Fabrication of Ag/TiO$_2$ Cotton Fabric to Enhance Photocatalytic Degradation of Anionic Dye

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ABSTRACT

Ag/TiO$_2$ composite fabric was prepared by coprecipitation with TiCl$_4$ as a titanium source and AgNO$_3$ as a silver source. The samples were characterized by scanning electron microscope (SEM), thermogravimetric analyzer (TG) and Fourier transform infrared spectrometer (FTIR). The photocatalytic activity of synthetic fabrics was measured by the degradation of anion dyes under ultraviolet light. The effects of silver loading concentration, fabric area, initial concentration, and photocatalytic time on photocatalytic activity were investigated. The experimental results showed that the degradation rate of Ag/TiO$_2$ composite fabric on anion dyes could reach 70.76% in 50 minutes, indicating that the prepared Ag/TiO$_2$ composite fabrics had high photocatalytic activity.

INTRODUCTION

The rapid development of the printing and dyeing industry has brought us a wealth of printing and dyeing products as well as pollution problems (Holkar et al. 2016, Anastasi et al. 2011). The research of efficient and economical sewage treatment technology has become a research hotspot. Traditional water treatment methods mainly include physicochemical methods and biological methods (Banks et al. 2020). However, these methods have several disadvantages such as low degradation efficiency and unsatisfactory effect, and cannot meet the increasingly strict wastewater discharge standards, which pose a serious threat to the water environment.

Photocatalytic technology, as a new green environmental protection technology, can oxidize and decompose organic molecules into carbon dioxide, water, and some inorganic small molecules under light irradiation (Lu & Zhao 2018). Because of its excellent photoactivity, chemical and thermal stability, and the ability to degrade toxic organic pollutants in water, TiO$_2$ has become one of the most promising environmental remediation materials (Riegel & Bolton 1995, Farbod & Khademalrasool 2011, Kaneco et al. 2006). It was widely used in wastewater treatment, organic degradation, air treatment, and other fields. However, the practical application of TiO$_2$ has been extremely limited. The wide bandgap (e.g. $\Gamma = 3.2$ eV) reduces the utilization rate of sunlight (Zhao et al. 2020, Habibi-Yang & Feizpoor 2019). Meanwhile, the recombination of electrons and holes that generate on the TiO$_2$ is unfavorable to the efficiency of the TiO$_2$ photocatalysts (Ma et al. 2020).

To overcome these shortcomings, a large number of studies have concentrated on the improvement of the photocatalytic efficiency and visible light utilization of TiO$_2$. At present, various strategies including noble metal deposition (Benz et al. 2020), semiconductor composite (Lv et al. 2014), metal or non-metal doping (Khan et al. 2017, Li et al. 2018), and load modification (Zhao et al. 2012) have been explored. Among them, noble metal (Pt, Ag, Au) deposition of TiO$_2$ significantly improves the electron capture efficiency, which is one of the most effective ways to improve its photocatalytic activities. Due to the large Fer between nano TiO$_2$ and noble metal, it is thermodynamically possible to transfer electrons brought by TiO$_2$ conduction to metallic particles, resulting in the formation of electron accumulation center on the surface of noble metal. This is a kind of photoelectron trap, which achieves a good separation of electrons and holes and greatly improves the photocatalytic activity of TiO$_2$ (Kulkarni et al. 2015). In this work, Ag was selected as the deposited noble metal. Considering the properties of easy doping, high electrical conductivity, and good light absorption ability, it is
one of the most suitable materials for industrial applications. What’s more, there is a synergy between Ag and TiO$_2$ at room temperature. Working as an electron receiver, Ag helps to reduce the recombination rate of electron-hole pairs. Ag/TiO$_2$ materials can receive light energy in both ultraviolet and visible light, optimizing the utilization of solar energy. A large number of studies have shown that silver deposition can effectively improve the photocatalytic of TiO$_2$ (Zheng et al. 2019, Rana et al. 2016).

**MATERIALS AND METHODS**

**Materials and Reagents**

The titanium tetrachloride (TiCl$_4$, 99.5%), nitric acid (HNO$_3$, 65-68%), and absolute ethanol were purchased from Aladin Industrial Corporation. The silver nitrate (AgNO$_3$) was obtained from Shanghai Fine Chemical Research Institute.

