environment. The illumination conditions are (1) with 125 W Hg lamp from up, the light intensity at the working ceramic surface was 0.1 mW/cm^2; (2) natural daylight in room for 4 h without direct sunlight beam irradiation, the light intensity at the working ceramic surface was 0.07–0.10 mW/cm^2. Sampling ceramic plates were taken out after illumination and were washed using 1 mL TYN solution, the washing solution was plated on LB agar plate, and counting colonies that appeared after 24 h incubation at 37 °C.

Fig. 1 is the TEM image of TiO_2 powder, used in this research. The particle size is in the range of 50–100 nm. Fig. 2 shows the thickness of the TiO_2 film on the surface of ceramic plate dried at room temperature. The thickness of film would be adjusted by the concentration of polyvinyl alcohol aqueous solution. Figs 3 and 4 demonstrate the evolution of the surface morphology of the TiO_2 film during calcinations. When the TiO_2 film was just dried at room temperature, it can be seen that the TiO_2 particles are well dispersed in the film and retain their tiny size (Fig. 3). The heat-treatment results in particles aggregation. Heat-treatment at 700 °C will bring significant particles aggregation and growth. A network-like microstructure is observed (Fig. 4a). In these coating layers (700 °C), the TiO_2 particles had not been fixed firm on the glaze. They are easy to be scratched and erased. Treated at 800 °C for 20 min (Fig. 4b), TiO_2 particles begin to fix on the top surface

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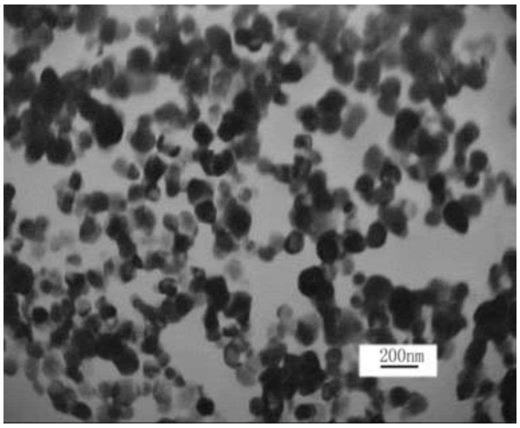


Figure 1 TEM image of TiO_2 powder.

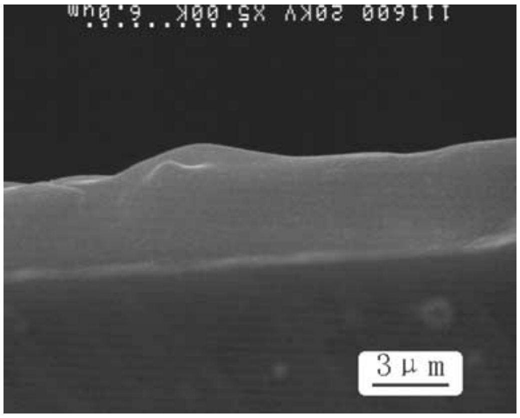


Figure 2 The thickness of the TiO_2 film on the surface of ceramic plate dried at room temperature.

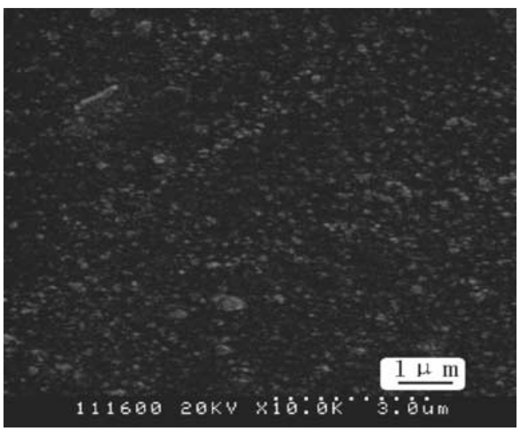
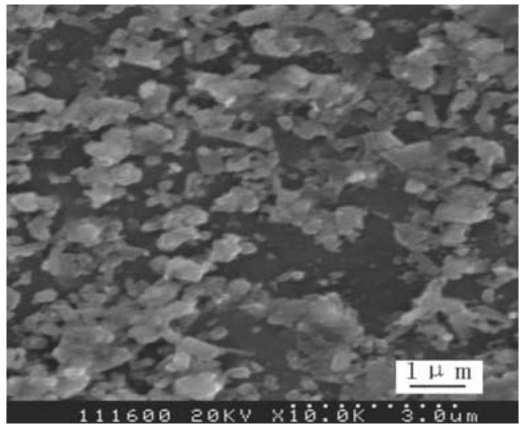
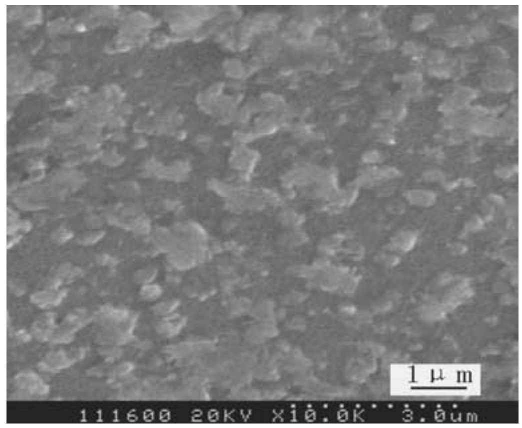


