

Research Article

Solar Photocatalytic Degradation of Typical Indoor Air Pollutants Using TiO₂ Thin Film Codoped with Iron(III) and Nitrogen

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Received 23 June 2014; Revised 23 August 2014; Accepted 25 August 2014

Academic Editor: Xinqing Chen

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A type of iron and nitrogen codoped titania thin film was prepared by sol-gel method to degrade three typical indoor air pollutants: formaldehyde (HCHO), ammonia (NH₃), and benzene (C₆H₆) under solar light. X-ray diffraction (XRD), UV-Vis spectroscopy, and energy dispersive spectra (EDS) were employed to characterize the photocatalysts. The results showed that the Fe/N codoped TiO₂ had a stronger absorption in the visible region than pure, Fe-doped, and N-doped TiO₂ and exhibited excellent photocatalytic ability for the degradation of indoor HCHO, NH₃, and C₆H₆. When the three pollutants existed in indoor air at the same time, the removal percentages of HCHO, NH₃, or C₆H₆ after 6 h photocatalytic reaction under solar light reached 48.8%, 50.6%, and 32.0%. The degradation reaction of the three pollutants followed the pseudo-first-order kinetics with the reaction rate constants in the order of 0.110 h⁻¹ for ammonia, 0.109 h⁻¹ for formaldehyde, and 0.060 h⁻¹ for benzene. The reaction rate constant decreased with the increase of initial reactant concentration, which reflected that there was oxidation competition between the substrate and its intermediate during the photocatalytic process.

1. Introduction

Indoor air quality within buildings has been paid great attention, since many metropolitans generally spend more than 80% of time in indoor environment [1]. Indoor air pollutants mainly include carbonyl compounds, volatile organic compounds, ammonia, particulate matter, and so forth. Among them, formaldehyde, ammonia, and benzene are the most representative, which come from the furnishings and decorating materials, causing nausea, chest tightness, wheezing, skin rashes, allergic reaction, and chronic poisoning [2].

Photocatalysis is an emerging and promising technology for the indoor air purification [3], and titania has been identified as the most effective and useful photocatalyst because of its outstanding physical and chemical properties [4–8]. However, with a wide band gap energy of 3.0–3.2 eV, titania cannot be activated to generate photoexcited electrons and holes to promote redox reaction unless it is irradiated by ultraviolet. 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, which hinders the application of TiO₂ as a photocatalyst with response to solar light [6, 9].

In the enhancement of the photoresponse of TiO₂ from ultraviolet to the visible range without decreasing photocatalytic activity, the modification to titania by doping with metal or nonmetal has been considered as one of the most promising methods [10–15]. Choi et al. conducted a systematic study of metal ions doping into TiO₂ for 21 metal ions [16]. Among various transition metal ions, Fe³⁺ was considered to be a successful doping element due to its half-filled electronic configuration [17]. Nitrogen and carbon doping have received attention due to low costs and the demonstration of band-gap narrowing, with significant improvement in visible light absorption capability [18]. Recent research results showed that the modification to titania by codoping may be a more effective method to improve the photocatalytic activity

under visible light [19, 20]. Zhao et al. prepared the B-Ni codoped photocatalyst using the modified sol-gel method. They pointed out that incorporation of B into TiO₂ could extend the spectral response to the visible region and that Ni doping could increase greatly the photocatalytic activity [21].

In this paper, a new solar photocatalyst, TiO₂ thin film codoped with iron(III) and nitrogen, was developed with flat glass as carrier to degrade three typical indoor air pollutants, formaldehyde, ammonia, and benzene, under solar light. The research finding provides a feasible way for enhancement of indoor air quality.

2. Experimental Procedure

2.1. Photocatalyst Preparation. Pure and doped TiO₂ thin films were prepared by sol-gel technique. The schematic diagram of preparing procedures of gels was described in Figure 1.

Then the plate glass was inserted vertically into the gel. After keeping for 30 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 gel was dried for 30 min at 100°C. At last, the glass was calcined for 4 h at 450°C (20°C/min).

2.2. Photocatalyst Characterization. The crystal structures of pure and doped TiO₂ were determined by a D-max-2500/PC X-ray diffractometer (XRD) equipped with Cu-K α radiation. The ultraviolet-visible (UV-Vis) absorption spectra of pure and doped TiO₂ thin films were recorded on a Shimadzu (Japan) UV-2550 spectrophotometer. The energy dispersive spectra of the Fe/N codoped TiO₂ thin film were recorded on JEM-2010 transmission electron microscopy (EDS).

