Preparation, characterization and photo activities of Nano-TiO2 thin film

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Abstract. TiO_2 sol is prepared by sol-gel method, nano-TiO_2 thin film on ceramic surface is prepared by dip-coating techniques and is tested by using XRD and AFM, and bactericidal activity of nano-TiO_2 thin film is separately studied by Natural fell bacterium experiments and Artificial fell bacterium experiments. The results show that the main type of crystallite for TiO_2 is anatase and the crystallite size of TiO_2 is 18.98 nm, and the surface shape is fairly uniformity; nano-TiO_2 thin film has good ability of bactericidal performance on Escherichia coli, Staphylococcus aureus, Bacillus subtilis and Pseudomonas aeruginosa.

Introduction

TiO2 is commonly known as titanium white, whose photocatalytic activity is very good, chemical stability is high, to the human body is harmless and the cost is low. It is an ideal inorganic antibacterial agent.

Since 1972 which Fujishima and Hondo found TiO2 sustainable water REDOX reaction in photovoltaic cells, TiO2 photocatalytic performance has become the research hot spot. After TiO2 is excited by about 365nm wavelength light, its price bring electronic will be excited to conduction band, form a hole with high oxidation activity and light excited electrons, and generate •OH and •O2 reacting with H2O and O2 . TiO2 thin film has good chemical stability and thermal stability, high catalytic activity, no secondary pollution, without excitant and safe non-toxic characteristics, It can decompose bacteria and contaminants using natural light. It is Long-term benefit for ecological environment. It can be used in light battery electrodes, water decomposition, organic carrier and vessel material, etc.

Currently, it is a development prospect of photoelectric materials, and is one of green environmental protection and bioceramic catalysts. Nano-TiO2 thin film is prepared by using sol-gel method in this paper, Using X-ray diffractometer and atomic force microscope nano-TiO2 thin film on the surface of ceramic tile, characterize XRD and AFM. The bactericidal performance of film is tested through natural drop experiment.

The experiment part

Preparation of Nano-TiO2 Thin Film

(1) Preparation of Nano-TiO2 Sol

A certain amount of anhydrous ethanol which was measured was put into the beaker, and the right amount of butyl titanate was slowly added into the beaker solution, then stirring magneticly for 120 min. After mixing, 2% of the total volume acetyl acetone was added as a chelating agent, then concentrated HNO3 was added, adjusting the pH of the solution, and then mixing 30 min, finally droping distilled water in the mixture to get the transparent sol solution.

(2) Preparation of Nano-TiO2 Thin Film

Ceramic tile glaze was used as a carrier of load, diping the glazed tile vertical in the sol, Dippulling method coating, taking out to deliquesce in the air, putting it in 100 ℃ constant temperature box for drying and heat preservation, then putting it in the muffle furnace for roasting. After Natural cooling, the nano-TiO2 Thin Film was got. Repeating the above operation, the different thickness nano-TiO2 Thin Films were got.

Characterization of Nano-TiO2 Thin Film

(1)XRD characterization

Adopting the Japanese guide tianjin company for BD - 6000 X-ray diffractometer, the ceramic surface of nano-TiO2 thin film was characterized with XRD.

(2) AFM characterization

Adopting the Japan Olympus atomic force microscope, the ceramic surface of nano-TiO2 thin film was characterized with AFM .

Bactericidal performance of Nano-TiO2 Thin Film

Natural bacteria experiment

The ceramic tile and ceramic tile blank sample (parallel to do three copies) were put indoor and ventilated bad place, keeping natural light irradiation conditions after a certain time (6 h, 24 h), Putting it in the destroy bacteria in a petri dish, the sterilized beef extract peptone medium was added, and amount to just cover ceramic tile was added, In the constant temperature of 37 ℃ incubator for 24 h, the number of colonies was recorded.

