Research Article

Study on the Thermal Treatment of Nano-Ag/TiO₂ Thin Film

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The photocatalytic degradation rates of methyl orange and antibacterial properties of nano-Ag/TiO₂ thin film on ceramics were investigated in this study. XRD was used to detect the structure of film to clarify the impacts on the rates and properties. The effect of film layers, heating temperature, heating time, and embedding of Ag⁺ on the degradation rates and antibacterial properties were ascertained. The nano-Ag/TiO₂ film of 3 layers with AgNO₃ 3% embedded and treated at 350°C for 2 h would exhibit good performance.

1. Introduction

Because of its nanoeffect, high activity, and characteristic [1] of the reuse in the immobile catalyzer application, the nano-TiO₂ thin film has great value in both theory study and application [2–4]. The ceramics with nano-TiO₂ thin film immobilized on glaze is a kind of new high-tech materials which is becoming the hotspot of high-tech product with a nice foreground [5]. Steady nano-TiO₂ water-sol was prepared in the study done before [6], and then put ceramics into the water-sol to load TiO₂ humid film, after that conducted thermal treatment. The photocatalytic and antibacterial performances of the film were dependent on the thermal treatment conditions.

The photocatalytic degradation rate of methyl orange and antibacterial property of nano-Ag/TiO₂ thin film on ceramics were used as main index in addition to XRD analysis in this investigation. The effects of film layers, heating temperature, heating time, and embedding of Ag⁺ on the degradation ratio and antibacterial property were studied.

2. Experimental

2.1. Preparation of TiO₂ Water-Sol. According to the literature [6], 5% nitric acid or 3% hydrochloric acid were used to peptize 0.1 or 0.2 mol/L H₄TiO₄ at pH = 1.4, then the mixture was agitated in water bath at 80°C until it became

translucent sol. The following reactions [7] took place in the procedure:

2.2. Preparation of TiO₂ Thin Film Immobilized on Ceramics Glaze. The ceramics were cut into 50 mm × 50 mm pieces and washed with deionized water, 5% NaOH solution, alcohol and distilled water, then dried at room temperature. The treated ceramics were put into the TiO₂ water-sol to load TiO₂ humid film. After that, they would be dried in an oven at 100°C. By repeating these operations, the films with requisite thickness were prepared. Finally they were heated in a Muffle Furnace from 100°C to appointed temperature at the rate of 4~5°C per min for 2 h.

2.3. Measurements

(1) Photocatalytic Degradation Performance. U-2010 ultra-violet-visible spectralphotometer made in Japan was used to test absorbance of methyl orange at 465 nm wavelength. The methyl orange and a piece of ceramics were put into a glass dish with a ZF-2 ultraviolet lamp (made in shanghai)

TABLE 1: Antibacterial property of the film embedded different Ag^+ .

	Blank	1% AgNO_3	1% AgCl
Antibacterial ratio (%)	31	99	51.5

TABLE 2: Antibacterial property of the film embedded different amount of Ag^+ .

Ag amount (AgNO_3)	0%	1%	3%	5%	7%
Antibacterial ratio (%)	25	81	92.5	95.5	96

at 253.6 nm wavelength lighting above. the degradation rate calculated in the following way [8].

$$\text{Degradation rate} = \frac{A_0 - A_t}{A_0} \times 100\%. \quad (3)$$

(2) *Antibacterial Performance.* According to the literature [9], the antibacterial rates were tested by the method according to Japanese standards which was used by TOTO Co. and INAX Co. for testing antibacterial efficacy of antibacterial materials.

(3) *X-Ray Diffraction Analysis.* Rigaku D/max2550VB+ X-ray diffraction analyzer made in Japan was used to observe the crystal structure of TiO_2 thin film after heated at different temperature [10].

3. Result and Discussion

3.1. Effect of Ag Embedding on the photocatalytic and Antibacterial Performance. According to Section 2.1, 5% nitric acid and 3% hydrochloric acid were used, respectively, to peptize 0.1 mol/L H_4TiO_4 at pH = 1.4, then the mixture was added with some silver nitrate (account for 1% weight of Ti) and stirred in water bath at 80°C until it became translucent sol. Then 2 types of ceramics with nano- Ag/TiO_2 thin film immobilized on glaze were prepared after 3 layers of humid film were loaded and treated at 550°C for 2 h according to Section 2.2.

