

## Research Article

# Degradation of Typical Indoor Air Pollutants Using Fe-Doped TiO<sub>2</sub> Thin Film under Daylight Illumination

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A type of iron-doped titania thin film was prepared by means of sol-gel method to degrade indoor formaldehyde (HCHO), ammonia (NH<sub>3</sub>), and benzene (C<sub>6</sub>H<sub>6</sub>) under sunlight. The photocatalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis spectroscopy, and energy dispersive spectra (EDS). The results showed that the iron was doped in the TiO<sub>2</sub> photocatalyst successfully. The absorption edge of doped TiO<sub>2</sub> had red shifts and the doped TiO<sub>2</sub> had a stronger absorption than the pure TiO<sub>2</sub> in the visible region. Fe-doped TiO<sub>2</sub> thin film prepared with the optimal preparation condition could remove indoor HCHO, NH<sub>3</sub> and C<sub>6</sub>H<sub>6</sub> effectively under solar light irradiation. The removal percentage of HCHO, NH<sub>3</sub> or C<sub>6</sub>H<sub>6</sub> after 9 h photocatalytic reaction under solar light reached 55%, 53.1%, and 37.5%, respectively, when they existed in the air individually. When the three pollutants were mixed in the air, the removal percentage decreased to 33.3%, 28.3%, and 28%. The degradation reaction of the three pollutants followed the pseudo first-order kinetics, which reflects that the photocatalytic reaction was controlled by the surface chemical reaction and the reaction rate was controlled by concentration of reactants.

## 1. Introduction

People are paying more and more attention to the pollution caused by indoor decoration with the improvement of living standard and indoor decoration gradually becoming popular [1–3]. Among the numerous indoor air pollutants, formaldehyde, ammonia, and benzene are the most representatives, which come from the furnishings and decorating materials, causing nausea, chest tightness, wheezing, skin rashes, allergic reaction, and chronic poisoning [4, 5].

Photocatalysis technology has been proved to be potentially advantageous for indoor air purification [6], and titania is the most common used photocatalyst for its high photocatalytic activity, stable physical and chemical properties, low cost, and nontoxicity [7–9]. However, with its high-energy band gap (ca. 3.0 eV for rutile and 3.2 eV for anatase), titania photocatalysis reacts only under ultraviolet light. But the ultraviolet light energy only accounts for 4%–6% of solar energy reaching the ground, so the solar energy cannot be utilized efficiently in the photocatalytic process [10–12]. In addition, the high degree for recombination between

photogenerated electron-hole pairs restricts the large-scale application of titania.

Doping is one of the important methods of improving visible light photocatalytic activity of titania [13–15]. Transition metal dopants have been widely used to improve the photoefficiency of the electronic process as well as the response to the visible part of the spectrum. Kim et al. reported that Fe-doped TiO<sub>2</sub> could extend the spectral response to the visible region and the photocatalytic activity was greatly enhanced [16]. Choi et al. conducted a systematic study of metal ions doping into TiO<sub>2</sub> for 21 metal ions. Among various transition metal ions, Fe<sup>3+</sup> was considered to be a successful doping element due to its half-filled electronic configuration [17].

In this paper, Fe-doped TiO<sub>2</sub> photocatalysts were attempted to degrade three typical indoor air pollutants: formaldehyde, ammonia, and benzene under daylight illumination. Usually, formaldehyde, ammonia, and TVOC exist in the indoor air at the same time, but there are few reports on the photocatalytic degradation of mixed indoor air pollutants. So, we not only studied the photocatalytic degradation of formaldehyde, ammonia, and benzene

when they exist in indoor air separately, but also studied photocatalytic degradation of the mixed formaldehyde, ammonia, and benzene in the indoor air. To avoid  $\text{TiO}_2$  powder suspending in the indoor air, the Fe-doped  $\text{TiO}_2$  thin films were prepared with flat glass as carrier. The research finding provides a feasible way for enhancement of indoor air quality.

