Research Article

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Crystallization of Nano-TiO₂ Films based on Glass Fiber Fabric Substrate and Its Impact on Catalytic Performance

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Abstract: Nano-TiO₂ film attracts great attention by its excellent photocatalytic activity performance. The application of nano-TiO₂ film based on fabric substrate in indoor household textiles is helpful for purifying air and degrading formaldehyde content in indoor environments. In this paper, the nano-TiO₂ films were prepared on fiberglass substrate by the sol-gel method, and the appearance of fabrics coated with nano-TiO₂ at conditions of both without calcination (room temperature) and high temperature calcination (300°C, 350°C, 400°C) was studied. In addition, X-ray diffraction technology was applied to analyze the crystallization of TiO₂ film, with further discussion of the photocatalytic performance of degrading helianthin under UV irradiation. The results show that with increase of calcination temperature, the color of the fabric gets darker and darker until the powder peeling and dyeing reaches the maximum degree, the fabric becomes fragile, the anatase crystal form of TiO₂ film tends to be complete, and the photocatalytic performance is improved. It is feasible to apply TiO₂ film on the surface of fabrics in the design of indoor household textiles.

Keywords: fabric, TiO₂ film, sol-gel method, photocatalytic activity, functional textiles

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1 Introduction

With the ever greater attention attached to interior decor by modern people, the impact of air pollution caused by paints on human health has received increasing attention. Studies have shown that the direct cause of the air quality decline in indoor environments is Volatile Organic Compounds (VOCs). The pollutants are mostly the paints, coatings, various building materials and furniture used in indoor living and workplace environments [1, 2]. People who live in such indoor environments for long periods of time will have a set of discomfort symptoms such as headache, nausea, drowsiness, etc., together called "sick building syndrome" in the medical field. In even more severe cases, these organic pollutants can have bad effects on the nervous system, respiratory system and cardiovascular system of the human body, and even cause cancer. Among these organic pollutants, formaldehyde is featured in relatively high concentration, wider sources, and with worse pollution effects, causing it to attract people's attention most [3, 4].

Many methods are available for removing indoor formaldehyde such as ventilation, physical adsorption [5, 6], plant absorption [7], and photocatalytic degradation [8], among which the ventilation method is the simplest and most effective. However, the ventilation method usually takes a long period of 3-15 years. It is obviously unrealistic to leave a newly decorated house idle for over 3 years. The plant absorption method also takes a long time because the absorption volume is quite small which makes the method have not that clear an effect. Physical adsorption methods, such as activated carbon adsorption, not only have the problem of small adsorption capacity, but also have a risk that the absorbed formaldehyde is easily re-released from due to changes of environment. Photocatalytic technology, which uses light as an energy-intensive catalyst, has been applied to the treatment of gaseous pollutants since the 1990s because of its low energy consumption and zero-secondary-pollution. Among these methods, TiO₂ is a good photocatalyst because of its good chemical

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stability, light corrosion resistance and non-toxicity performance, and so is often used for catalytic degradation of formaldehyde. The application of TiO_2 film on textiles, such as curtains, air conditioning filters, sofa covers, carpets, etc., can decompose indoor formaldehyde [9]. However, TiO_2 is low in response to visible light and has different sizes of particles for which only the large particles are catalytic under ultraviolet irradiation, and only those of nano-scale are stimulated under ordinary light.

Meanwhile, many methods are also available for preparing TiO_2 films, among which the simplest way is to apply (wipe) TiO_2 nanoparticles onto a substrate and obtain TiO_2 films by drying and baking. The key to this method is to prepare a TiO_2 nanoparticle colloid, for which the sol-gel method is the most commonly used because it has the advantages that it can be a compound in room temperature, is an easily controlled reaction, produces high purity output, exhibits good uniformity and accurate chemical composition, provides easy doping, and involves simple equipment and processes [10, 12]. After calcining the TiO_2 film prepared by the sol-gel method at a certain temperature, the organic matter in the sol-gel can be basically volatilized and decomposed so that the TiO_2 particles in the film can be presented in the form of a nanocrystalline network sponge shape with a large surface area and roughness that are good for absorbing other active substances [13].