**Preparation of Ag/TiO$_2$ Cotton Fabric**

Add 2 g of TiCl$_4$ into 10 mL absolute ethanol, and mark it as solution A. Add AgNO$_3$ (0%, 2%, 5%, 8%, 10%, 15%) into 40 mL absolute ethanol and altering the pH level to 2, marking it as solution B. Soak the washed cotton cloth into B solution. Lastly, add solution A to B at a slow rate of about 2 sec per drop while constantly stirring the solution. After stirring for about 2 hours, wash the fabric with distilled water and dry it in the oven (60°C, 15 mins).

**Characterization of Ag/TiO$_2$ Cotton Fabric**

FTIR was used to detect the chemical groups of unmodified and Ag/TiO$_2$ cotton fabric in the wavelength range of 500-4000 cm$^{-1}$. We use TG to analyze the thermal performance and decomposition kinetics. The microstructure and morphology of the prepared fabric were analyzed by SEM.

**Photocatalytic Activity of Ag/TiO$_2$ Cotton Fabric**

The photocatalytic activity of Ag/TiO$_2$ fabric was evaluated by testing the degradation of anionic dye solution as a model pollutant by using UV light. The photocatalytic activity of the Ag/TiO$_2$ fabric area varies from 15 cm$^2$ to 35 cm$^2$. The effect of initial concentration on the photocatalytic activity of the dye solution varies from 5 mg.L$^{-1}$ to 25 mg.L$^{-1}$. The distance of the UV lamp was kept 15 cm above the dye solution. We use the ultraviolet-visible spectrophotometer to measure the absorbance of the solution every 5 minutes.

**RESULTS AND DISCUSSION**

**Morphology of the Fabric**

The morphology of the non-modified, pure TiO$_2$ and 15% Ag/TiO$_2$ fabric is shown in Fig. 1. The surface of the pure TiO$_2$ and 15% Ag/TiO$_2$ composite fabric looked uneven with particles attached, indicating that TiO$_2$ and Ag were successfully supported on the fabric. The surface agglomeration of

![Fig. 1: The morphology of the non-modified (a), pure TiO$_2$ (b), 15% Ag/TiO$_2$ (c) fabric.](image-url)
pure TiO$_2$ fabric is obvious, which may be because TiO$_2$ is attracted and then agglomerated by polar groups of cotton fabric. The surface of the Ag/TiO$_2$ composite fabric also has some pellets. However, compared with pure TiO$_2$, doping Ag reduced the particle agglomeration and the dispersion degree is higher.

**Chemical Structure**

In Fig. 2, no new absorption peak appeared in the infrared spectra of a, indicating that Ag-doped would not affect Ti-O bond, O-O bond and Ti-Ti bond in the TiO$_2$ structure. 3338 cm$^{-1}$ is the stretching vibration peak of O-H on the fabric surface, which confirmed the strong interaction of water molecules on the surface of TiO$_2$. The peak at 1644 cm$^{-1}$ is caused by the bending vibration of O-H and is due to the absorption of water molecules. The peaks in the range of 526-664 cm$^{-1}$ are caused by the stretching vibration and variable angle vibration of Ti-O. It indicated that Ag/TiO$_2$ indeed existed on the surface of the fabric. The peak near 2901 cm$^{-1}$ is C-H stretching vibration, and the peak at 1167, 1108, and 1050 cm$^{-1}$ is C-O-C stretching vibration, which is in line with the characteristic peak of the infrared spectrum of cotton fiber.

**Thermo Gravimetric Analysis**

Fig. 3 shows the thermogravimetric characterizations of non-modified cotton and 15% Ag/TiO$_2$ fabric. The results show that the decomposition of 15% Ag/TiO$_2$ fabric is earlier than unmodified fabric. At room temperature of 275°C, there is dehydration of physically adsorbed water and evaporation of waxes and other small molecules. Between 275°C and 355°C, both of them had a large mass loss, which is caused by the decomposition of fibrous macromolecules of organic matter. It is obvious that the residual value of the weight of unmodified cotton is lower than that of 15% Ag/TiO$_2$ fabric, which proved that the thermal stability of the modified fabric is improved.