2.3. Photodegradation of Gaseous Indoor Pollutants. Photocatalytic experiments with the prepared photocatalysts were carried out in a self-designed, cuboid, airtight, glass reactor (60 × 60 × 20 cm) with two holes, which were connected to sampling tubes of KC-6D air sampler. An electric fan was installed on the bracket of the airtight reactor in order to circulate the mixture of gaseous pollutants and air. Eight pieces of coated glass were placed vertically and evenly in the reactor. A predetermined amount of pollutant was injected in vessel under dark. The sunlight illumination was started following a dark period of 2 h which was sufficient to attain adsorption equilibrium with the pollutants. The residual concentration of pollutant was periodically measured every 60 min.

3. Results and Discussion

3.1. Results of Characterization

3.1.1. XRD Spectra. Figure 2 shows the XRD patterns of undoped TiO₂, Fe-doped TiO₂ with the doping proportion (mole ratio) is 1.00%, N-doped TiO₂ with the doping proportion (mole ratio) is 25.0%, and Fe/N codoped TiO₂ with the doping proportions (mole ratio) of iron and nitrogen is

1.00 and 25.0%, respectively. The results showed that all the samples had anatase structure mainly with the formation of characteristic diffraction peaks at $2\theta = 25.28^\circ, 37.80^\circ, 48.05^\circ, 53.89^\circ, 55.06^\circ, \text{ and } 62.69^\circ$, corresponding to (101), (04), (200), (105), (211), and (204) crystal surface. Compared to undoped TiO₂, the patterns of doped TiO₂, especially Fe/N codoped TiO₂, 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 as follows:

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

where D is crystallite size (nm), λ is X-ray wavelength (1.5406 Å), β is width of the obtained peak at half maximum, and θ is contour peak angle (radian). According to the Scherrer's formula, the crystallite sizes of the photocatalysts can be ranked in an order of Fe/N codoped TiO₂ (6.28 nm) < Fe-doped TiO₂ (7.35 nm) < N-doped TiO₂ (10.72 nm) < pure TiO₂ (12.02 nm).

3.1.2. UV-Vis Spectra. Figure 3 shows the ultraviolet-visible (UV-Vis) absorption spectra of the undoped TiO₂ thin film, Fe-doped TiO₂ thin film (the doping mole ratio is 1.00%), N-doped TiO₂ thin film (the doping mole ratio is 25.0%), and Fe/N codoped TiO₂ thin film (the doping mole ratios of iron and nitrogen are 1.00% and 25%, resp.). According to Figure 3, all the doped TiO₂ have stronger absorption than the undoped TiO₂ in the visible region. Among the photocatalysts, Fe/N codoped TiO₂ thin film has the strongest absorption in the visible region.

3.1.3. EDS Spectra. Figure 4 shows the energy dispersive spectra of the Fe/N codoped TiO₂ with the doping mole ratio of iron and nitrogen are 1.00 and 25.0%, respectively. The result showed that the iron and nitrogen were doped in the TiO₂ photocatalyst successfully. The mole ratio of Fe and Ti was very close to 1%, and the mole ratio of N and Ti was very close to 25%.

3.2. Photocatalytic Experiment

3.2.1. The Optimal Doping Amount of Iron and Nitrogen. The solar photocatalytic activity of doped TiO₂ thin films was determined by testing the degradation ratio of formaldehyde after 6 h photocatalytic reaction. Figure 5 shows the effect of Fe(III) doping amount on the photocatalytic activity of Fe-doped TiO₂ thin films, and Figure 6 shows the effect of N doping amount on the photocatalytic activity of N-doped TiO₂ thin films. From Figures 5 and 6, we could see that the solar photocatalytic performance of doped TiO₂ thin films exceeded that of pure TiO₂ thin film, indicating that both of Fe and N dopant could increase the solar photocatalytic activity. Among the Fe-doped TiO₂ thin films, the film with the doping mole ratios of iron was 1.00% and owned the best solar photocatalytic activity. And the solar photocatalytic activity of N-doped TiO₂ thin film with the doping mole ratio of nitrogen was 25.0% and was the best among the N-doped