The calcination temperature of the TiO_2 film not only affects the particle size, but also affects the crystal structure and microstructure of the catalyst. Because the corresponding temperature requirements for the formation of different crystalline forms are different, there are very few examples of the formation of crystalline forms on fabrics because most textiles are not heat-resistant and the calcination method cannot be used to crystallize nano- TiO_2 film [14, 15]. Fiberglass fabrics were selected to prepare the carrier of loaded TiO_2 film because fiberglass fabrics are inexpensive with good light transmittance and high-temperature calcination resistance, and bonding between the film and the carrier improves the stability of the load.

In this paper, high temperature resistant fiberglass fabric was selected as the substrate, and TiO_2 thin film was prepared by the sol-gel method, and then coated on the surface of fiberglass fabric. In this way, the effects of different calcination temperatures on the crystal formation types of TiO_2 film and its photocatalytic properties were studied, thereby providing a strong basis for the development of TiO_2 textile as a kind of air purification functional fabric.

2 Experiment

2.1 Material

2.1.1 Reagents

N-N dimethylformamide ($\text{HCON}(\text{CH}_3)_2$, analytical purity, Tianjin Fuchen Chemical Reagent Factory), TiO_2 powder (TiO_2 analytical purity, China Pharmaceutical Group Chemical Reagent Co., Ltd.), sodium hexametaphosphate powder, $((\text{NaPO}_3)_6$, analytical purity, Tianjin Damao Chemical Reagent Factory), polyvinylidene fluoride powder (PVDF, analytical purity, Xingxing Plastic Raw Materials Co., Ltd.), helianthin powder ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$, Tianjin Damao Chemical Reagent Factory), deionized water (self-prepared in laboratory).

2.1.2 Fabric

The uncalcined fiberglass fabrics carrying TiO_2 film ($2\text{cm} \times 2\text{cm}$, $4\text{cm} \times 4\text{cm}$), the fiberglass fabrics carrying TiO_2 film that were calcined at 300°C ($2\text{cm} \times 2\text{cm}$, $4\text{cm} \times 4\text{cm}$), the fiberglass fabrics carrying TiO_2 film that were calcined at 350°C ($2\text{cm} \times 2\text{cm}$, $4\text{cm} \times 4\text{cm}$), and the glassfiber fabrics carrying TiO_2 film that were calcined at 400°C ($2\text{cm} \times 2\text{cm}$, $4\text{cm} \times 4\text{cm}$).

2.1.3 Instruments

PA2004 electronic analytical balance (Changzhou Keyuan Electronic Instrument Co., Ltd., 85-2 type magnetic stirrer (Jintan City Geotechnical Automation Instrument Factory), electrothermal blast dryer (Shanghai Yiheng Science Instrument Co., Ltd.), vacuum atmosphere furnace (Zhuochi Mafo Furnace Factory Shop). IN-STRON 33 universal tensile testing machine, XRD-6100 desktop X-ray diffractometer (Shimadzu Manufacturing Institute of Japan), UV-5100 ultraviolet-visible spectrophotometer (Shanghai Meta-analysis Instrument Co., Ltd.), Osram ultraviolet curing lamp high-pressure mercury lamp (Yugu Technology, Zhongshan City, Guangdong Province), 85-2 digital thermostatic magnetic stirrer (Jintan City Geotechnical Automation Instrument Factory).

2.2 Preparation of nano-TiO₂ Film

Nano-TiO₂ films were coated on fiberglass substrates by sol-gel coating. First, 180 ml of N-N dimethylformamide and 18% TiO₂ powder (TiO₂) were taken, and the TiO₂ powder was added into 2/3 of the N-N dimethylformamide in a beaker. Then the obtained solution mixture was placed in an electric stirrer and evenly stirred for 40 minutes at a speed of 1000 r/min. Next, 5% sodium hexametaphosphate solid powder was added to the mixture and the stirring continued for 60 minutes. At the same time, polyvinylidene fluoride powder (polyvinylidene fluoride: N-N dimethylformamide = 1:10) was added into a beaker containing the other 1/3 of the N-N dimethylformamide, stirred with a glass rod until it was uniform and stationary in a transparent colloid state without bubbles. Finally, the first beaker of dispersed homogeneous solution of TiO₂ was added into the second beaker containing the transparent colloid and stirred, completing the sol preparation.

