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Enhanced adsorption and photocatalytic degradation of high-concentration methylene blue on Ag_2O-modified TiO_2-based nanosheet

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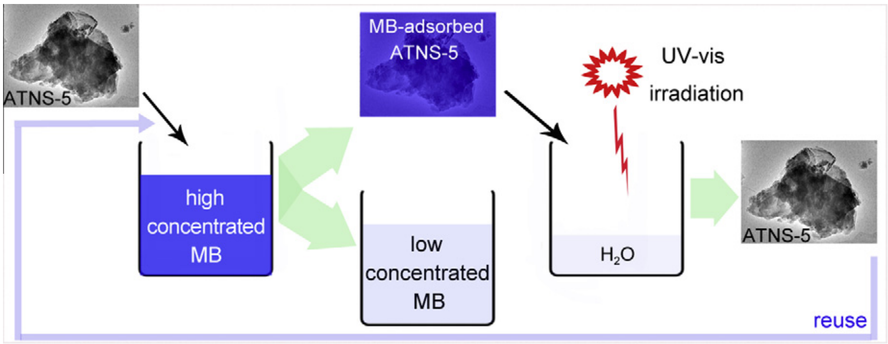
HIGHLIGHTS

- ▶ TiO_2-based nanosheet (TNS) was modified by Ag_2O photocatalyst.
- ▶ Ag_2O-modified TNS possesses enhanced adsorption and photocatalytic activity.
- ▶ The maximum adsorption capacity of Ag_2O-modified TNS for MB is up to 172.4 mg/g.
- ▶ High-concentration MB can be removed by adsorption–photocatalytic degradation.
- ▶ Ag_2O-modified TNS exhibits good reusability for removing high-concentration MB.

GRAPHICAL ABSTRACT



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ABSTRACT

TiO_2-based nanosheet (TNS) was modified with Ag_2O, and the adsorption and photocatalytic performances of modified nanosheet were characterized by the removal of high-concentration methylene blue (MB). When TNS was loaded with a proper amount of Ag_2O, the adsorption capacity is enhanced to 2.2 times, with a maximum of 172.4 mg/g determined from Langmuir isotherm. The adsorption results also show that a small amount of Ag_2O-modified TNS can quickly enrich large amounts of MB molecules onto its surface via adsorption. Furthermore, Ag_2O-modified TNS exhibits novel separation efficiency of photogenerated carriers evidenced by photoluminescence measurements, and enhanced photocatalytic activity proved by the degradation of MB. The good reusability of Ag_2O-modified TNS implies a potential application for dealing with high-concentration dyes by adsorption–photocatalytic degradation.

1. Introduction

A large amount of dye wastewater is released into the environment annually [1,2]. It is reported that even very low-concentration of dye can greatly reduce the light transmittance of aqueous solution and affect the aquatic ecosystem [3]. Moreover, some azo, fluorine dyes, and their degradation products such as aromatic amines are highly carcinogenic and mutagenic [4]. In addition, the dye molecules are usually inert and non-biodegraded [5]. Therefore, dye wastewater has become one of the most serious environmental problems. TiO_2 photocatalytic technology has been regarded as a promising method to treat all kinds of organic pollutants [6,7]. However, photocatalytic degradation bases on the premise that the reaction system should be transparent or at least with certain light transmittance. In general, the individual photocatalytic degradation is only suitable for the removal of dye wastewater with low concentration, and usually insufficient and failed to treat high-concentration dye solution [4]. This is why the combination of adsorption and photocatalysis has attracted increasing attentions [8–10].

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Adsorption can be carried out to enrich dyes from a large volume of wastewater to a small amount of adsorbents, and then the adsorbed dyes can be removed by photocatalytic degradation [11]; meanwhile, the adsorption capacity of adsorbent may be recovered. Therefore, it is of great significance to develop materials with dual function of both high adsorption ability and good photocatalytic activity. Some inert adsorbents such as activated carbon [12,13], mesoporous silica [14], and alumina [15]. have been widely used to modify TiO_2. Unfortunately, there are some drawbacks for this method such as the regeneration efficiency of the prepared composites is usually unsatisfactory [16,17], because dye molecules are mainly adsorbed on inert adsorbent surface while photocatalytic reaction occurs on the surface of photocatalysts. It may be a practical way to modify TiO_2-based photocatalysts with catalyst instead of inert adsorbent. TiO_2-based nanosheet (TNS) exhibits good adsorption ability and photocatalytic activity for some dye pollutants in our previous study [18], which can be used as the substrate material. Since TNS has relatively low adsorption capacity as compared with inert adsorbents [19], compensating for the lack of its adsorption capacity exhibits particular importance at the same time by improving its photocatalytic activity.

