Facile formation and photocatalytic performance of flexible WO₃/TiO₂/wool fabric composite

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Abstract. In this work, a visible-light driven flexible WO₃/TiO₂/wool fabric composite photocatalyst was prepared and the photocatalytic performance was studied. Compared with other mole ratios of WO₃/TiO₂, the 0.18-WO₃/TiO₂ composite exhibited the strongest photocatalytic activity. Then, the WO₃/TiO₂/wool composites loaded by 0.18-WO₃/TiO₂ were used to degrade C.I. KN-R with different initial concentrations. The results showed that the C.I. KN-R could be almost complete degradation with lower concentrations (50 mg/L and 100 mg/L) after irradiation under visible light in 120 min. For higher initial concentration, more amounts of catalysts or longer reaction time may be required to achieve a complete degradation. Moreover, the stability and reusability of WO₃/TiO₂/wool composites were measured.

1. Introduction

The photocatalytic degradation of organic pollutants in water over TiO₂-based photocatalysts has attracted considerable interests for their high physical and chemical stability, non-toxicity, safety, low cost, and resistance to photocorrosion [1–3]. However, TiO₂ can only be excited by UV light because of its wide band gap [4]. Moreover, the recombination rate of the photogenerated electrons and holes is high [5]. Coupling TiO₂ with other metal oxide to construct a heterojunction structure, such as Fe₂O₃/TiO₂ [6], SnO₂/TiO₂ [7], WO₃/TiO₂ [8], MgO/TiO₂ [9] and so on, has been reported to be an effective approach that can improve the photocatalytic performance of TiO₂ by expanding the excitation wavelength range, promoting the charges separation and inhibiting the recombination of electrons and holes. Among these metal oxides, WO₃ has been mostly designed to be a promising co-catalyst for its narrower band gap (about 2.4~2.8 eV) and stronger absorption of visible light [10–12]. Moreover, WO₃ has a suitable conduction band potential and acts as an efficient charge separator by trapping the photogenerated electrons from TiO₂ [13], which has been assumed to facilitate the charge separation and thus may enhance the photoactivity of TiO₂.

Recently, to enhance the re-collecting and reuse abilities of the composite photocatalysts, some researches about flexible substrates such as fabrics or fibers have been reported [14–16]. The textiles used to support the photocatalysts have superior physical and mechanical properties, rich porous
structure and low cost. The special loose and porous structure could promote the absorption of dye molecules and be convenient for the recycling of the photocatalysts [17].

In this study, the wool fabric has been employed as a substrate to synthesize flexible WO3/TiO2/wool composite photocatalysts by dipping the wool fabric into the suspension of WO3/TiO2 composite which was synthesized by hydrothermal method. The photocatalytic performance, stability and reusability of the WO3/TiO2/wool composite photocatalysts were evaluated by using the C.I. KN-R as a model organic pollutant under visible light illumination.

2. Experimental

All the chemicals and reagents used in this investigation are analytical grade and used without further purification. Deionized water was used to prepare aqueous solutions.

2.1. Synthesis of WO3/TiO2 composites

4.50 mL Ti(OBu4) was dissolved in 4.5 mL ethanol with vigorous stirring to form a mixture. 45 mL HNO3 (0.1 mol/L) was slowly dripped into the mixture, which was stirred for 30 min at room temperature to obtain Ti precursor. W precursor was achieved by 5 mmol WCl6 dissolving in 50 mL ethanol with vigorous stirring for 1 h. The precursors with different W/Ti mole ratio were transferred to a Teflon vessel. The solution pH was adjusted to 1 and then reacted at 160 °C for 6 h by hydrothermal method. The obtained precipitates were filtered and washed with ethanol and distilled water, then dried at 60°C in a laboratory oven for 1h. Subsequently, the precipitates were calcined at 500 °C for 2h to obtain WO3/TiO2 composites. The mole ratios of WO3/TiO2 in the composites were 0.01, 0.10, 0.18, 0.25 and 0.43 and the products were named as 0.01-WO3/TiO2, 0.10-WO3/TiO2, 0.18-WO3/TiO2, 0.25-WO3/TiO2, 0.43-WO3/TiO2, respectively.