The 10cm × 10cm fiberglass fabric was placed in the sol-gel beaker for 30 minutes in the baking chamber. Then, it was taken out and put into the drying oven with a temperature of 100°C to bake for 5 minutes, followed by putting it back in the beaker for a second time to coat for 30 minutes, and dried in the oven until fully dried. Next it was taken out for washing in water, and put back into the drying oven at 80°C to dry, thereby completing the preparation of the TiO₂ film by the sol-gel coating method. Finally, the fabrics were calcined in a vacuum furnace for 3 hours at 300, 350 and 400°, respectively [16, 17]. After calcination, nano-TiO₂ films based on fiberglass fabrics were obtained.

2.3 Characterization (XRD)

First, the non-calcined fiberglass fabrics carrying TiO₂ film and the fiberglass fabrics calcined at 300°C, 350°C and 400°C were cut into 2cm × 2cm squares of the same specification. They were fixed on four slides using tape. The X-ray diffractometer was opened and the slides were inserted into the gripper. Then the rotation was observed along with the gripper of the diffractometer, and data for vertical diffraction energy line values for the fiberglass fabric from 0 degrees to 90 degrees was recorded and saved.

3 Photocatalytic Performance Test

A typical anionic dye helianthin (MO) was applied as a simulated pollutant to evaluate the photocatalytic activity of nano-TiO₂ films prepared under visible and ultra-violet

light irradiation. Step 1 was to dissolve 0.5g helianthin powder into 500 ml deionized water, using the magnetic stirrer to shake for 20 minutes; then, two beakers were used to hold 150 ml helianthin solution and 100 ml deionized water, respectively. The ultraviolet spectrophotometer was set for 468 nm wavelength and pre-heated for 20 minutes, and the high pressure mercury lamp of the OSRAM ultraviolet curing lamp was preheated for 10 minutes. Step 2 was to extract an appropriate amount of deionized water and place it in a 10mm glass colorimeter. This colorimeter was put in the second cell of the ultraviolet spectrophotometer and the key of ZERO was reset to zero. Next, the colorimeter was taken out to pour out the deionized water. Then the helianthin solution which had not been irradiated by ultraviolet light was extracted by dropper and put into the 10mm colorimeter (note that the colorimeter is the same one, no need to change to a new one). The initial transmittance and initial absorbance of the helianthin solution were measured by ultraviolet spectrophotometer. Step 3 was to put the sample into the whole beaker of helianthin solution and irradiate it under the high-pressure mercury lamp with 250W OSRAM UV curing lamp (paying attention that the location of the irradiation point correctly faced the center of the beaker). The absorbance of helianthin solution was tested every 30 minutes by extracting a certain amount of the solution with a dropper. The duration of the process was six hours.

4 Results and Discussion

4.1 Appearance Analysis

Figure 1 shows the calcined samples of fiberglass fabrics coated with nano-TiO₂ at different temperatures. Sample (a) is a non-calcined sample coated with TiO₂ film, which is white, granular and wrinkled. After coating, the fiberglass fabric has clear lines, and is obviously interlaced with staggered warp and weft yarns. The mercerization and glossiness of the fiberglass are reduced by coating with TiO₂, which also brings with it a rigid feel to the fabric. Sample (b) is calcined at 300°C in a high-temperature vacuum-furnace. The color of the fabric turns brown and white. Because of the uneven coating of TiO₂, the calcined fiberglasss become more uneven. Some areas show brown and yellow color with lower chroma and lightness. Some show brown or gray white with higher lightness. The texture of the fabric is hard and difficult to drape, and there is a slight powder drop phenomenon. Sample (c) has darker color (dark brown as a whole), light brown in some

Figure 1: Samples of nano-TiO₂ films based on fiberglass fabric substrates

uneven areas, aggravated powder dropping phenomenon, and more fragile and stiff fabric texture. Sample (d) has an overall black-gray color, with part of the area dark brown. Comparing the fabric samples, with increase of calcination temperature, the color of fabrics gradually deepens, the phenomena of powder dropping and dyeing reach the maximum, and the texture of fabrics becomes fragile.

