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Preparation of fibrous TiO_2 photocatalyst and its optimization towards the decomposition of indoor ammonia under illumination

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Abstract

Aqueous dispersion containing TiO_2 particles was firstly prepared and then mixed with silicone or acrylic additives to establish a treating bath. And the fibrous TiO_2 photocatalysts were produced by padding three woven fabrics including cotton, polyester and flax fabrics as support materials with this treating bath and some factors affecting the preparation process were discussed. Moreover, the fibrous TiO_2 photocatalysts were characterized by X-ray diffractometer, infrared Fourier transform spectrometer and scanning electron microscope, and evaluated with respect to the removal efficiency of ammonia under UV irradiation in air stream by a specifically designed photocatalytic reactor and environmental condition simulated chamber. The results showed that ammonia gas could well be decomposed by the fibrous TiO_2 photocatalysts based on cotton and flax fabrics. Increasing the dosage of TiO_2 aqueous dispersion led to the improved ammonia decomposition level of the fibrous TiO_2 photocatalysts. The additives caused the reduced ammonia decomposition level of the fibrous TiO_2 photocatalysts, but provided it with the enhanced resistance to water washing. The ammonia photocatalysis of the fibrous TiO_2 photocatalysts was not much affected by curing temperature and dyed cotton fabrics when preparing.

Keywords: TiO_2 photocatalysts; Woven fabrics; Preparation; Indoor ammonia; Decomposition

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1. Introduction

The different kinds of chemicals are used widely as additives in concrete construction of buildings in recent years. Antifreeze admixtures are important additives added to the concrete during mixing, which depress the freezing point of the water and accelerate the hydration rate of the cement. It is believed that continuous decomposition of antifreeze admixtures based on urea compounds in concrete wall can take place at room temperature and be transformed to gaseous ammonia under alkaline and warm condition. In general, the produced gaseous ammonia can release to indoor environment through slow diffusion in concrete wall and have result in the increasing indoor air pollution. Too high concentration of indoor ammonia has attracted people's close concern, and how to reduce the risk caused by ammonia in indoor air becomes a big issue in some countries particularly China. The standards and regulations to control indoor ammonia pollution have been enacted and developed in China [1]. On the other hand, several researchers investigated indoor ammonia emission sources [2] and measured ammonia concentration in indoor air [3,4]. These studies reported that concentrations of ammonia were measured in different rooms in houses and in a range of public buildings using a variety of testing method. In addition, remedial measures against high concentrations of ammonia in buildings were also suggested [5].

It is believed that oxidation is currently considered to be the most effective technology to decompose airborne pollutants. Ultraviolet (UV) related technologies are very effective compared with other oxidation processes on removing the contaminants in air at considerably mild conditions. The hydroxyl free radical is the major species that initiates most of

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the UV-related processes to the oxidation of compounds in gaseous streams. Therefore, the UV-related processes are referred as advanced oxidation processes (AOPs). Among the UV-related processes, UV/TiO_2 process has been considered to be a promising alternative for decomposition of various refractory contaminants in gaseous streams in the past decades.

Coating of TiO_2 by impregnation is most widely used by most researchers because the technique is easy and does not require any complicated equipment. The selection of based material may influence the activity, homogeneity and adhesion of TiO_2 catalyst on the surface. However it is difficult for the replacement of spent TiO_2 catalyst from the reactors for practical uses. Therefore, various based materials including paper [6] as well as nonwoven textile [7] have been developed for the possible applications of TiO_2 photocatalytic process in the future. The photocatalytic oxidation of ammonia was carried out over UV-irradiated TiO_2 spread as a thin uniform membrane at room temperature [8]. But there is little detailed information in current literature concerning preparation of the fibrous TiO_2 photocatalysts by using textile finishing process and its application to decontamination of indoor ammonia from the concrete wall in civil building.

In this study, in order to produce a heterogeneous photocatalyst with the TiO_2 fixed to a woven fabric support, aqueous dispersion containing TiO_2 was first prepared and then mixed with silicone or acrylic additives to establish a treating bath. Three woven fabrics including cotton, polyester and flax fabrics were treated with this bath by using pad-dry-cure process, respectively, and different fibrous TiO_2 photocatalysts were obtained. Some factors affecting the preparation process, such as fiber nature, dosage of aqueous TiO_2-dispersion, additives, curing temperature and dyed fabrics were discussed. Moreover, the fibrous TiO_2 photocatalysts were evaluated with respect to the removal efficiency of ammonia in air stream by a specifically designed photodegradation system consisting of the photoreactor and environmental condition simulated chamber. In addition, the resistance to water of fibrous TiO_2 photocatalysts was examined in accordance with textile test method.

2. Experimental

2.1. Preparation of TiO_2 aqueous dispersion

Degussa P-25 TiO_2 powder was employed without further treatment. It is said that Degussa P-25 TiO_2 powder is approximately spherical and nonporous with greater than 99.5% purity and contained about 80% of anatase and 20% of rutile and the average particle size of the TiO_2 particles was 30 nm [7]. All other chemicals were of reagent grade.