Figure 1 indicates that Ag^+ improves the degradation rate. The reason is that Ag could restrain recombination of cavity and electron and improve photocatalytic performance of the film. Besides that, degradation rate of the film embedded AgNO_3 is higher than the one embedded AgCl . It is because that grain size of TiO_2 in film prepared by HNO_3 was also smaller than that prepared by HCl [6].

Table 1 indicates that antibacterial rate of the film embedding AgNO_3 is higher than the one embedding AgCl . There may be 2 reasons: first, the former actually has two types of Ag, Ag_2SO_4 and AgNO_3 , either of which has higher solubility constant than AgCl . So that there would be more Ag dissolving into bacterium solution, which could lead to higher antibacterial rate; Second, it is easier for AgCl to turn into elementary substance or silver oxide under light either of which has lower solubility constant than AgCl itself.

FIGURE 1: The film embedded different Ag^+ to the photocatalytic degradation ratio of methyl orange. FIGURE 2: The film embedded different amount of Ag^+ to the photocatalytic degradation ratio of methyl orange.

According to the method stated at the beginning, but the amount of embedding Ag was change, the films with 1%, 3%, 5% AgNO_3 were prepared.

Figure 2 indicates that the film's photocatalytic performance is improved with the increasing of embedding Ag amount.

Table 2 indicates that the film's antibacterial rate is improved with the increasing of embedding Ag amount. The increasing of embedding Ag amount means that there would be more Ag^+ dissolving into bacterium solution. Beside that, although the amount of Ag embedding on film increased from 3% to 5%, 7%, the antibacterial rate was not obviously improved, it is because that the concentration of Ag in

FIGURE 3: The different film layers to the photocatalytic degradation ratio of methyl orange ((a) 0.1 mol/L sol; (b) 0.2 mol/L sol).

the film dissolving into bacterium solution tends to be a constant.

3.2. Effect of Thickness on the Photocatalytic and Antibacterial Performance. According to Section 2.1, 5% nitric acid was used to peptize 0.1 mol/L and 0.2 mol/L H_4TiO_4 at pH = 1.4, then the mixed system was agitated in water bath at 80°C until it became translucent sol. Several types of ceramics with nano- TiO_2 thin film immobilized on glaze were prepared after 1, 3, 5 layers of humid film were, respectively, loaded and heated at 550°C for 2 h according to Section 2.2.

Figure 3(a) indicates that with the film layers added, the film's photocatalytic performance is improved. Layers' increasing means the amount and surface area of TiO_2

TABLE 3: The photocatalytic properties of 0.1 mol/L sol film and 0.2 mol/L sol film (150 min).

	1 layer	3 layers	5 layers	7 layers
0.1 mol/L sol degradation ratio (%)	5.4	12.8	17.6	18.9
0.2 mol/L sol degradation ratio (%)	8.1	9.5	1.6	6.5

TABLE 4: Antibacterial property of the film with different layers.

Layers	Blank	1 layer	3 layers	5 layers	7 layers
Antibacterial ratio (%)	35	48.5	76	71	72

loaded on films also increase. Figure 3(b) indicate that the film's photocatalytic performance is not improved with the film layers' adding as well as Figure 3(a). Its degradation rate reaches the maximum at 3 layers. It is because that loading superabundant TiO_2 on the glaze would lead to reduction of the TiO_2 surface area. Table 3 indicates that when the sol concentration is higher, the film with fewer layers would have better photocatalytic performance; when the sol concentration is lower, the film with more layers would have better photocatalytic performance.

According to the method stated at the beginning, but 1% AgNO_3 was added into 0.1 mol/L sol to prepare Ag/TiO_2 films with 1, 3, 5 layers.

Table 4 indicates that antibacterial rate of the films is improved with the increasing of its layers which means that the amount of Ag embedding in films increases. It is also found that antibacterial rates of the film with 5 layers and 7 layers are not improved but lower than the one with 3 layers. It may because of superposition of the TiO_2 's network structure prevent the Ag^+ in the bottom films from dissolving into the bacteria solution.

3.3. Effect of Heating Temperature on the Photocatalytic and Antibacterial Performance. According to Section 2.1, 5% nitric acid was used to peptize 0.1 mol/L H_4TiO_4 at pH = 1.4, then the mixed system was agitated in water bath at 80°C until it became translucent sol. Several types of ceramics with nano- TiO_2 thin film immobilized on glaze were prepared after 3 layers of humid film was loaded and, respectively, heated at 350°C, 450°C, 550°C, and 650°C for 2 h according to Section 2.2.