Some research findings indicate that the adsorption capacity of TiO_2-based materials can be enhanced by surface modification with other semiconductor catalysts. For example, the enhancement of adsorption was realized by loading WO_3 on TiO_2 surface [20–22]. It was ascribed to the high acidity of WO_3 [23], and the loading can markedly increase the surface acidity of modified TiO_2. As a result, the adsorption for cationic dyes was enhanced [21]. It has reported that Ag_2O also exhibits high acidity [24], thus it should be a potential material to modify TNS as to obtain enhanced adsorption capacity. In addition, it is documented that the loaded Ag_2O is transformed into stable Ag_2O–Ag structure when photocatalytic degrading organic pollutants [25–27]. Both Ag_2O and the formed noble metal Ag can act as traps to capture photogenerated electrons, which are beneficial to the separation of electron–hole pairs [27–31]. Thus, it is reasonable that Ag_2O-modified TNS may be an ideal material working as adsorbent and photocatalyst simultaneously. However, few investigations about the coupled adsorption–photocatalytic property of Ag_2O-loaded TNS have been reported.

In this paper, TNS was prepared by a hydrothermal method, and then it was successfully modified by the semiconductor photocatalyst Ag_2O. Methylene blue (MB), a representative of dyestuffs resistant to biodegradation, was selected as a model for the study. It is found that a proper amount of Ag_2O loading on TNS surface can markedly enhance the adsorption capacity and photocatalytic activity of Ag_2O-modified TNS. Furthermore, the modified TNS is stable after several cyclic experiments, implying a potential and promising application for the removal of dyes from high-concentration solution.

2. Materials and methods

2.1. Preparation

TiO_2 precursor was prepared via a solvothermal method by the following procedure. 12 mL of tetrabutyl titanate was mixed with 40 mL of isopropyl alcohol and 2 mL of acetic acid, and then 3 mL of deionized water was dripped into the mixed solution under intense stirring. The produced gel was transferred to a Teflon-lined autoclave (100 mL) and heated at 130 °C for 6 h. After being cooled to room temperature, the resultant powder was collected on a filter and dried at 70 °C for 24 h. TiO_2-based nanosheet (TNS) was prepared using the same method reported in our previous study [18], and the only difference is the used TiO_2 nanoparticles were replaced by our home-prepared TiO_2.

A series of Ag_2O-modified TNS were obtained as follows. 0.8 g TNS was added into 100 mL of required concentration of $AgNO_3$ solution (0.85, 1.7, 2.55, 3.4 or 5.1 g/L) and vigorously stirred for 10 min, then 200 mL of sodium tetraborate solution (molar ratio of sodium tetraborate to silver nitrate = 4) was dropped in and stirred constantly at room temperature for 12 h. Finally, the product was washed with deionized water and dried at 80 °C for 12 h. The series of samples were denoted as ATNS-5, ATNS-10, ATNS-15, ATNS-20, and ATNS-30 according to the Ag/Ti atomic ratio of 5%, 10%, 15%, 20%, or 30% in the synthesis systems, respectively.

2.2. Characterization

Transmission electron microscopy (TEM) images were obtained by a JEOL JEM-2010 (HT) instrument at the accelerating voltage of 200 kV. X-ray diffraction (XRD) spectra were collected on a D8-advance X-ray diffractometer with Cu Kα radiation. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. Data were recorded with a step interval of 0.02° and a scan rate of $1^\circ\ \mathrm{min}^{-1}$ in the 2θ range from 5° to 70°. X-ray photoelectron spectroscopy (XPS) data were recorded with a VG Multilab-2000 spectrometer using Mg Kα irradiation. The Brunauer–Emmett–Teller (BET) surface areas were measured by nitrogen adsorption isotherm measurements at 77 K on a JW–BK instrument. Photoluminescence (PL) spectra were recorded via a F-4600 fluorescence spectrophotometer with an excitation wavelength of 325 nm. Total organic carbon of the solution and MB-adsorbed ATNS-5 were measured by a Vario TOC cube total organic carbon analyzer (Elementar Analysensysteme GmbH, German). The concentrations of MB were estimated according to the absorbance measured by a Shimadzu UV–vis 2550 spectrophotometer.

2.3. Adsorption capacity and photocatalytic activity

First, different concentrations of MB solutions were prepared by adding MB into deionized water, and the solution pH was determined to be 6.68. In each experiment, 0.1 g catalyst was added into 100 mL aqueous solution of MB with different concentration. After stirring in the dark for 1 h, the MB-adsorbed catalyst was separated by centrifugation for a further treatment, and the equilibrium concentration of MB was determined by UV–vis spectrophotometer. The adsorption capacity q_e (mg/g) of catalyst after adsorption equilibrium was calculated by the following equation:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

where C_i is initial concentration, C_e is equilibrium concentration of MB, and V and m are the volume of solution and the mass of catalyst, respectively.

Photocatalytic activities of catalysts were evaluated by the degradation of MB. In a typical reaction, 0.1 g catalyst was added into 100 mL aqueous solution of MB (160 mg/L) and stirred in the dark for 1 h to reach adsorption equilibrium. Then, the system was irradiated with a 160 W high-pressure mercury lamp. At regular irradiation time intervals of 1 h, 1.6 mL sample was withdrawn from the dispersion and centrifuged to remove the catalyst, and the concentration of MB was determined by UV–vis spectrophotometer. In order to quantitatively evaluate the photocatalytic activity of photocatalyst, reaction rate constant k is determined by the first-order kinetic equation as follows:

$$\ln(C_0/C) = kt \tag{2}$$

where C_0, C indicates the MB concentration at irradiation time $t = 0$ and reaction time t, respectively.