TiO_2 aqueous dispersion was prepared by mixing 1.5 g of Degussa P-25 TiO_2 powder and the appropriate amounts of deionized water in an ultrasonic mixer. After 5 h of ultrasonic mixing, 0.125 g of polyglycol was added into aqueous dispersion and mixed under continuous magnetic stirring for 30 min. The TiO_2 aqueous dispersion was prepared containing 3% by weight of Degussa P-25 TiO_2 and 0.25% by weight of polyglycol. The average particle size was measured in TiO_2 aqueous dispersion to be 0.212 μm using a LA-300 particle sizer (Horiba Instrument Ltd., Japan).

2.2. Preparation and characterization of fibrous TiO_2 photocatalysts

Three commercially scoured and bleached woven fabrics including cotton, polyester and flax fabrics were used, respectively, as support materials for TiO_2 particles in this study because of their good flexibility, huge surface and high absorbing power. Two commercial grade of textile additives including reactive amino silicone softener AM-200 and self-crosslinking acrylic binder TOW from Fuzhou Botex Chemicals Co., Ltd. (Fujian, China) were used for fixing TiO_2 particles on the woven fabrics mentioned above. These fabrics were further treated with a solution containing 2 g L^{-1} sodium carbonate and 2 g L^{-1} soap at the boil for 30 min, then thoroughly washed with cold water and dried at ambient temperature. The fabric samples were padded twice (take up $75 \pm 1\%$) with a treating solution containing various amounts of TiO_2 aqueous dispersion produced above and AM-200 or TOW on a laboratory-padding mangle. After being padded, the samples were immediately dried at 100 °C for 2 min, and then cured at different temperatures for 1 min and form the fibrous TiO_2 photocatalysts.

The composition of the fibrous TiO_2 photocatalysts was verified by using a Rigaku Xd/Max-2500 X-ray diffractometer operating with Cu Kα radiation and a Nicolet Magna-560 Fourier infrared transform spectrometer (4 cm^{-1} resolution), respectively. Scanning electron microscopic observations on specimens of the fibrous TiO_2 photocatalysts were also done on a Hitachi S-670 electron microscope.

2.3. Decomposition of indoor ammonia

The photodegradation system used in this research was designed and consists mainly of a small stainless steel environmental condition simulated chamber (1 m^3) and a glass photoreactor. The schematic diagram of photodegradation system is shown in Fig. 1.

Four concrete wall pieces were prepared with 65.5 kg cement, 3.73 kg FDJ antifreeze admixtures containing 34% of urea (Tianjin Bocheng New Type Building Materials Company, China) and a large amount of fine sand, gravel and water, and used for simulating the indoor concrete wall. The same concentration of antifreeze admixtures was also used in construction process of actual rooms in China. It is noticed that proportion of wall piece weight to the volume of environmental chamber equals that of actual indoor concrete weight to indoor volume and the proportion of the emitting surface area of wall piece to the volume of environmental chamber equals that of the emitting surface area of actual indoor concrete wall and indoor volume in the given rooms by partial covering of plastic film on wall pieces. The specifications of concrete wall pieces are presented in Table 1.

The photocatalytic reactor was a 38 cm long glass plug flow tubular reactor with an effective volume 2.5 L. It contained a 2 cm i.d. quartz tube inside cooling water and housing a UV

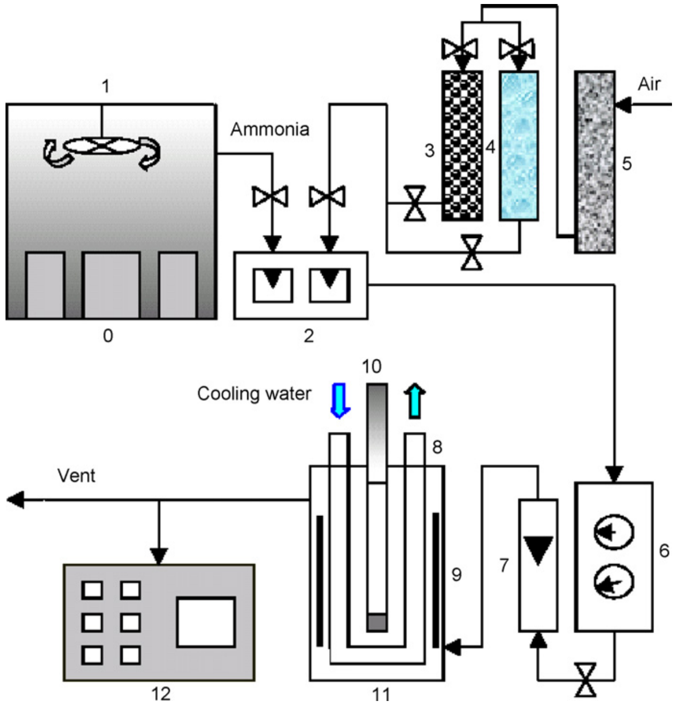


Fig. 1. The schematic diagram of photocatalytic and testing system for ammonia in air. 0: wall pieces; 1: environmental chamber; 2: gas mixer; 3: dewater reagent; 4: water bottle; 5: activated carbon filter 6: thermo/humidity meter; 7: flow meter; 8: quartz shelter (inside cooling water); 9: fibrous TiO_2 photocatalysts; 10: UV lamp; 11: reactor; 12: ammonia detector.