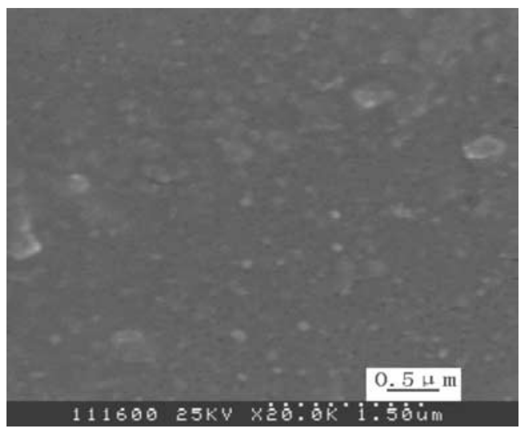
Figure 3 SEM image of TiO_2 film dried at room temperature.



(a)



(b)



(c)

Figure 4 (a) SEM image of glaze surface with TiO_2 film at 700 °C. (b) SEM image of glaze surface with TiO_2 film at 800 °C (20 min). (c) SEM image of glaze surface with TiO_2 film at 800 °C (60 min).

of glaze. The surface of the ceramic plate is gloomy. Increase the duration of treatment, promotes the particles move into the glaze layer. Fig. 4c is the image of glaze surface heat-treated at 800 °C for 60 min. It is observed that the particles of TiO_2 had settled in the inner position of the glaze layer. The surface of the ceramic plate is very bright. The settlement depth of TiO_2 particle in the glaze layer depend on the temperature and time of the heat-treatment, it will influence the photo-catalysis effect of TiO_2-coated ceramic plates. Further detailed research on this issue is still ongoing. Fig. 5 is the XRD pattern of TiO_2 particles in the glaze layer heat-treated at 800 °C. The peak at 25.3 °, belong to the plane (101) of TiO_2 anatase phase, is remarkable on the amorphous background. It indicates the TiO_2 particles in the glaze layer retain the anatase crystalline.

Fig. 6 is the photocatalysis effect of TiO_2-coated ceramic plate (calcined at 800 °C, 60 min) on E.coli under Hg-lamp irradiation condition. The survival ratio of E. coli on the TiO_2-coated ceramic plate in dark condition was not affected, indicating the TiO_2-coated ceramic plate is not poisonous for E. coli if UV irradiation is absent. The UV light irradiation on a blank ceramic plate will kill about 35% E. coli for 4 h. Applying the UV irradiation on the TiO_2-coated ceramic plate, the survival

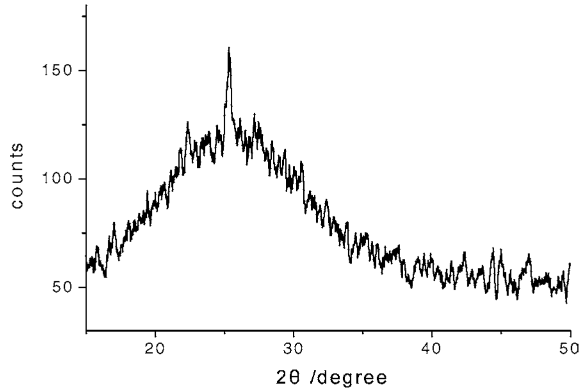


Figure 5 XRD pattern of glaze surface with TiO_2-coated at 800 °C.

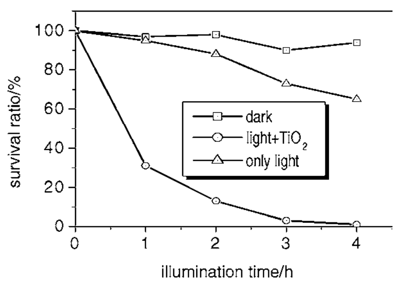


Figure 6 Effect of the irradiation time on S% of *E.coli* in ceramic plates.

ratio of E. coli decreases to 30% within one hour; and approaches a negligible level after 4 h. The efficiency is remarkably higher than that without TiO_2-coated ceramic plate. The results of three group samples that the ceramic plates were illuminated by natural daylight in room for 4 h, no direct sunlight beam on it are summarized as Table I. The survival ratio of E. coli on the TiO_2-coated ceramic plates decreases to a very low level.

The present available method of E. coli disinfection requires either a thermal treatment up 100 °C, or a chemical treatment with disinfection reagents. The TiO_2 photocatalytic treatments are proved an efficient method at room temperature and ambient conditions. These features render TiO_2-coated materials applicable to environment protections, especially in medical buildings, hygienic wares and table wares.

In summary, this paper reports a convenient and low cost method to prepare the TiO_2-coated ceramic plate with the TiO_2 nanoparticles. The microstructure and crystalline phases of TiO_2 in the glaze were investigated; the TiO_2 particles retain the anatase phase, forming a net via aggregation in the glaze layer. The TiO_2-coated ceramic plates can kill the E. coli under the irradiation of mercury lamp, or under the room daylight. This method is easy to transfer to the commercial applications.

TABLE I Survival ratio of *E. coli* on the ceramic plates under daylight condition

	Survival ratio (%)	
Sample number	TiO_2-coated ceramic	Blank ceramic
1	2.6	71.3
2	1.4	73.6
3	2.1	67.1

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