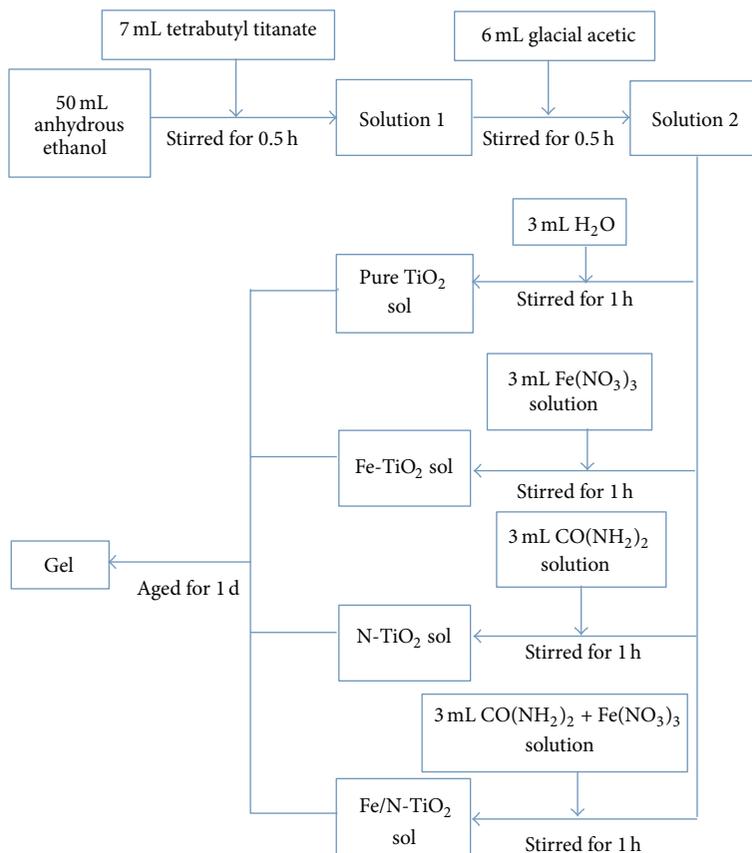


FIGURE 1: The schematic diagram of preparing procedures of gels.

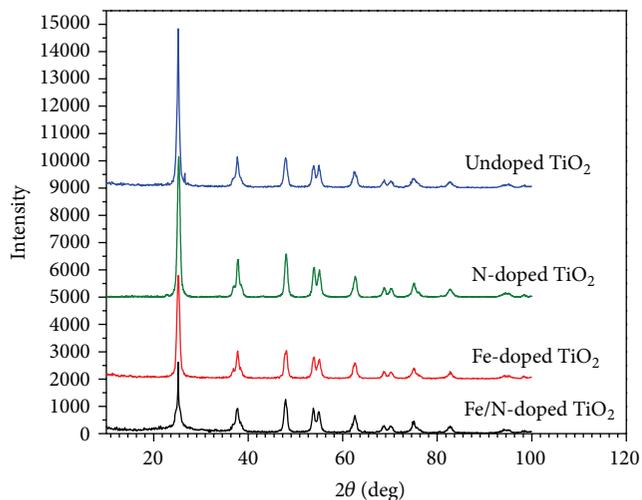
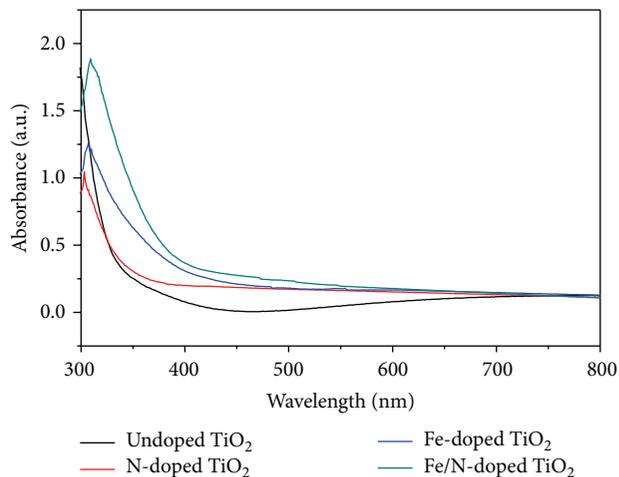
FIGURE 2: XRD spectra of TiO_2 catalysts.