2.2. Preparation and Characterization of WO3/TiO2/wool composites

Before the preparation of WO3/TiO2/wool composites, it is necessary to pre-treat the wool fabric with H2O2 to destroy the scale layer on the surface, because the existence of scale layer makes the fabric hydrophobic. The pretreatment process is as follows: sodium silicate 0.70% (o.w.f), sodium carbonate 0.20% (o.w.f), 30% hydrogen peroxide 40ml/L, bath ratio 1:25, 50 °C, 1h.

After treatment, the surface of wool fabric becomes rough, which is benefit for the loading of WO3/TiO2 composites. Briefly, 0.10 g WO3/TiO2 composites were dispersed into 100 mL deionized water with vigorous stirring to form suspension, then 0.5 g of the above pretreated wool fabrics were immersed in the suspension and heated at 50 °C for 1 h. Finally, the wool fabrics were took out and dried at 100°C for 2h. The above steps were repeated three times to obtain the WO3/TiO2/wool composite photocatalysts. Morphological images of the obtained composite were conducted on a scanning electron microscope (SEM, JSM-5600LV, Japan).

2.3. Photocatalytic degradation experiments

The degradation experiments were carried out in a BL-GHX-V photochemical reaction apparatus (Shanghai Bilon Instrument Co., Ltd.) with the visible light irradiation (1000W Xenon lamp). For the degradation of 50 mg/L C.I. KN-R (50 mL), the amount of WO3/TiO2 composites was 0.20 g/L. While, for the degradation of 100 mg/L C.I. KN-R (50 mL), the amount of WO3/TiO2/wool composites was 10 g/L. The composite photocatalysts were dispersed in C.I. KN-R solutions and stirred sufficiently in dark for 30 min to achieve the adsorption/desorption balance. HCl or NaOH were used to adjust the pH of the reaction solutions. After predetermined time intervals, the suspensions were collected and centrifuged (10000 rpm, 10 min) to remove the residual catalysts, and analyzed immediately by using a UV–vis spectrometer. All the experiments were performed at 25±1 °C.

The degradation efficiency of dye was calculated by the equation:

\[ \text{Degradation efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1) \]
The degradation of C.I. KN-R followed a pseudo-first-order reaction and its kinetics can be expressed as:

\[ \ln\left(\frac{C_t}{C_0}\right) = -K \times t \quad (2) \]

where \( K \) is the rate constant (min\(^{-1}\)), \( C_0 \) and \( C_t \) are the concentrations at initial state and after reaction for \( t \) min, respectively.

3. Results and discussion

3.1. Effect of mole ratios of WO\(_3\)/TiO\(_2\)

The effect of mole ratios of WO\(_3\)/TiO\(_2\) on the degradation efficiency of C.I. KN-R was investigated (Figure 1). It can be seen from Figure 1, the degradation efficiency increased with increasing the mole ratios of WO\(_3\)/TiO\(_2\) from 0.01 to 0.18. When the mole ratio is 0.18, the degradation efficiency of C.I. KN-R could reach 92.33% after 120 min of illumination. However, the degradation efficiency of C.I. KN-R would decrease gradually if the mole ratios of WO\(_3\)/TiO\(_2\) increased to 0.43. The results showed that the photocatalytic activity of 0.18-WO\(_3\)/TiO\(_2\) composite would be strongest. Therefore, the WO\(_3\)/TiO\(_2\)/wool composites would be prepared by using the WO\(_3\)/TiO\(_2\) composites synthesized under this condition.