Table 1
Specification of concrete wall pieces

Dimension of each wall piece	0.520 m × 0.300 m × 0.200 m
Total weight of four wall pieces	312 kg
Total volume of four wall pieces	$0.1248\ m^3$
Total emission area of four wall pieces	$1.248\ m^2$
Total content of urea in four wall pieces	1.114 kg
Amount of ammonia emitted from four pieces in theory	6.13×10^5 mg

365 nm lamp obtained from Shanghai Philips-Yaming Company (Shanghai, China). The fibrous TiO_2 photocatalysts with an area of $0.022\ m^2$ was wound and fixed on the inner wall of the photoreactor.

Environmental chamber and photoreactor were thoroughly cleaned with a solution containing $2\ g\ L^{-1}$ sodium carbonate and deionized water, respectively. Gaseous ammonia emitted from wall pieces in environmental chamber and clean air were mixed in a gas mixer and maintained constant for providing ammonia gas with a steady concentration. The temperature of the mixed gas flow in the photoreactor was kept at $25 \pm 1\ ^\circ C$ and humidity of the mixed gas flow reached steady by adjusting water bubbling humidity regulator and measured through flow meter and CR-052 thermo/humidity meter (Crecer Company, Japan). A NH_3 gas detector TG-2400KBP (Bionics Instrument Co., Ltd., Japan) was used to determine the concentration of gaseous ammonia in the air stream from the photoreactor. The reaction was not considered to reach balance until the concentration of gaseous ammonia in the photoreactor was kept steady for 5 min. The ammonia concentration in the photoreactor at this time was referring to the balance concentration of ammonia. Photocatalytic decomposition percentage of ammonia ($D_p\%$) at constant humidity and temperature was calculated as follows:

$$D_p\% = \frac{C_0 - C}{C_0} \times 100$$

where $D_p\%$ is the photocatalytic decomposition percentage of ammonia, C_0 the initial concentration of ammonia ($mg\ m^{-3}$) and C is the residual concentration of ammonia ($mg\ m^{-3}$).

3. Results and discussion

3.1. Characterization of the fibrous TiO_2 photocatalysts

3.1.1. XRD analysis

The X-ray diffraction curve of the fibrous TiO_2 photocatalysts and untreated woven fabrics were presented, respectively, in Fig. 2.

As seen from Fig. 2, it is found that three major peaks (14.84°, 16.38° and 22.68°) of cellulose fiber including cotton and flax and three major peaks (17.68°, 22.8° and 26.66°) of polyester were coincident with data published in literature [9]. More importantly, a relatively strong reflection peak (a: 25.28°) and three weak peaks (b: 37.84°, c: 47.98° and d: 53.90–55.12°) of anatase TiO_2 were also observed. TiO_2 grain size can be

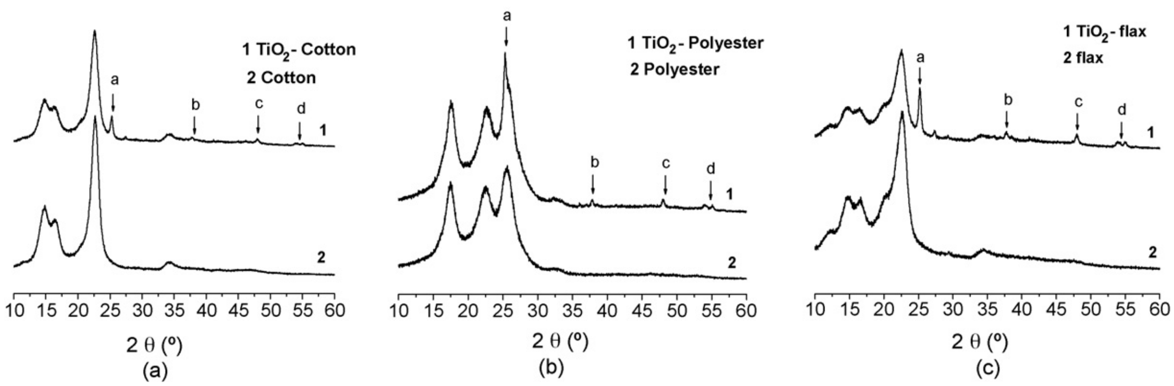


Fig. 2. XRD spectrum of three fibrous TiO_2 photocatalysts and untreated woven fabrics. (a) Cotton; (b) polyester; (c) flax.