**Factors Influencing the Photocatalytic Activity**

**Effect of Doped Silver Content on Photocatalytic Degradation**

Fig. 4 shows that under the same irradiation time, the photocatalytic efficiency of Ag/TiO$_2$ composite fabric with different silver loads is improved to different degrees compared with pure TiO$_2$ fabric. At the same time, Ag increases the content of hydroxyl and O$_2$, promoting the redox reaction. However, the composite of Ag and TiO$_2$ has a saturation value. The photocatalytic activity of the fabric peaked when the silver load was 5%. This may be because too much silver forms excessive contact sites. Ag itself constantly accepted electrons, however, it could not transmit electrons to O$_2$, and its ability to accept holes was constantly enhanced, leading to the combination of electrons and holes captured by Ag (Parastar et al. 2013). Other studies have shown that excessive Ag will cover the surface of TiO$_2$, resulting in the decrease
of hole concentration (Suwarnkar et al. 2014).

**Effect of Initial Concentration of Dye on Photocatalytic Degradation**

In Fig. 5, the influence of initial dye concentration on photocatalytic degradation is shown. As shown in this figure, when the dye concentration is lower than 15 mg L⁻¹, the degradation rate increases with an increase in the initial concentration. This may be because the degradation process conforms to the first-order reaction kinetics in a certain range of dye concentration. Dye molecules competitively adsorbed on the catalyst surface, which accounted for the increase of reaction rate and degradation rate. When the concentration is higher than 15 mg L⁻¹, the initial degradation rate slows down, and the final degradation rate decreases. Excessive dye molecules adsorbed on TiO₂, preventing the reaction of dye molecules with free radicals and electron holes.

**Effect of Fabric Area on Photocatalytic Degradation**

The effect of fabric area on anionic dye degradation under...
UV irradiation is shown in Fig. 6. When the fabric area is below 25 cm$^2$, the initial degradation rate increased rapidly with the increase of fabric area, and the degradation rate was also improved. The increase of fabric area was equivalent to the increase in the amount of catalyst and catalytic active centers. The result is the opposite when the fabric area is larger than 25 cm$^2$. This may be because when the fabric area is too large, the light transmittance is affected, the light absorption and the O$_2$ contact of the lower layer are reduced, resulting in the decrease of photocatalytic activity.

**Effect of Irradiation Time on Photocatalytic Degradation**

Fig. 7 shows the degradation of dye at different irradiation times. With the increase of illumination time, the degradation degree of anionic dyes increased. And the degradation rate of 5% Ag/TiO$_2$ composite fabric was higher than that of pure TiO$_2$ fabric, indicating that Ag was an effective catalyst. When the UV light lasted for more than 50 minutes, the degradation rate of the two fabrics no longer significantly increased, indicating the photocatalytic reaction basically approached equilibrium.

**Catalytic Mechanism Analysis**

The possible catalytic mechanism is shown in Fig. 8. When Ag/TiO$_2$ is exposed to ultraviolet light (hv > 3.2 eV), electrons are stimulated and transfer from the valence band (VB) to the conduction band (CB), leaving holes in the valence
band. The silver then acts as an electron receiver, capturing electrons from TiO$_2$ and storing them on its surface. Ag can effectively attract and conduct electrons, and effectively prevent electrons from recombining with holes. The adsorbed oxygen molecules on the silver are quickly captured by electrons, reduced to form superoxide radical (O$_2^-$), and further react with H$^+$ to form hydroxyl radical (•OH). On the other hand, the holes of Ag$^+$ can react with H$_2$O to form •OH. The e$^-$ and h$^+$ get more chances to react with O$_2$ and H$_2$O. •OH and O$_2^-$ have high oxidation capacity, which can oxidize and degrade organic molecules to H$_2$O and CO$_2$. The degradation reactions are shown in the following equations.

CONCLUSIONS

These experiments studied the photocatalytic degradation of anionic dye with Ag-doped TiO$_2$ cotton fabric (produced by coprecipitation method) under UV irradiation. The effects of Ag-doped, initial concentration, fabric area, and irradiation time were investigated. The experiments confirmed that Ag/TiO$_2$ was successfully doped on cotton fabric and the photocatalytic property of the modified fabric was improved. In this study, results showed that the optimal silver content doped on TiO$_2$ was 5%, the fabric area was 25 cm$^2$, the initial concentration was 15 mg.L$^{-1}$, and the optimal irradiation time
was 50 mins. Under the best conditions, the degradation rate could reach 70.76%.

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