FIGURE 3: UV-Vis absorption spectra.

TiO_2 thin films. So the Fe/N codoped TiO_2 thin film was prepared with the doping mole ratio of iron and nitrogen that was 1.00 and 25.0%, respectively.

3.2.2. Degradation of Formaldehyde, Ammonia, and Benzene.

Formaldehyde, ammonia, and TVOC exist in the indoor air at

the same time usually. So, we not only studied the photocatalytic degradation of formaldehyde, ammonia, and benzene when they exist in indoor air separately but also studied the photocatalytic degradation of the mixed formaldehyde, ammonia, and benzene in the indoor air. Figure 7 shows the degradation ratios of separate formaldehyde, ammonia,

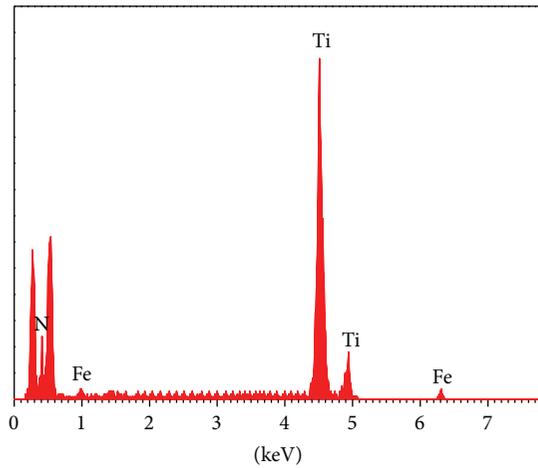


FIGURE 4: EDS spectra.

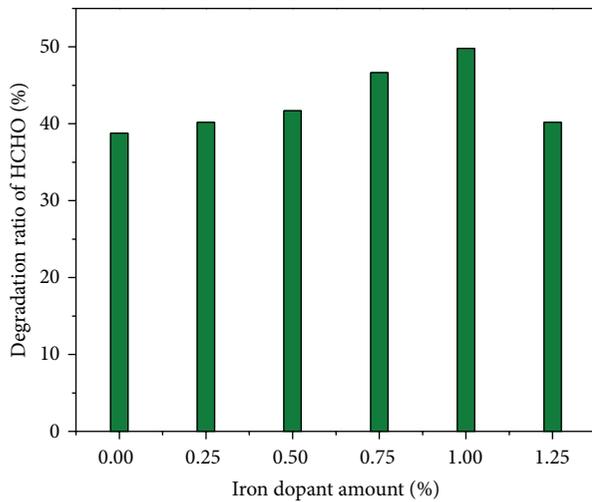
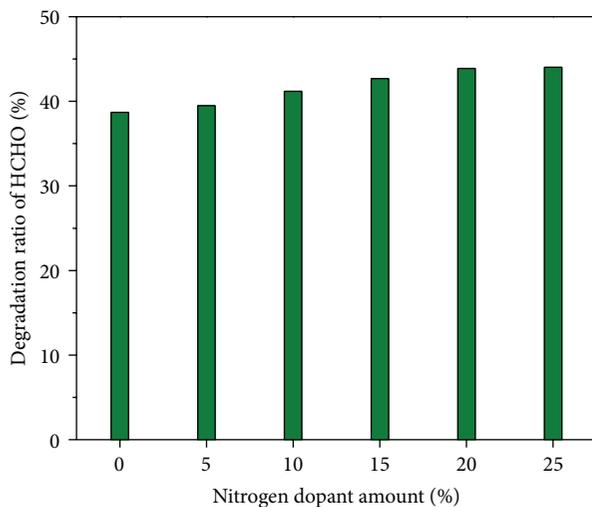
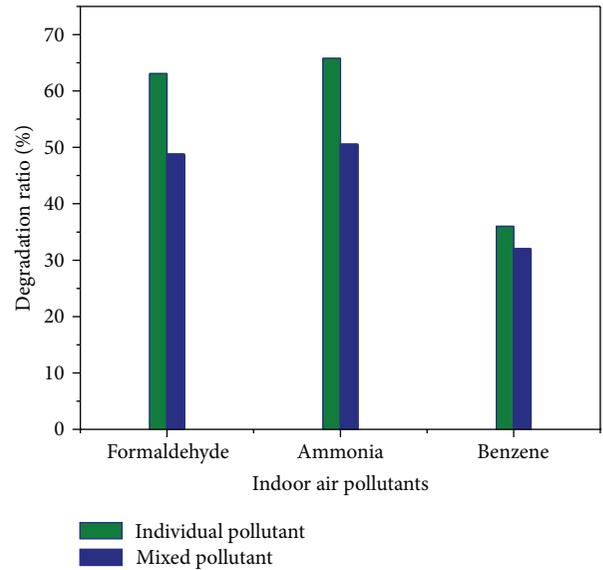
FIGURE 5: Effect of iron doping amount on photocatalytic activity of Fe-doped TiO₂.FIGURE 6: Effect of nitrogen doping amount on photocatalytic activity of N-doped TiO₂.