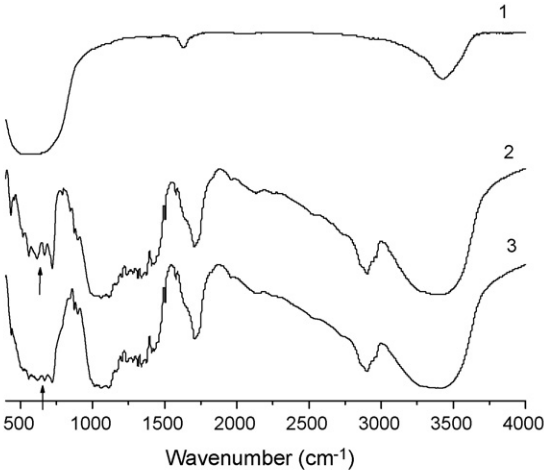


Fig. 3. FT-IR spectrum of untreated cotton fabric and fibrous TiO_2 photocatalysts. 1: TiO_2; 2: cotton fabric; 3: TiO_2–cotton.

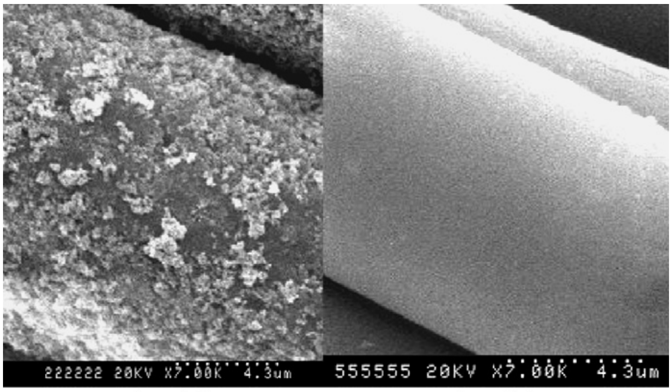
determined from the broadening corresponding X-ray spectral peaks by Scherrer's formula $L = 0.90\lambda/(\beta \cos \theta)$, where L is the grain size, λ the wavelength of X-ray radiation, and β is the line width at half maximum height. Based on XRD analysis, the average grain size of anatase TiO_2 is 30.1 nm.

3.1.2. FT-IR analysis

Fig. 3 (lines 1–3) shows the spectra of TiO_2, cotton fabric and cotton TiO_2 photocatalyst, respectively. Fig. 3 (line 1) illustrates that the IR spectrum of the TiO_2 in the range of 400–4000 cm^{-1}, which agrees with the reported data [10]. Fig. 3 (line 3) is for the cotton TiO_2 photocatalysts, which is not the same as Fig. 3 (line 2) due to IR band difference at 500–800 cm^{-1} suggesting the presence of TiO_2 in cotton fabric. This indicates that TiO_2 particles have been effectively loaded on surface of cotton fabric through finishing method.

3.1.3. SEM analysis

Figs. 4–6 illustrate scanning electron micrographs of three fibrous TiO_2 photocatalysts (panel a) and three untreated woven fabrics (panel b), respectively. Comparing three fibrous TiO_2 photocatalysts, it is noticed that they were formed by TiO_2 particles covering on the surface of the fiber, and seem to be somewhat rough and uneven. Therefore, it is proved that TiO_2 particles were loaded onto three fibers by using pad-dry-cure process, but their distribution onto fiber surface was not quite even, possible because of aggregation of some fine TiO_2 particles. Moreover, of these fibrous TiO_2 photocatalysts, TiO_2 particles distributed more evenly on cotton fiber than on polyester and flax fiber. In addition, TiO_2 particles film formed on polyester fiber seem to be thinner than those on flax fiber, especially cotton fiber, this is due mainly to the difference in the surface structure, hydrophilic and adsorbing capacity among three fibers.



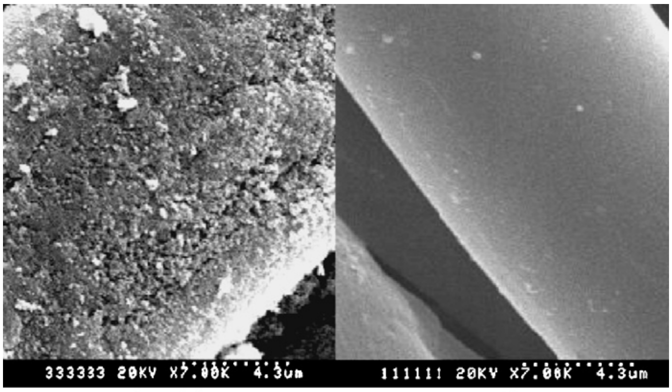
(panel a) (panel b)

Fig. 5. SEM of polyester–TiO_2 photocatalysts (panel a) and untreated polyester fabric (panel b).

3.2. Background experiment

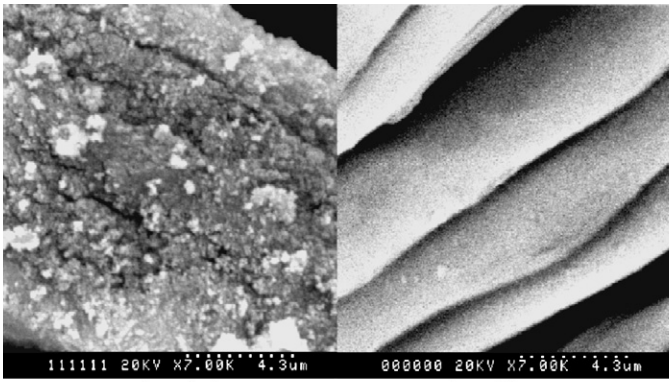
The photocatalytic decomposition of ammonia by the 365 nm UV irradiation, gas flow rate of 0.5 L min^{-1}, relative humidity 45 ± 2%, temperature 25 ± 1°C and in the presence of three woven fabrics, especially, polyester fabric without TiO_2 particles were found to be negligible within the reaction time studied in this research, as shown in Fig. 7.

