Halloysite-TiO₂-Ag composites: Preparation, characterization and photodegradation

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Abstract. Halloysite (HNTs)-TiO₂-Ag composites were fabricated by depositing anatase TiO₂ and nano Ag particles on the HNTs surfaces. The composite was characterized with corresponding instrumental analysis methods. Compared with HNTs-TiO₂ composites, the HNTs-TiO₂-Ag composites exhibited better photocatalytic activity in the decomposition of MB and the persistent organic pollutant 4-nitrophenol (4-NP) under UV irradiation. After 2.5 hours of UV light irradiation, HNTs-TiO₂-Ag composites removed about 97.63% and 51% of MB and 4-NP, respectively.

1. Introduction

Dyes are widely used in environmental, chemical, textile, cosmetics and other fields. [1]. However, dyes are very difficult to handle because they are difficult to be degraded into non-toxic small molecules, and they are very stable to light and heat. [2]. Dyes can cause serious damage to ecological balance and human health when discharged into nature. Adsorption technology is widely used to remove some dyes, especially those that are not easy to biodegrade. Various adsorbents such as carbon nanotubes, graphene oxide, zeolites, clays, biomass and polymeric materials have attracted the attention of researchers[3].

Halloysite (HNTs) is a natural alumino silicate clay mineral with large specific surface area, unique hollow microtubular structure and good biocompatibility and thermal stability. HNTs is generally composed of multiple layers, its external diameter is 10-20 nm, and the inner diameter is about 40-100 nm. It has a chemical formula of Al₂Si₂O₅(OH)₄·nH₂O, which is similar to kaolinite except for the presence of an additional water monolayer between the adjacent clay layers[4]. HNTs occurs mainly in two polymorphs: the anhydrous form, with and interlayer of 7 Å, and the hydrated form, with expanded interlayer spacing of 10 Å, as a result of the incorporation of water in the inter lamellar space[5]. HNTs tubes consist of gibbsite octahedral sheet (Al–OH) groups on the internal surface and siloxane groups (Si–O–Si) on the external surface[6]. Due to the different chemical groups, the HNTs has a negative charge on the outer surface and a positive charge on the inner surface in the pH range 2-8. HNTs has a highly negatively charged outer surface, which makes it have superior adsorption, pore filtration, and ion exchange properties. These excellent properties make HNTs possible as an adsorbent, a drug carrier, and a fixed catalytically active molecule.

TiO₂ is the most excellent photocatalytic material due to its non-toxicity, high photocatalytic
activity and reusability. However, TiO$_2$ nanoparticles are prone to aggregate, resulting in an adverse effect on the photocatalytic activity\cite{7}. Consequently, great efforts have been made to block the aggregation of TiO$_2$ nanoparticles, such as coating method. The Ag nanoparticles are deposited on the TiO$_2$ nanoparticles, the fabrication of metal-semiconductor oxide composites can improve the photocatalytic activities of semiconductor oxide photocatalysts. The electron transfers from semiconductor oxides to metal nanoparticles can occur, which can decrease the number of electron/hole recombination events and improve the photocatalytic performance of semiconductor oxide-based catalysts\cite{8}.

In the present work, the HNTs-TiO$_2$-Ag composites are prepared by sol-gel method and the structure of the composite was characterized by various testing methods. In addition, in order to explore the photocatalytic performance of the material, the work studied the photocatalytic degradation of MB and 4-NP systematically.

2. Materials and methods

2.1. Materials
The HNTs were obtained from Hebei Province, China. MB dye and 4-NP were provided by Tianjin Damao Chemical Reagent Co., Ltd. All other reagents are of analytical grade.

2.2. The Preparation of HNTs-TiO$_2$-Ag composites
Glacial acetic acid (4 mL) and deionized water (10 mL) were added in 30 mL absolute ethanol, followed by the addition of 8.5 g silver nitrate. And then, the concentrated nitric acid was added to the solution to make the pH within 2-3. The solution was protected from light and stirred for 10 min at the room temperature.

15 g of Tetrabutyltitanate was mixed with a certain amount of absolute ethanol. The mixture was mechanically stirred for 20 min at 25°C. HNTs (6 g) were slowly added in the mixture. The obtained suspension was continuously stirred for 1 h. The solution was added dropwise to the suspension and the sol can be obtained after stirring for 1 h. The sol was stored at 25°C to form better nanoparticles. Firstly, the products were centrifuged with ethanol and oven-dried. And then, HNTs-TiO$_2$-Ag composites were calcined in Muffle furnace at 300°C.

2.3. Fourier transform infrared spectroscopy
The spectra of composites were obtained on a BIO-RAD FTS 3000 IR Spectrum Scanner. The resolution of the instrument was 4 cm$^{-1}$, the analysis range was 300-4000 cm$^{-1}$, and the wave number accuracy was 0.01 cm$^{-1}$. The wavelength range of each absorption band was observed and analyzed and the functional groups in the molecule were inferred.

2.4. X-ray diffraction
HNTs, HNTs-TiO$_2$ and HNTs-TiO$_2$-Ag powders were placed in a sample reservoir to hold the sample reservoir in the diffractor. Scanning was operated using a Bruker D8-S4 X-ray diffractometer. The test parameters were: Cu target, scanning speed was 4 ° / min, the range of diffraction angle is 2θ = 10-70 °, Cu Ka wavelength was 1.542 Å.