## 2. Materials and Methods

**2.1. Photocatalyst Preparation.** Pure and Fe-doped  $\text{TiO}_2$  thin films were prepared by sol-gel technique. The sol was prepared with tetrabutyl titanate as precursor, anhydrous ethanol as solvent, deionized water or  $\text{Fe}(\text{NO}_3)_3$  solution as reactive substance, and glacial acetic acid as stabilizer. 7 mL of tetrabutyl titanate was dissolved in 50 mL of anhydrous ethanol. The mixed solution was sealed with plastic wrap and stirred for 0.5 h at room temperature to form solution 1. 14 mL glacial acetic acid was dropped into solution 1 with constant stirring for 0.5 h in air to form solution 2. Then 6 mL deionized water or  $\text{Fe}(\text{NO}_3)_3$  solution of different concentrations was added dropwise in solution 2 within 60 min under vigorous stirring at room temperature to form the sol, followed by aging for 24 h to prepare the gel. The plate glass was inserted vertically into the gel. After keeping 10 seconds, it was pulled out of the gel with the speed of 12 cm/min. Thus, the gel film was formed on the glass surface. Then the glass coated with the sol was dried for 20 min at  $100^\circ\text{C}$ . At last, the glass was calcined for 2 h at  $500^\circ\text{C}$  ( $20^\circ\text{C}/\text{min}$ ).

**2.2. Photocatalyst Characterization.** The crystal structure of pure and Fe-doped  $\text{TiO}_2$  was determined by a D-max-2500/PC X-ray diffractometer (XRD) equipped with Cu-K $\alpha$  radiation. Morphology of Fe-doped  $\text{TiO}_2$  thin film was examined by HITACHI (Japan) S-4800 scanning electron microscopy (SEM). The ultraviolet-visible (UV-Vis) absorption spectra of pure and Fe-doped  $\text{TiO}_2$  thin films were recorded on a Shimadzu (Japan) UV-2550 spectrophotometer. The energy dispersive spectra of the Fe-doped  $\text{TiO}_2$  thin film were recorded on JEM-2010 transmission electron microscopy (TEM).

**2.3. Degradation Test of Gaseous Indoor Pollutants.** The degradation test was performed on a self-designed, cuboid, airtight, glass reactor ( $60 \times 60 \times 20$  cm) with a hole, which was connected to sampling tube of KC-6D air sampler. An electric fan was installed on the bracket of the airtight reactor in order to circulate the mixture of pollutants (individual formaldehyde, ammonia, benzene, or the mixture of three pollutants) and air. Eight pieces of coated glass were placed vertically and evenly in the reactor. A predetermined amount of formaldehyde was injected in vessel under dark. The photoreactor was then kept in darkness for 2 h to allow the adsorption of formaldehyde into photocatalyst to approach the state of equilibrium. The photoreactor was then exposed to sunlight to activate the photocatalytic degradation. The experiments were carried out in good sunny days of summer (June to July) with a maximum temperature of  $30^\circ\text{C}$  (between

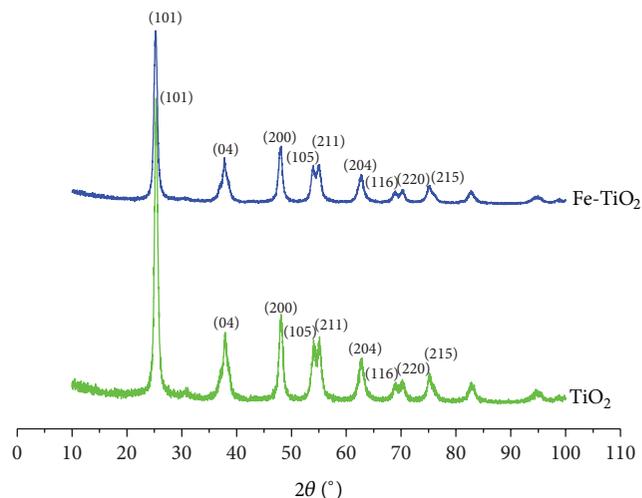


FIGURE 1: XRD spectra of  $\text{TiO}_2$  catalysts.

8 a.m. to 5 p.m.). The intensity of indoor sunlight was in the range between 500 and 1000 lux. The concentration of formaldehyde, ammonia, and benzene was periodically measured every 60 min. The formaldehyde concentration was measured with the 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) spectrophotometric method. The ammonia concentration was measured with Nessler's reagent spectrophotometric method. The benzene concentration was measured by the benzene detector.