It can be seen from Fig. 7 that the concentration of ammonia in photoreactor gradually decreased at the beginning stage of reaction, but then came back to about initial concentration level



(panel a) (panel b)

Fig. 4. SEM of cotton–TiO_2 photocatalysts (panel a) and untreated cotton fabric (panel b).



(panel a) (panel b)

Fig. 6. SEM of flax–TiO_2 photocatalysts (panel a) and untreated flax fabric (panel b).

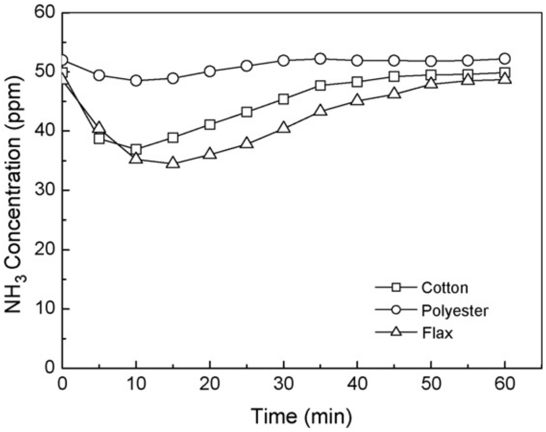


Fig. 7. The photolysis of ammonia by the 365 nm lamp with three woven fabrics without TiO_2.

during the reaction time in the presence of cotton and flax fabrics. This may be due to the limited adsorption of ammonia on the cellulose fiber surface. On the other hand, polyester fabric caused little change in the ammonia concentration during the reaction time. It indicates that ammonia could not be directly decomposed by UV light of 365 nm. The main reason is that the maximum wavelength for breaking the N–H bond is 220 nm [8], which is shorter than 365 nm employed in this research. Additionally, the adsorption of ammonia on TiO_2 particles may improve the decomposition of ammonia since the adsorption of ammonia on TiO_2 catalysts is an important step in the heterogeneous decomposition. However the adsorption was also studied in this research and found to be minimal; therefore, the removal of ammonia contributed the adsorption on TiO_2 particles during UV/TiO_2 process can be neglected. The activity of the TiO_2 catalysts on the fabrics can be assumed to be constant during the course of reaction because that their lifetime should be long enough to enable their participation in photocatalytic oxidation of ammonia.

3.3. Nature of woven fabrics

For a given treatment condition, cotton, polyester and flax fabrics were treated at the same concentration (30 g L^{-1}) of aqueous TiO_2-dispersion, respectively, in order to select the best support material for the fibrous TiO_2 photocatalysts and results were shown in Fig. 8.

It should be noted from Fig. 8 that the decomposition values of three fibrous TiO_2 photocatalysts based on different woven fabrics gradually increased with prolong of the irradiation time. This is due to the degradation of ammonia with fibrous TiO_2 photocatalysts under the UV irradiation in a photoreactor during the reaction. Previous work [8] confirmed that ammonia was oxidized to more nitrogen (N_2) and a little dinitrogen oxide (N_2O) over UV-irradiated TiO_2 at room temperature in the presence of oxygen. In this research, both nitrate and nitrite were not identified in the aqueous extraction of the used fibrous TiO_2 photocatalyst by ion chromatography.

Fig. 8 also depicts the difference in ammonia destruction among three fibrous TiO_2 photocatalysts. It is found that from

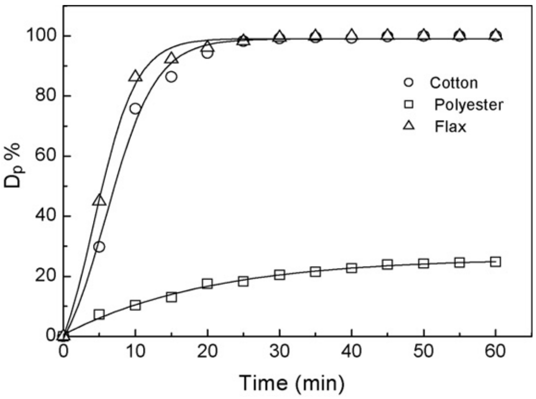


Fig. 8. Effect of different fabrics on D_p% of fibrous TiO_2 photocatalysts.