(2) Artificial inoculation experiment

Blank tile and ceramic tile sample were put on super clean bench, using ultraviolet light. Both the front and opposite were sterilized for 20 min. Respectively taking of 0.5 ml bacteria liquid of concentration for 106cfu•mL-1 to vaccinate in 7.5×4 cm2 blank samples surface with the ceramic tile ceramic tile and pave, covering its surface using fresh plastic film, irradiating a certain period of time （1.0 h、2.0 h、4.0 h、8.0 h、12.0 h、24.0 h）by 30W fluorescent lamp, 45cm of Irradiation distance, 37±1 ℃ of experiment temperature, 60 % of relative humidity. 9.5 ml diluent bacterium fluid flush rinsing was used on the surface of the ceramic tile ceramic tile and sampling to sterilization in a petri dish, after mixing, 1：10 was dilutted , then choosing 1 ~ 2 suitable bacteria liquid concentration, taking 0.1 ml as colony number to count, Each dilution degrees vaccination three nutrient AGAR medium were put in constant temperature of 37℃ for 24 h, Calculating the sterilization rate.

(3) The calculation formula of sterilization rate

$$a = (A - B)/ B * 100\% \qquad (1)$$

in the type :

sterilization rate;

the ceramic tile on the surface of Blank colony count ；

the ceramic tile on the surface of nano—TiO2 samples colony count.

The results and discussion

XRD analysis of Nano-TiO2 Thin Film

The XRD characterized on the surface of the ceramic tile of Nano -TiO2 thin film. As shown in figure 1:

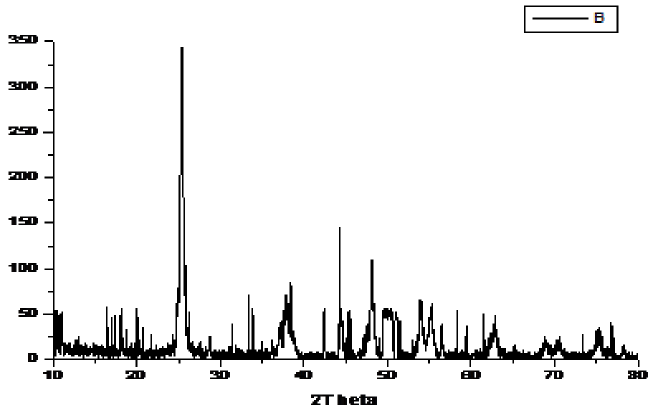

Fig. 1 XRD analysis of Nano-TiO_2 Thin Film

XRD analysis result was shown that，anatase phase nano-TiO2 was generated in Film，among them，diffraction angle was 2 θ =25.3583°，Using anatase phase in the theta 2 θ = 25.3583 ° diffraction peaks of XRD data, by Scherre formula:

D= Kλ / (B cosθ) (2)

B2=BM2－BS2 (3)

in the type：

D-Grain size;

K-constant ，0.89;

λ -X wavelength;

θ -Bragg Angle （Half the diffraction Angle ）;

B-wide X ray caused by refinement of nanometer particles ;

BM-the measured width is changed;

BS- wide Instrument.

The crystallite size of Nano-TiO2 particles were calculated.,concluding that the particle of TiO2 was 18.98 nm.

AFM analysis of Nano-TiO2 Thin Film

The surface of the ceramic tile of nano -TiO2 thin film was characterizated by the AFM. As shown in figure 2：