FIGURE 7: Degradation ratios of formaldehyde, ammonia, and benzene.

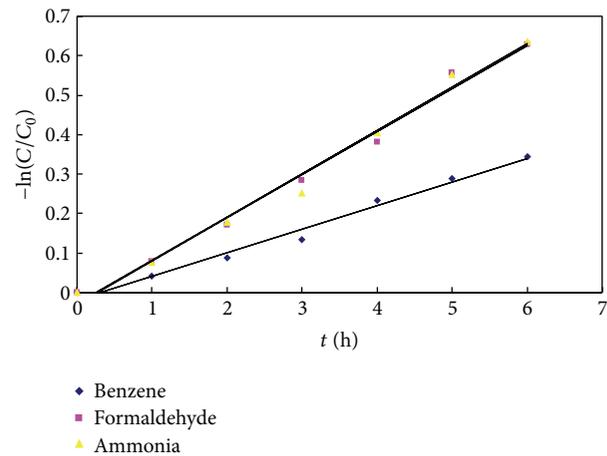


FIGURE 8: Kinetics of degradation reaction of the mixed pollutants.

and benzene and the mixture of three pollutants after 6 h of photocatalytic reaction under solar light.

As shown in Figure 7, appropriate amount of Fe³⁺ and N codoped into the TiO₂ thin film was helpful to further improve photocatalytic activity. The removal percentage of separate HCHO in the presence of the Fe/N codoped TiO₂ thin film was 63.1%, which was much greater than that in the presence of Fe-doped TiO₂ thin film (49.8%) and N-doped TiO₂ thin film (44.0%). The cooperation of Fe³⁺ and nitrogen could induce the formation of new energy levels close to the conduction band and valence band, respectively, leading to the much narrowing band gap. Besides, Fe³⁺ could trap the photogenerated electrons, while nitrogen could trap the photogenerated holes; thus, the codoping of Fe³⁺ and nitrogen could further restrain the recombination of the photogenerated electron and hole and enhance photocatalytic activity [22].

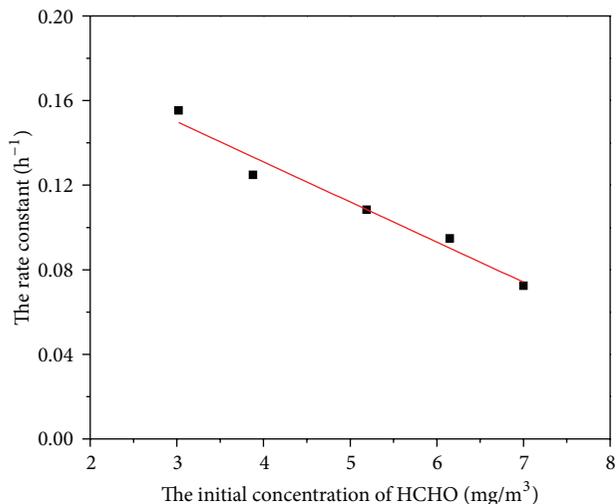


FIGURE 9: The relationship of reaction rate constant and initial concentration of HCHO.