Fig. 8 that the fibrous TiO_2 photocatalysts based on cotton or flax fabrics are much higher than the fibrous TiO_2 photocatalysts based on polyester fabric in terms of the ammonia decomposition percentage (D_p%). This may be owing to the big difference in chemical properties and microstructure characteristics between cellulose and polyester fiber. It is the fact that hydrophilic cotton and flax fiber has high moisture regain because they are composed of cellulose molecules bearing hydroxyl groups; meanwhile, they have relatively loose microstructure, particularly in flax fiber [11] as a result of high amorphous regions and lower crystalline regions. Moreover, the same long cellulose chain molecules are organized in relation to each other in certain portions of their lengths, and disorganized in others [12,13]. In contrast, there are little polar substitutes in molecule chain of hydrophobic polyester fiber. Furthermore, polyester fiber has a low moisture regain of 0.1–0.4%, and a glass rod-like shape with smooth surface [14]. Therefore, it is believed that cotton and flax fibers may exhibit much higher adsorption affinity for ammonia by means of their good hydrophility and loose microstructure than polyester fibers under the same environmental condition. The relatively high adsorption of ammonia onto cotton and flax fibers may accelerate photocatalytic oxidation of ammonia on their surface. Also, the hydroxyl groups in cellulose molecule chain are generally considered as the weak acid substitutes, they may benefit the adsorption and photocatalytic degradation of ammonia on surface of cotton fiber to certain extent by the neutralization effects. In addition, it is possible that more TiO_2 particles were loaded onto the surface of cotton and flax fabric than polyester fabric because of their difference in hydrophilic and adsorbing capacities when padding with the same concentration of treating bath for a given process. Another probable explanation is related to the generation of hydroxyl radicals on the surface of TiO_2 particulates based on different fabrics. When the TiO_2 particulates are excited by wavelengths below 365 nm light irradiation, first step is the generation of photoelectrons and photoholes on TiO_2 particulates (Eq. (1)) followed by reaction (Eq. (2)) to yield the same active oxygen species, such as hydroxyl radicals. And then these hydroxyl radicals can attack organic substrates to lead to their degradation and mineralization [14,15]:

$$TiO_2 + h\nu \rightarrow (e_{cb}^-) + (h_{vb}^+) \rightarrow e^- + h^+ \quad (1)$$

Table 2
Relationship between woven fabrics and reaction rate constants for the photocatalysis of ammonia

Support materials	Cotton	Polyester	Flax
Reaction rate constant, k_i (min^{-1})	0.147	0.009	0.169
Correlation coefficients, R	0.9914	0.9852	0.9884

$$h^+ + OH^-(or H_2O)_{surf} \rightarrow OH^\bullet(+H^+) \quad (2)$$

In the case of fibrous TiO_2 photocatalysts based on cellulose fabrics, cellulose fiber may provide reaction (Eq. (2)) with more water than polyester fiber so as to facilitate the production of hydroxyl radicals, resulting in the improved photocatalytic oxidation of ammonia. A previous study has reported that decomposition of ethanol by UV/TiO_2 process was enhanced with an increase in the relative humility [16].

Suppose that the adsorption of gaseous ammonia on the surface of the fibrous TiO_2 photocatalyst is very limited, the photo-oxidation of ammonia under UV irradiation can be well described by using the pseudo-first-order kinetics with respect to its concentration. In this study, the pseudo-first-order rate constants, k_i of decomposition of ammonia in a photoreaction system within 20 min of exposure time were calculated and listed in Table 2.

Table 2 presents that the decomposition rate constants of the fibrous TiO_2 photocatalyst based on cotton fabric is similar to that of the fibrous TiO_2 photocatalyst based on flax, and much higher than that of the fibrous TiO_2 photocatalyst based on polyester. This agrees well with results obtained in Fig. 8.

3.4. Dosage of aqueous TiO_2-dispersion

Experimental results of gaseous ammonia photodecomposition by using cotton TiO_2 photocatalysts produced with different dosage of aqueous TiO_2-dispersion between 30 and 100 g L^{-1} in treating bath are given in Fig. 9.

It can be observed in Fig. 9 that photocatalytic decomposition percentage of ammonia is increased with the prolongation of reaction time; and increasing tendency becomes level after about 15 min of the induction period, which is affected by characteristics of TiO_2 photocatalysts and fabrics, as well as initial reaction conditions. This means that most of ammonia in reactor was removed with cotton TiO_2 photocatalysts after the induction period. Also, it is noticed that increasing the amount of aqueous TiO_2-dispersion from 30 to 100 g L^{-1} in the treating bath is accompanied with an enhancement in degradation of ammonia. This is due to the fact that the increasing dosage of aqueous TiO_2-dispersion in the padding solution leads to more TiO_2 particles loaded on the fiber surface, which improved the decomposition efficiency of ammonia to a certain extent.

3.5. Additives

In order to improve the wash resistance of the cotton TiO_2 photocatalysts, a padding bath containing 30 g L^{-1} AM-200 or 30 g L^{-1} TOW and 100 g L^{-1} TiO_2 aqueous dispersion was prepared for producing the fibrous TiO_2 photocatalysts based on the cotton fabric by curing at 170 °C for 1 min. And then, the fibrous TiO_2 photocatalysts were washed with an aqueous solution containing 2 g L^{-1} anionic detergent and 2 g L^{-1} sodium carbonate through SW-12 washing testing machine (Shandong Laizhou Instruments Co., Ltd., China). The washed fibrous TiO_2 photocatalysts were used for the decomposition of gaseous ammonia in photocatalytic system. For comparison, control experiments in which two additives were absent in the padding bath were carried out, experimental results of which were presented in Figs. 10 and 11.