2.5. Transmission electron microscope
Drops of HNTs-TiO$_2$ and HNTs-TiO$_2$-Ag aqueous suspensions were delivered onto the copper grid and air dried. The samples were analysed using a TEM JEM-1200EX.

2.6. Photodegradation Experiments
The glass bottles that contain adsorbents and dyes (MB) were exposed to ultraviolet light. The concentration of MB was measured by an ultraviolet spectrophotometer at regular intervals. The degradation rate is represented by (C$_0$−C$_t$)/C$_0$, C$_0$ is the initial concentration of methylene blue and C$_t$
is the concentration measured after photocatalytic degradation for a certain period of time[9]. MB dye was replaced with 4-NP (0.01 g/L) and the degradation rate of 4-NP could be measured.

3. Results and discussion

3.1. Morphology
The morphologies of the composites are obtained by TEM. In Fig. 1(a-b), TiO₂ particles or clusters are deposited on the HNTs. The size of the TiO₂ particles or clusters is about 10-40 nm. In Fig. 1(c-d), Ag and TiO₂ particles The size of the particles is about 10-20 nm, and they are evenly distributed on the surface of the HNTs tube with little agglomeration. It can be seen from the figure that the addition of nano Ag weakens the aggregation of TiO₂.

3.2. FTIR
Fig. 2 exhibits the FTIR spectra of HNTs, HNTs-TiO₂ and HNTs-TiO₂-Ag. The double peaks at 3696 and 3623 cm⁻¹ are due to the stretching vibrations of Al-OH groups at the surface of HNTs[10,11]. The hydroxy bending vibration absorption peak of HNTs appear at 916.02 and 1028.084 cm⁻¹[12]. The above mentioned peaks all appear in FTIR of HNTs-TiO₂ except for HNTs-TiO₂-Ag. Due to the loading of Ag particles, the absorption peaks at 3696 and 3623 cm⁻¹ are blue-shifted and moved to 3660 and 3704cm⁻¹, respectively.

![TEM micrograph of the HNTs-TiO₂(a-b) and HNTs-TiO₂-Ag(c-d).](image-url)
3.3. XRD
The X-ray diffraction patterns of the HNTs, HNTs-TiO₂ and HNTs-TiO₂-Ag are obtained. As you can see from the figure, the powder of HNTs-TiO₂-Ag display distinct peaks at 2θ values of about 25.3, 37.9, 47.6, 54.8 and 62.7[13]. The diffraction peak of the nanosilver is at a 2θ value of 38.1[14]. The above data indicates that Ag and TiO₂ particles are attached to the halloysite nanotubes, which is consistent with the TEM and FTIR results. The diffraction peak of Ag is not very obvious. This may be caused by: (i) The diffraction peaks of Ag are not obvious due to the low Ag content; (ii) The diffraction peak of Ag overlaps the diffraction peak of TiO₂[8].

Fig 2. FTIR spectra of HNTs, HNTs-TiO₂ and HNTs-TiO₂-Ag.
3.4. Photodegradation

As shown in Fig. 4, after photocatalysis for 2.5 h, the absorbance decreased from 2.318 to 0.055 for HNTs-TiO$_2$-Ag composite. The degradation rate of HNTs-TiO$_2$-Ag composite to methylene blue was 97.63%, while the degradation rate of HNTs-TiO$_2$ composite was 51.08%. The removal of MB is the result of both adsorption and photocatalysis, but HNTs-TiO$_2$-Ag exhibits better dye removal performance[15]. As shown in the Fig. 5, after photocatalysis for 2.5 h, the degradation rate of 4-NP by HNTs-TiO$_2$-Ag composites was 51%, while the degradation rate of HNTs-TiO$_2$ composite was 20.75%. The results show that the addition of Ag particles can improve the photocatalytic performance of the composites.

![Fig 3. X-ray diffraction patterns of HNTs, HNTs-TiO$_2$, and HNTs-TiO$_2$-Ag.](image)

**Fig 3.** X-ray diffraction patterns of HNTs, HNTs-TiO$_2$, and HNTs-TiO$_2$-Ag.

![Fig 4. Photocatalytic degradation of MB on HNTs-TiO$_2$ and HNTs-TiO$_2$-Ag.](image)

**Fig 4.** Photocatalytic degradation of MB on HNTs-TiO$_2$ and HNTs-TiO$_2$-Ag.

![Fig 5. Photocatalytic degradation of 4-NP on HNTs-TiO$_2$ and HNTs-TiO$_2$-Ag.](image)

**Fig 5.** Photocatalytic degradation of 4-NP on HNTs-TiO$_2$ and HNTs-TiO$_2$-Ag.

4. Conclusions

In this paper, TiO$_2$ and Ag particles were successfully deposited on the surface of HNTs by sol-gel
method. The doping of the Ag particles reduces the agglomeration of the TiO₂ particles, which improves the photocatalytic performance of the photocatalyst to some extent. The prepared HNTs-TiO₂-Ag composite has excellent adsorption performance and photocatalytic performance and can improve the removal of dyes. In terms of sewage treatment, HNTs-TiO₂-Ag composite show good application value.

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