4.2 XRD Analysis

The results show that the calcination temperature of nano-TiO₂ film, as a heterogeneous photocatalytic carrier, not only affects the particle size, but also affects the crystal structure and microstructures of the catalyst. In general, only anatase, rutile and amorphous forms can be found in TiO₂ films, and slate crystalline forms can only be formed under special conditions.

Figure 2 shows the XRD diffraction patterns of the crystalline structure of TiO₂ films at room temperature without calcination and at three different calcination temperatures. The results show that the formation and crystallization of TiO₂ are different at different calcination temperatures. Figure 2a shows the X-ray diffraction (XRD) of non-calcined fiberglass fabrics loaded with TiO₂ films with obvious diffraction peaks. The position of the strongest peak is $2\theta = 22.7^\circ$. There is a deviation from the theoretical value of the diffraction angle of the anatase structure of TiO₂ at 25.3° , and the curves are cluttered background noise,

(a) Uncalcined (room temperature)

(b) 300°C calcination

(c) 350°C calcination

(d) 400°C calcination

Figure 2: XRD diffraction pattern of TiO₂ film generating crystal under different calcination conditions

Table 1: Absorbance of textile samples carrying TiO₂ film at different calcination temperatures

Time/ min	Sample#1 (Room temperature)	Sample#2 (300°C calcination)	Sample#3 (350°C calcination)	Sample #4 (400°C calcination)
0	3.000	2.928	2.913	2.862
30	1.862	1.542	1.431	0.924
60	1.266	1.098	0.954	0.756
90	1.104	1.026	0.921	0.741
120	1.089	1.017	0.825	0.720
150	1.086	1.014	0.807	0.689
180	1.086	0.996	0.806	0.680
210	1.080	0.994	0.806	0.680
240	1.080	0.994	0.800	0.680
270	1.080	0.993	0.802	0.672
300	1.080	0.993	0.800	0.672
330	1.080	0.993	0.800	0.672
360	1.080	0.993	0.800	0.672

which indicates that the non-calcined TiO₂ film is amorphous and does not crystallize. The XRD diffraction pattern also has a strong peak at about 10 degrees, which may correspond to nano-TiO₂ particles with mesoporous structure.

Figure 2b shows the XRD analysis of the TiO₂ films calcined at 300°C. Compared with Figure 2a, the peak values on the angle X axis become dense and continuous, and the peak values begin to fluctuate and the diffraction peaks increase. Compared with the standard XRD card of anatase phase TiO₂, there are weak characteristic diffraction peaks on anatase phase TiO₂ crystal plane at $2\theta = 25.3^\circ(101)$, $38^\circ(004)$, $47.7^\circ(105)$ and $47.7^\circ(105)$. The grains have been transformed from amorphous to anatase phase and a small amount of anatase crystal forms have been formed.

Figure 2c shows the XRD analysis of TiO₂ films calcined at 350°C. Under this condition, the peak value becomes more continuous and compact, and the fluctuation is more obvious than that of the previous analysis. The peak angle on the X-axis increases, and the diffraction peak is further enhanced. Strong characteristic diffraction peaks appearing on (101), (004), (105) represent the crystalline plane of the anatase phase TiO₂, and the crystallization degree of the anatase crystalline form of the TiO₂ film was improved. Figure 2d shows the XRD analysis of the TiO₂ films calcined at 400°C. The peak value of characteristic diffraction increases further. At 400°C, the TiO₂ films have formed a complete anatase crystalline form, but no rutile phase has been observed.

In conclusion, with increase of calcination temperature, the anatase crystal form generated by TiO₂ films

tends to be complete. It can be assumed that if the coated fabrics can withstand high temperatures above 500°C, there will be the possibility of forming rutile crystals. Anatase TiO₂ has better photochemical activity than rutile and slate crystals, and it has the most suitable thermal dynamic field of valence band and conduction band. If nano-TiO₂ film coated fabric is used as indoor textiles to purify air by photocatalysis, the calcination temperature at 400°C is most appropriate.