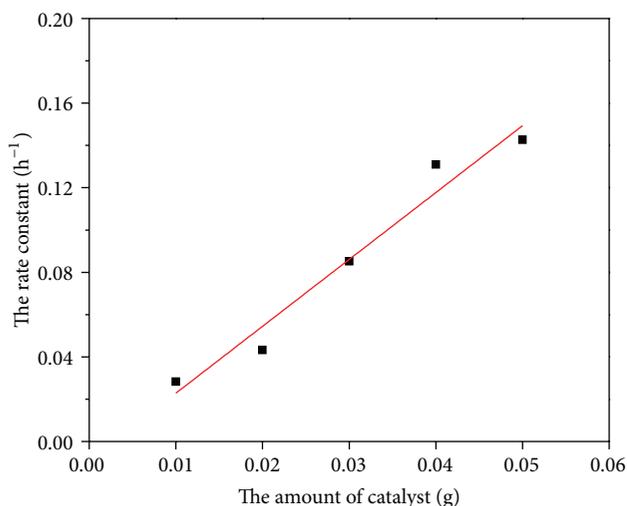


FIGURE 10: The relationship of reaction rate constant and the amount of catalyst.

Whether the three pollutants, formaldehyde, ammonia, and benzene, existed separately or mixed, they could be removed effectively using the Fe/N codoped TiO₂ thin film. But the removal percentage of formaldehyde, ammonia, and benzene in gas mixture (48.8%, 50.6%, and 32.0%) after 6 h photocatalytic reaction under solar light was lower than those of formaldehyde, ammonia, and benzene existing in air separately (63.1%, 65.8%, and 36.0%). This is due to gas molecules occupying fully the 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 Fe/N codoped TiO₂ thin film. 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 pollutant (C) to the initial concentration (C_0), k is the reaction rate constant, and t is the irradiation time. The experimental data were fitted by plotting $-\ln(C/C_0)$ against irradiation time. The fitting result was shown in Figure 8.

As shown in Figure 8, almost good linear relationships with the correlation coefficient $R^2 > 0.98$ were observed, indicating that the degradation reaction of formaldehyde, ammonia, and benzene followed the pseudo-first-order kinetics. The reaction rate constants of three pollutants were in the following order: ammonia (0.110 h^{-1}), formaldehyde (0.109 h^{-1}), and benzene (0.060 h^{-1}). This shows that the photocatalytic reaction is controlled by surface chemical reaction and reaction rate is controlled by reactant concentration.

3.2.4. Effect of Initial Reactant Concentration and Amount of Catalyst on the Reaction Rate. Since the photocatalytic reaction rate is controlled by reactant concentration, the photocatalytic degradation experiments with different initial concentration of HCHO (3.02 mg/m^3 , 3.88 mg/m^3 , 5.19 mg/m^3 , 6.15 mg/m^3 , and 7.00 mg/m^3) as degradation objects were conducted in order to understand controlling mechanism, and the results were shown in Figure 9. From Figure 9, we could see that there was good linear relationship between the rate constant and initial reactant concentration. The relation equation was $k = 0.207 - 0.0189C_0$, $R^2 = 0.956$. The rate constant decreased with the increase of initial reactant concentration. This reflected that there was oxidation competition between substrate concentration and its intermediate.

In addition, the amount of the photocatalyst is also the important influencing factor of photocatalytic reaction. Figure 10 shows the effect of the amount of Fe/N codoped TiO₂ (0.01 g, 0.02 g, 0.03 g, 0.04 g, and 0.05 g) on the photocatalytic degradation rate of formaldehyde. The results showed that the photocatalytic reaction rate constant increased with the increase of the amount of photocatalyst. The relation equation was $k = 3.16m - 0.0088$ with the correlation coefficient $R^2 = 0.964$, and m was the amount of catalyst.

4. Conclusions

The Fe/N codoped TiO₂ thin film was prepared by means of sol-gel method. The Fe/N codoped TiO₂ exhibited much higher photocatalytic activities than the pure one and those doped with Fe(III) or nitrogen alone under solar light. Indoor

HCHO, NH₃, and C₆H₆ could be removed effectively using the Fe/N codoped TiO₂ thin film under solar light. The removal percentages of three indoor pollutants with solar light irradiation for 6 h reached 63.1%, 65.8%, and 36.0% for separate formaldehyde, ammonia, and benzene and 48.8%, 50.6%, and 32.0% for mixed formaldehyde, ammonia, and benzene. The photocatalytic degradation reaction kinetic of mixed 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. Overall, using the Fe/N codoped TiO₂ thin film to purify indoor air under solar light is very promising.

Conflict of Interests

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

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