Fig. 10 shows additives especially TOW that leads to a significant decrease in the decomposition levels of ammonia in photocatalytic reactor at the initial reaction time, compared with the control experiment. This may be the reason why that these additives especially TOW belong to acrylic polymer compounds and they are able to cause the more aggregation of some fine TiO_2 particles on the surface of cotton fiber by their adhesive performance. Another possible explanation is associated mainly with the improved hydrophobic capacity of cotton fabric surface due to the covering of additives especially, amino silicon softener AM-200 on it.

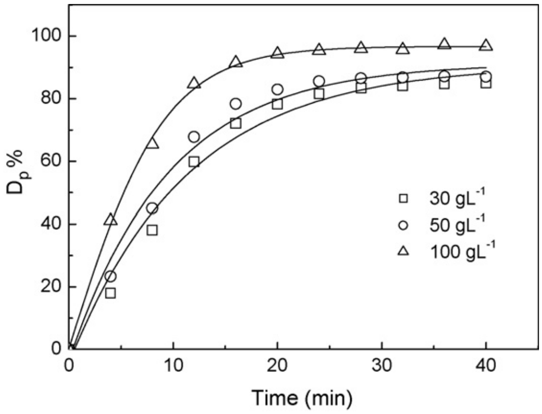


Fig. 9. Effect of aqueous TiO_2-dispersion dosage on D_p% of cotton TiO_2 photocatalysts. Without additives; curing condition: 170 °C, 1 min.

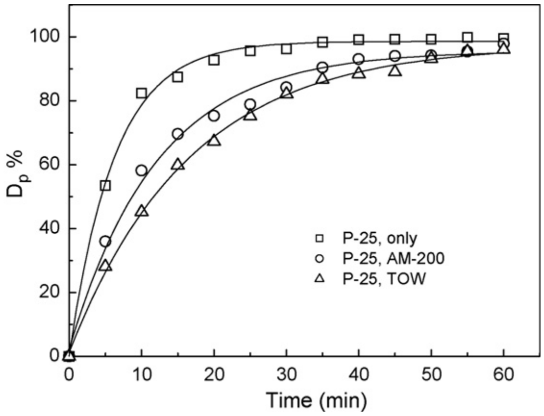


Fig. 10. Effect of additives on D_p% of cotton TiO_2 photocatalysts. TiO_2-dispersion: 100 g L^{-1}; curing condition: 170 °C, 1 min; before washing.

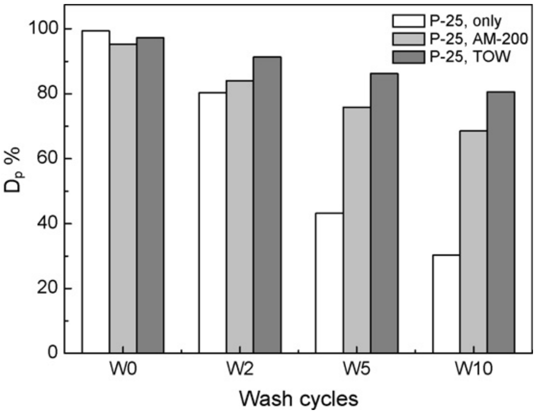


Fig. 11. Relationship between wash cycles and D_p% of cotton TiO_2 photocatalysts. Washing condition: liquid ratio 1:50, 20 °C, 15 min/cycle.

As shown in Fig. 11, the increasing washing cycles give rise to a gradual decline in ammonia decomposition of cotton TiO_2 photocatalysts, especially without the additives in reaction time of 60 min due to the removal of some TiO_2 particles from the surface of cotton fabrics during washing. Moreover, the cotton TiO_2 photocatalysts with the acrylic binder TOW or silicon softener AM-200 are much higher than the one without the additives in terms of the ammonia decomposition at the same washing condition, particularly during 5 and 10 wash cycles. This is because that TiO_2 particle is physically attached to the surface of the fabric and does not penetrate into the cotton fiber in the absence of the additives. On the other hand, the application of the additives, particular in the acrylic binder TOW make it possible that TiO_2 particle is strongly fixed to the surface of the fiber by their powerful crosslinking capacity and film formation at the curing procedure [17].

3.6. Curing temperature

Two cotton woven fabrics with the thickness of 113 and 142 g m^{-2} and the similar texture were employed, respectively, as the support materials for the fibrous TiO_2 photocatalysts to investigate the impact of curing temperature on the ammonia decomposition.