## 3. Results and Discussion

### 3.1. Results of Characterization

**3.1.1. XRD Spectra.** Figure 1 shows the XRD patterns of undoped  $\text{TiO}_2$  and Fe-doped  $\text{TiO}_2$  with the doping proportion (mole ratio) which is 1.00%. The result showed that both samples had anatase structure mainly with the formation of characteristic diffraction peaks at  $2\theta = 25.28^\circ$ ,  $37.80^\circ$ ,  $48.05^\circ$ ,  $53.89^\circ$ ,  $55.06^\circ$ , and  $62.69^\circ$ , corresponding to (101), (04), (200), (105), (211), and (204) crystal surface. Compared to undoped  $\text{TiO}_2$ , the patterns of Fe-doped  $\text{TiO}_2$  became weak and broadening, which indicated that the crystallite sizes decreased. From the obtained XRD peaks the crystallite size of the catalysts was determined by applying Scherrer's formula. The formula is given below:

$$D = \frac{0.89\lambda}{(\beta \cdot \cos \theta)}, \quad (1)$$

where  $D$  = crystallite size (nm),  $\lambda$  = X-ray wavelength (1.5406 Å),  $\beta$  = width of the obtained peak at half maximum, and  $\theta$  = contour peak angle (radian). According to Scherrer's formula, the crystallite size of Fe-doped  $\text{TiO}_2$  was 13.1 nm, which was less than that of undoped  $\text{TiO}_2$  14.6 nm.

**3.1.2. SEM Image.** Figure 2 shows the SEM photograph of Fe-doped  $\text{TiO}_2$  thin film with the doping proportion (mole ratio)

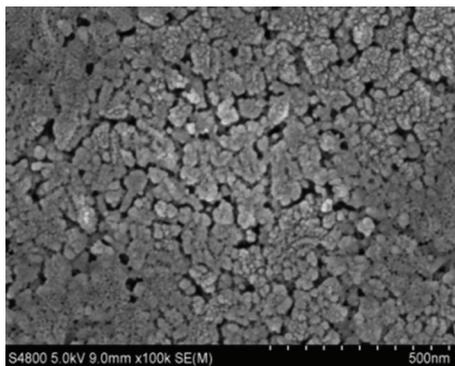


FIGURE 2: SEM photograph of Fe-doped  $\text{TiO}_2$  thin film.

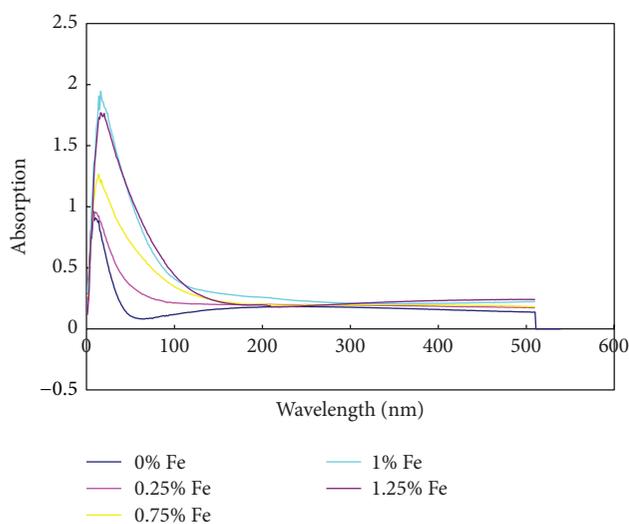


FIGURE 3: UV-Vis absorption spectra.

which is 1.00%. From the image, the thin film was coated on the plate glass smoothly and uniformly.

**3.1.3. UV-Vis Spectra of Photocatalyst.** Figure 3 shows the ultraviolet-visible (UV-Vis) absorption spectra of the undoped and different Fe-doped  $\text{TiO}_2$  thin films (the doping mole ratios are 0.25%, 0.75%, 1.00%, and 1.25%). According to Figure 3, the absorption edge of Fe-doped  $\text{TiO}_2$  has red shifts and the doped  $\text{TiO}_2$  has a stronger absorption than the pure  $\text{TiO}_2$  in the visible region. Since doped  $\text{TiO}_2$  can absorb light in a wider range of wavelength and use more light energy than undoped  $\text{TiO}_2$ , a high photocatalytic activity should be expected.