Before the thermal treatment, TiO_2 of the film is amorphous. Figure 4 indicates that TiO_2 of the film heated at 350°C begins turning to anatase at 2-Theta = 25.3°, the amorphous and anatase TiO_2 coexist. According to the literature [11], TiO_2 of the film heated at 500°C begins turning to rutile. It accords with the indication of Figure 4 that there is not rutile but anatase appearing in the film at 450°C and both of them coexist in the film at 550°C. With the heating temperature reaches 650°C, the amount of rutile TiO_2 increases, and there is still some anatase TiO_2 existing. According to the Scherrer Formula [12], the average diameter of TiO_2 crystal grain is 29.8 nm, it is nano-film.

FIGURE 4: X-ray diffraction patterns of TiO_2 thin film at different annealing temperature.

FIGURE 5: The different film annealing temperature to the photocatalytic degradation ratio of methyl orange.

Figure 5 indicates that the order of the film's degradation rate from max. to min. is $350^\circ\text{C} > 450^\circ\text{C} > 650^\circ\text{C} > 550^\circ\text{C}$. Generally speaking, anatase TiO_2 has better more active photocatalytic performance than the rutile. With the heating temperature goes up, crystal grains of the film grow bigger, its surface area reduces and adsorption capability becomes weaker. Meanwhile the amount of the rutile increases. All of these leads to the decline of the photocatalytic performance. But it would be improved as if there is a amount of rutile existing in the film [11]. It is the reason for that the film heated at 650°C has higher degradation rate than the one heated at 550°C . It may be the same reason for the film with the amorphous and anatase TiO_2 coexisting has more active photocatalytic performance than the one with pure anatase TiO_2 .

FIGURE 6: The different film annealing time to photocatalytic degradation ratio of methyl orange.

TABLE 5: Antibacterial property of the film at different annealing temperature.

	Blank	100°C	350°C	450°C	550°C	650°C
Antibacterial ratio (%)	45	76.9	90.2	80	77.8	53.8

According to the method stated at the beginning, but 1% AgNO_3 was added into the sol to prepare Ag/TiO_2 films heated at different temperature.

It could be found in Table 5 that the antibacterial rate of the film is going up with the heating temperature from 100°C to 350°C , but the film heated at 100°C is not firmly attached on the glaze, it could fall off easily under the scraping of fingers. The antibacterial rate of the film is going down with the heating temperature from 350°C to 650°C , it may because AgNO_3 in the film turn into elementary substance or silver oxide which has lower solubility constant than AgNO_3 and Ag_2SO_4 themselves.

3.4. Effect of Heating Time on the Photocatalytic and Antibacterial Performance. According to Section 2.1, 5% nitric acid was used to peptize 0.1 mol/L H_4TiO_4 at $\text{pH} = 1.4$, then the mixed system was agitated in water bath at 80°C until it became translucent sol. Several types of ceramics with nano- TiO_2 thin film immobilized on glaze were prepared after 3 layers of humid film was loaded and, respectively, heated for 0 h, 0.5 h, 1 h, 2 h, and 3 h at 550°C according to Section 2.2.

Figure 6 indicates that heating time has not marked effect on degradation rate of the films. With the heating time going up, degradation rate is increasing and reaches the max. at 0.5 h, after that crystal grains of the film grow bigger with the increasing of heating time; besides that the amount of rutile is also increasing. All of these leads to poor photocatalytic performance.

FIGURE 7: The Antibacterial property of the film at different annealing time.

According to the method stated at the beginning, but 1% AgNO_3 was added into the sol to prepare Ag/TiO_2 films heated for different hours.

Figure 7 indicates that antibacterial rate of the films is improved within the heating time 0 h to 2 h and is steady within 1 h to 2 h, but when the heating time keep up increasing, the antibacterial rate goes down markedly. It may because more and more AgNO_3 in the film gradually turn into elementary substance or silver oxide.

4. Conclusion

Embedding of Ag^+ helps to improve the photocatalytic and antibacterial performance, the optimum amount and type of Ag embedding in the film is 3% AgNO_3 . With the film layers' adding, the film's photocatalytic and antibacterial performance are improved. The optimum layers of film is 3. To compromise the photocatalytic and antibacterial performance, 350°C is chosen as the optimum heating temperature. Heating time from 0 h to 3 h has not marked effect on degradation rate of the films. But heating time has concern with the film's antibacterial rate, the optimum heating time would be 2 h.

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