3.2. The photocatalytic performance of WO\(_3\)/TiO\(_2\)/wool composites

The SEM images of wool fabric before and after WO\(_3\)/TiO\(_2\) composites loading were shown in Figure 2. Figure 2a showed that the wool fabric had a smooth surface and no obvious particulate substance existed on the surface. Figure 2b showed that the surface of wool fibers became rough and the scale layer up-warped. The images of the wool fabric loaded with WO\(_3\)/TiO\(_2\) composite particles were shown in Figure 2c and Figure 2d. As expected, the particles were successfully dispersed on the surface and gap of the wool fabric.
Figure 2 showed the degradation efficiency of C.I. KN-R with the concentrations range from 50 to 500 mg/L. The degradation efficiency was decreased from 99.13% to 60.64% with the increase of initial concentrations (Figure 3a). When the initial concentration is low (50 mg/L and 100 mg/L), the degradation of C.I. KN-R would be nearly complete. The results suggested that the active radicals produced during the photocatalytic process were sufficient. The degradation efficiency of C.I. KN-R dropped rapidly if the initial concentration is high (300 mg/L and 500 mg/L) for the amount of active radicals produced was not enough to completely oxidize the dyes. The reasons may be that the amount of active radicals produced almost the same when preserving other reaction condition but changing the initial concentrations [18]. Much more molecules of C.I. KN-R adsorbed on the surface of the WO3/TiO2/wool composites and then the competitive adsorption of OH− on the same site decreased if the concentration is high. Therefore, the amount of ·OH and ·O2− on the surface of catalyst decreased [19]. So, for higher concentrations, more amounts of catalysts would be required to produce enough oxidants for degrading C.I. KN-R completely.

Figure 3b confirmed that the degradation rate of C.I. KN-R follow the first-order reaction kinetics model. The regression equations and kinetic constants at different initial concentrations were calculated. It can be seen from Table 1, the K values decreased from 0.04786 min⁻¹ to 0.00951 min⁻¹, while the half-reaction time (t₁/₂) [20] increased from 14.48 min to 72.89 min, correspondingly. The results indicated that longer reaction time would be required to degrade C.I. KN-R completely with higher concentrations.

The reusability as an important parameter that used to measure the activity and stability of WO3/TiO2/wool composites was tested. As showed in Figure 4, degradation efficiency of C.I. KN-R dropped slightly after five recycle runs, which indicated that the photocatalytic activity of WO3/TiO2/wool composites were stable. The good stability illustrated that the WO3/TiO2/wool
composites can resistant to photocorrosion in the photocatalytic process and can be applied to water purification.

**Figure 3** (a): Degradation efficiency of C.I. KN-R with different initial concentrations; (b): The slope of the plot of ln \( C_t/C_0 \) versus reaction time.

**Table 1.** Regression equations and kinetic constants at different initial concentrations

| Initial Concentrations (mg/L) | Regression equations | \( R^2 \) | K (min\(^{-1}\)) | \( t_{1/2} \) (min) |
|-------------------------------|----------------------|----------|-----------------|------------------|
| 50                            | \( y=0.04598x-0.50130 \) | 0.96067  | 0.04598         | 15.07            |
| 100                           | \( y=0.04786x-1.13505 \) | 0.93703  | 0.04786         | 14.48            |
| 300                           | \( y=0.01730x-0.44498 \) | 0.99068  | 0.01730         | 40.07            |
| 500                           | \( y=0.00951x-0.19930 \) | 0.97831  | 0.00951         | 72.89            |

**Figure 4** Degradation efficiencies of C.I. KN-R in recycled runs.
4. Conclusions

In summary, the preparation and investigation on the photocatalytic performance of \( \text{WO}_3/\text{TiO}_2 \) composites and \( \text{WO}_3/\text{TiO}_2/\text{wool} \) composites under visible light irradiation were conducted. The 0.18-WO\(_3\)/TiO\(_2\) composite showed the strongest photocatalytic activity among the different mole ratios of \( \text{WO}_3/\text{TiO}_2 \). For the \( \text{WO}_3/\text{TiO}_2/\text{wool} \) composites loaded by 0.18-WO\(_3\)/TiO\(_2\), a nearly complete degradation of C.I. KN-R (50 mg/L and 100 mg/L) was achieved in 120 min. It was found that more amounts of catalysts or longer reaction time would be required to produce enough oxidants for degrading C.I. KN-R completely if the initial concentration is high. Moreover, the \( \text{WO}_3/\text{TiO}_2/\text{wool} \) composites possessed excellent stability with consecutive runs and showed promise as new flexible photocatalysts for environmental remediation.

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