**3.1.4. EDS Spectra.** Figure 4 shows the energy dispersive spectra of the Fe-doped  $\text{TiO}_2$  thin films with the doping proportion (mole ratio) which is 1.00%. The result showed that the iron was doped in the  $\text{TiO}_2$  photocatalyst successfully, and the mole ratio of Fe and Ti was very close to 1%.

TABLE 1: Degradation ratios of individual formaldehyde, ammonia, and benzene.

Iron dopant amount (mole fraction) %	Degradation ratio of HCHO (%)	Degradation ratio of $\text{NH}_3$ (%)	Degradation ratio of $\text{C}_6\text{H}_6$ (%)
0	35.2	39.5	26
0.25	37.1	41.0	28.6
0.75	40.4	50.3	35.2
1.00	55.0	53.1	37.5
1.25	38.9	46.2	34.2

### 3.2. Photocatalytic Experiment

**3.2.1. Degradation of Individual Formaldehyde, Ammonia, and Benzene.** Table 1 shows the degradation ratios of formaldehyde, ammonia, and benzene after 9 h photocatalytic reaction under solar light when they exist in air individually. The results showed that the photocatalytic activities of Fe-doped  $\text{TiO}_2$  thin films were higher than pure  $\text{TiO}_2$  thin film and the photocatalytic activity of Fe-doped  $\text{TiO}_2$  thin film increased with the doping amount of iron when iron dopant amount was smaller than 1.00%. When the doping amount of iron was 1.00%, the photocatalytic activity was the highest. The degradation ratios of formaldehyde, ammonia, and benzene reached 55%, 53.1%, and 37.5%, respectively. This is due to the fact that new impurity levels are introduced between the conduction and valence bands; with the substitution for  $\text{Ti}^{4+}$  by  $\text{Fe}^{3+}$  in the structure of  $\text{TiO}_2$ , the electrons can be promoted from the valence band to these impurity levels [18]. It can induce more photogenerated electrons and holes to participate in the photocatalytic reactions. So Fe-doped  $\text{TiO}_2$  has narrowed band gap than pure  $\text{TiO}_2$  and could increase the absorption in the visible-light region, which is consistent with the result of UV-Vis absorption spectra analysis. Besides,  $\text{Fe}^{3+}$  can effectively inhibit the recombination of photogenerated electrons and holes and enhance the photocatalytic activity. But the photocatalytic activity of Fe-doped  $\text{TiO}_2$  reduced when the mole fraction of  $\text{Fe}^{3+}$  was more than 1%, because the excess amounts of  $\text{Fe}^{3+}$  might cover the surface of  $\text{TiO}_2$ , increased the number of recombination centers, decreased the photo quantum efficiency, and led to low photoactivity.

**3.2.2. Degradation of the Mixture of Formaldehyde, Ammonia, and Benzene.** Since the photocatalytic activity of Fe-doped  $\text{TiO}_2$  thin film with the doping amount of iron was 1.00% which was the highest, the photocatalytic degradation experiment of mixed formaldehyde, ammonia, and benzene was conducted with this optimal Fe-doped  $\text{TiO}_2$  thin film. The results showed that although the three pollutants were mixed in the air, they were still removed effectively after 9 h photocatalytic reaction under solar light. The degradation ratios of formaldehyde, ammonia, and benzene in gas mixture were 33.3%, 28.3%, and 28% separately, but they were lower than the degradation ratios of formaldehyde, ammonia, and benzene existing in air separately (55.0%, 53.1%, and 37.5%). This is due to the fact that gas molecules occupy fully the

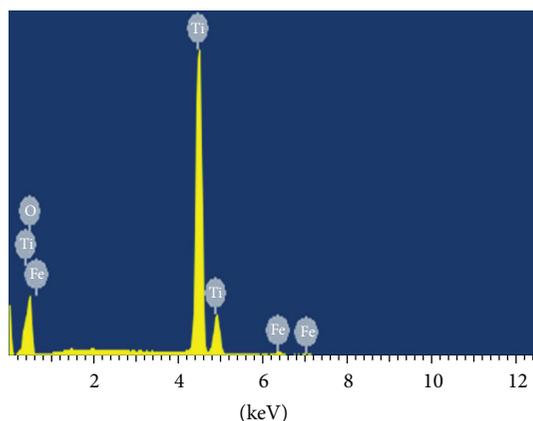


FIGURE 4: EDS spectra.

active sites of the photocatalyst, different molecules compete with each other, and the intermediate product of different pollutant accumulating on the photocatalyst surface prevents the effective contact of gas molecules and photocatalyst.