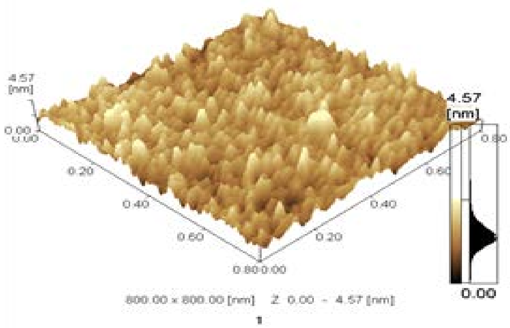

Fig. 2.(a) three dimensional image

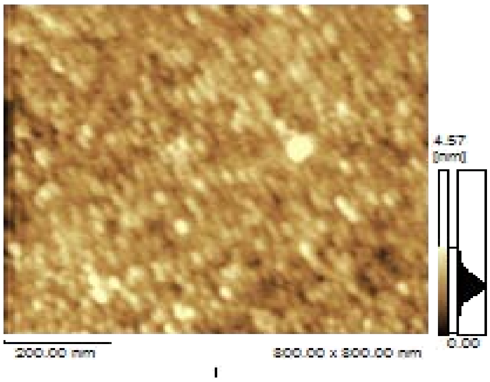

Fig. 2 (b) two dimensional image

AFM analysis result was shown that, the surface of nano-TiO2 thin film was bright and clean, without abnormal big particles, without reunion phenomenon, the particle size of nano-TiO2 thin film was at the nanometer scale, particle size was uniform, The average particle size was 20 nm , The film had a flat organizational structure.

The bactericidal performance of Nano-TiO2 thin film in the natural bacteria experiment

In natural bacteria experiment, the Nano-TiO2 thin film of the Ceramic tile surface was lighted by the irradiation about 6 h、24 h, the sterilization result was shown in table1：

Table1 Natural bacteria experiment result

Natura light time [h]	6	24
Colony counts of the blank tile surface [a]	22	67
Colony counts of the sample tile surface [a]	3	6
Sterilization rate [%]	86.4	91.0

As shown in table1: in the same culture condition, the colony count of the sample ceramic tile surface was less than the blank ceramic tile surface, instructed load Nano-TiO2 thin film Ecological ceramic tile had antiseptic effect, as the growth of the natural light irradiation time, sterilization rate had increased, after natural light irradiation 24 h , sterilization rate had reached to 91.0%. It show that load Nano-TiO2 thin film Ecological ceramic tile had a very good sterilization effect on the natural light irradiation without the strong ultraviolet irradiation.

The bactericidal performance of Nano-TiO2 thin film in the artificial inoculation experiment

In the artificial inoculation experiment, nano-TiO2 thin film of ceramic tile surface was lighted by fluorescent lamp for different time, the sterilizing performance was resulted in Four kinds of the same concentration and different bacteria liquid show as figure 3:

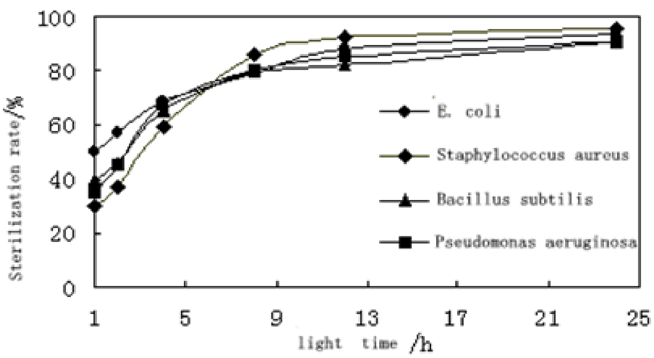

Figure 3 the sterilizing performance of Nano-TiO2 thin film in the same concentration and different bacteria liquid

Figure3 was shown that the sterilizing rate which Nano-TiO2 thin film was to Escherichia coli, staphylococcus aureus, bacillus subtilis, pseudomonas aeruginosa was changed with the changing time in the same concentration.

Learning from figure 3, in the light of time of 1 h, membrane of e. coli bactericidal performance was the highest, but as the extension of time, the e. coli sterilization performance increased slowly, its sterilizing rate had reached 93.72 % when the light time of 12h; the sterilizing rate of bacillus subtilis, pseudomonas aeruginosa reach above 90 % when the light time of 24h.

So it could be seen that, Nano-TiO2 thin film had good sterilizing performance on e. coli, staphylococcus aureus, bacillus subtilis and pseudomonas aeruginosa .

Conclusion

Nano-TiO2 thin film which is prepared by sol-gel method show that anatase phase nano-TiO2 is generated in its thin film by using XRD and AFM. Its particle is 18.98 nm, and its size is uniform. Loading nano-TiO2 thin film Ecological ceramic tile can play a very good sterilization effect in the natural light irradiation without the strong ultraviolet irradiation. Nano-TiO2 thin film have good sterilizing performance on e. coli, staphylococcus aureus, bacillus subtilis and pseudomonas aeruginosa .

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