4.3 Photocatalytic Performance Analysis

Under UVA radiation, the photocatalytic performance of the nano-TiO₂ film calcined at different temperatures was evaluated by photodegrading MO dye. Table 1 shows the absorbance (A) of different sample MO solutions. According to Beer-Lambert's law and absorbance, the concentration of MO solution was calculated. And according to the absorbance value and photocatalytic degradation rate of different samples, the formula is

$$C = [(C_0 - C_t)/C_0] \times 100\%$$

In this formula: C is the degradation rate of helianthin; C_0 is the concentration of helianthin solution before illumination; C_t is the concentration of helianthin solution at the time when the illumination time is t . According to calculation and comparison based on the above values, Figure 3 was obtained. Figure 3 is a comparison of photocatalytic degradation rates of nano-TiO₂ films at different calcination temperatures.

Through analysis of the photocatalytic degradation efficiency curves of the four samples in Figure 3, rules for

Figure 3: The degradation rate curves of TiO₂ film's photocatalytic activity

how the degradation rate varies with ultraviolet irradiation time can be obtained. The variation pattern of the four samples of helianthin degradation efficiency with time is basically the same, reaching maximum degradation rate at 60-120 minutes and then showing no big change beyond that. As for the uncalcined TiO₂ film, the highest degradation rate was 63.8%, and the TiO₂ film photocatalytic degradation rate of helianthin reached 77.6% at high temperature of 400°C. The photo-catalytic performance of the four samples was ranked as follows: Sample 4 > Sample 3 > Sample 2 > Sample 1. The photocatalytic performance of the TiO₂ film based on fiberglass fabric was enhanced with the increase of calcination temperature.

The main reasons why the catalytic performance of TiO₂ film is not ideal are as follows: first, the nano-film is not thick enough. It has been shown in currently existing research that thickness is one of the most sensitive factors affecting the photocatalytic ability of TiO₂ film. The photocatalytic performance of the film below 120nm increases as thickness is increased [18–20]. Second, no flowing photocatalytic reaction device has been adopted. In this experiment, a fixed photocatalytic reaction device was applied, and the liquid wasn't stirred during the whole experiment process, which resulted in insufficient contact of helianthin with the TiO₂ film, thereby causing too slow a reaction speed.

In summary, comparing with Sample 1 of the fiberglass fabric carrying TiO₂ film before calcination, with the increase of calcination temperature, the nano-TiO₂ film gradually formed the anatase crystal form, which accelerated the photocatalytic reaction rate and improved the photocatalytic degradation rate. This indicates that the formation of nano-TiO₂ crystal form accelerates the photocat-

alytic reaction and makes the degradation more thorough, indicating that the formation of TiO₂ crystal form is beneficial to the photocatalytic reaction.

5 Conclusions

A nano-TiO₂ film based on fiberglass fabric substrate was prepared by the sol-gel coating method. Appearance changes of the fabric under four different calcination conditions of uncalcined, 300°C calcination, 350°C calcination, and 400°C calcination were compared, and it was found that with the increase of calcination temperature, the color of the fabric got darker and darker until the powder peeling and dyeing reached maximum degree, and the fabric became fragile.

The crystallization of nano-TiO₂ film samples based on fiberglass fabric substrate was tested under four calcination conditions (uncalcined, 300°C calcination, 350°C calcination, 400°C calcination). It was found that with increase of calcination temperature, the crystal form tends to become complete, thereby forming anatase crystal form.

The photocatalytic properties of nano-TiO₂ film samples based on fiberglass fabric substrate were tested under four calcination conditions (uncalcined, 300°C calcination, 350°C calcination, 400°C calcination). It was found that with increase of calcination temperature, the crystal form tends to become complete, thereby accelerating the photocatalytic reaction speed and enhancing the photocatalytic degradation rate.

The crystal form that the TiO₂ film which is based on fiberglass fabric substrate generates under high tem-

perature calcination facilitates the photocatalytic reaction. As the base fabric, high-temperature resistant materials should be selected to degrade formaldehyde in the air on one hand, and satisfy demands on comfortable feel, good decorative effect, and good mechanical properties of the fabric on the other hand.

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