**3.2.3. Kinetics of Photocatalytic Reaction.** Formaldehyde, ammonia, and benzene exist in the indoor air at the same time usually, so the kinetics of photocatalytic reaction was studied with the experimental data of mixed pollutants over the optimal designed Fe-doped TiO<sub>2</sub> thin film; that is, Fe(III) dopant amount was 1%. Langmuir-Hinshelwood (L-H) equation has been widely used to describe the process of photocatalytic reaction. At low reactant concentration, which is a reasonable assumption for most indoor air pollution problems, the L-H model is simplified to a pseudo first-order expression:

$$\ln\left(\frac{C}{C_0}\right) = -kt, \quad (2)$$

where the reactant residue ( $C/C_0$ ) is a ratio of the instantaneous concentration of gaseous formaldehyde( $C$ ) to the initial concentration ( $C_0$ ),  $k$  is the reaction rate constant that is determined by linear regression of the data  $\ln(C/C_0)$  versus the exposure time ( $t$ ). The experimental data were fitted by plotting  $-\ln(C/C_0)$  against irradiation time. The fitting result was shown in Figure 5.

From Figure 5, we could see that the degradation reaction of formaldehyde, ammonia, and benzene followed the pseudo first-order kinetics with the correlation coefficient  $R^2 = 0.96, 0.98, \text{ and } 0.99$ , respectively. The reaction rate constants of formaldehyde, ammonia, and benzene were  $0.043 \text{ h}^{-1}$ ,  $0.035 \text{ h}^{-1}$ , and  $0.035 \text{ h}^{-1}$ , respectively. This shows that the photocatalytic reaction is controlled by surface chemical reaction and reaction rate is controlled by reactant concentration.

## 4. Conclusions

The Fe-doped TiO<sub>2</sub> thin film was prepared by means of sol-gel method. The solar light catalytic activity of TiO<sub>2</sub>

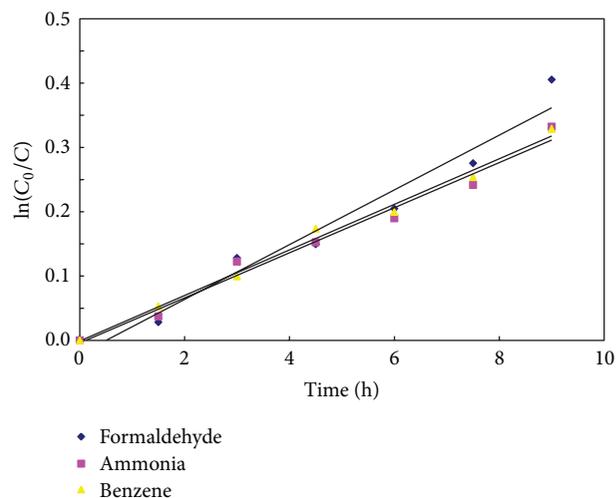


FIGURE 5: Kinetics of degradation reaction of the mixed pollutants.

was improved significantly by doping with iron (III). Using the optimal Fe-doped TiO<sub>2</sub> photocatalyst, the formaldehyde, ammonia, and benzene could be removed effectively whether existing separately or mixedly in the air. But the degradation ratios of formaldehyde, ammonia, and benzene in gas mixture after 9 h photocatalytic reaction under solar light (33.3%, 28.3%, and 28%) were lower than those of formaldehyde, ammonia, and benzene existing in air individually (55%, 53.1%, and 37.5%). So the photocatalytic degradation of indoor air pollutants using solar light is very promising. The photocatalytic degradation reaction kinetic of three pollutants followed the pseudo first-order kinetic model, the photocatalytic reaction was controlled by the surface chemical reaction, and the reaction rate was controlled by concentration of reactants.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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