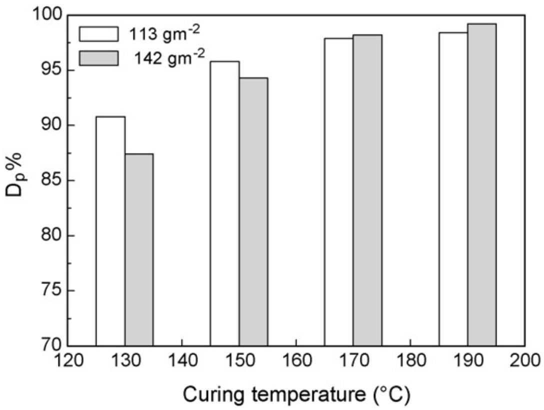


Fig. 12. Effect of curing temperature on D_p% of the fibrous TiO_2 photocatalysts.

Fig. 12 shows that the ammonia decomposition of two fibrous TiO_2 photocatalysts are insignificantly increased with elevation of curing temperature from 130 to 190 °C. This result demonstrates that increment of curing temperature is able to enhance the degree of attachment of TiO_2 particles to cotton fiber. It may be mainly owing to slightly reduced aggregation and uneven distribution of TiO_2 particles on the surface of the fiber at higher curing temperature. Another possible reason is that increasing curing temperature can improve the interactions and absorption between TiO_2 particle and the fiber and resulting in more TiO_2 particle fixed on it. In addition, there is little difference in the ammonia decomposition between two fibrous TiO_2 photocatalysts with the different thickness of the fabrics, especially at higher temperature such as 170 and 190 °C.

3.7. Dyed cotton fabrics

In order to investigate the sensitizing feasibility of dye molecules fixed on the fabrics to the TiO_2 photocatalysts under irradiation and examine the effect of dyed fabrics as support materials on photo-oxidation of ammonia, four cotton fabrics dyed with 2% owf concentration of four azo dyes including C.I. Reactive Yellow 86, C.I. Reactive Red 2, C.I. Direct Blue 15 and C.I. Direct Red 13, respectively, were treated with a finishing solution containing 100 g L^{-1} aqueous TiO_2-dispersion by using pad-dye-cure process under the same technical condition as mentioned above and then used for the photodecomposition of ammonia. For comparison, control experiment in which the bleaching cotton fabric was used in the padding bath was performed, experimental results of which are presented in Fig. 13.

Comparing several decomposition curves of ammonia in Fig. 13, it is found that the fibrous TiO_2 photocatalysts based on the cotton fabrics dyed with direct dyes are almost the same as that of control sample, but somewhat higher than those dyed with reactive dyes in terms of ammonia decomposition values. This may be attributed to the differences in dye characteristics such as molecule structure and distribution mode on the surface of cotton fiber. Therefore, it is believed that the dye molecules on the fabrics have no sensitizing power to TiO_2 photocatalysts based on the cotton fabrics under irradiation, and the dyed

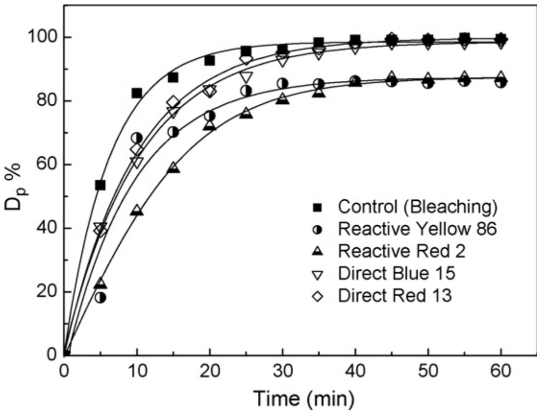


Fig. 13. Effect of dyed cotton fabrics on D_p% of the fibrous TiO_2 photocatalysts.

fabrics have a little influence on photo-oxidation of ammonia with the fibrous TiO_2 photocatalysts in this study.

4. Conclusions

The fibrous TiO_2 photocatalysts were produced with woven fabrics as the base materials by using pad-dry-cure process. And combination of the fibrous TiO_2 photocatalysts with UV irradiation of 365 nm wavelengths can effectively eliminate gaseous ammonia in the reactor. The fibrous TiO_2 photocatalysts based on cotton or flax fabric exhibited more removal efficiency of gaseous ammonia than one based on polyester. It is believed that the decomposition of ammonia is improved by increasing dosage of aqueous TiO_2-dispersion when preparing the fibrous TiO_2 photocatalysts.

Additives containing silicon or acrylic polymer can provide the fibrous TiO_2 photocatalysts with a significant decrease in the decomposition levels of ammonia in photocatalytic reactor at the initial reaction time, but they cause a higher resistance of the fibrous TiO_2 photocatalysts to water washing. In addition, the fibrous TiO_2 photocatalysts produced at higher curing temperature or with the dyed fabrics as support materials do not exhibit the powerful capacity in the ammonia decomposition. To sum up, the accepted ammonia decomposition efficiency and resistance to wash the fibrous TiO_2 photocatalyst was found when it was prepared with 100 $g\ L^{-1}$ aqueous TiO_2-dispersion and 30 $g\ L^{-1}$ additives at 170 °C curing temperature by using cotton woven fabric as the base material.

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