Photocatalytic Degradation of Dye Wastewater by NG/TiO₂ Composite

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Abstract. N-doped graphene (NG)/TiO₂ composites were prepared by a hydrothermal method using HF as the surface etchant and urea as the nitrogen source. The morphology and structure of the NG/TiO₂ composites were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), UV-visible diffuse reflectance spectroscopy (UV-Vis DRS) and specific surface area (BET). The pore size distribution of the composite and the effect of NG addition on the photocatalytic properties were studied. The photocatalytic properties of the composite were evaluated under UV and sunlight conditions respectively. The results show that TiO₂ is uniformly loaded on the surface of NG, and NG/TiO₂ is mesoporous material. The introduction of NG can effectively improve the photocatalytic properties, 5wt% NG/TiO₂ has the best photocatalytic degradation effect on methylene blue. The degradation rate of methylene blue is 96.30% at 30 min under UV and 99.87% at 180 min under sunlight.

Introduction

With the development of the textile printing and dyeing industry, the environmental pollution of dye wastewater has become increasingly serious. Dye wastewater has the characteristics of large chroma, high concentration and difficult to degrade[1]. Photocatalytic oxidation is one of the common methods for treating dye wastewater[2-4]. TiO₂ is widely used in the field of photocatalysis because of its strong oxidizing ability, high chemical stability, low cost, non-toxicity and environmental protection[5-6]. However, due to its high recombination rate of photoexcited charge carriers, the quantum efficiency is low. Moreover, nano-TiO₂ tends to agglomerate, thus reducing the specific surface area and the adsorption of dyes, resulting in low photocatalytic efficiency. Therefore, it is an urgent problem to restrain the recombination of photocatalysis and improve the adsorption of dye.

The sp² hybrid structure of C atoms in graphene makes graphene have a two-dimensional structure. It has high conductivity (1.5×10⁴ cm²/(V·s)), high stability, and a large specific surface area (theoretical value of 2630 m²/g). Because the nitrogen atom has the same atomic radius as the carbon atom, the nitrogen atom can be doped as an electron donor, and the N-doped graphene (NG) shows many new properties, such as adjusting the conductive type, increasing the free carrier density, increasing the adsorption active sites on the surface of graphene, etc[7-8]. NG can provide carriers for TiO₂ photogenerated electrons, reduce the recombination of photoexcited carriers, and improve the efficiency of photocatalytic reaction. Therefore, NG/TiO₂ composites may be ideal new photocatalysts.

Experimental

Materials

Titanium sulfate (Ti (SO₄)₂, ≥ 97.0 %), hydrofluoric acid (HF, ≥ 40.0 %), absolute ethanol (≥ 99.7 %), urea (≥ 99.5 %), graphite powder(≥ 99.9 %), potassium permanganate (KMnO₄, ≥ 99.5 %), sodium nitrate (NaNO₃, ≥ 99.0 %), sulfuric acid (H₂SO₄, 95.0～98.0%), and methylene blue, were all
purchased from Sinopharm Chemical Reagent Co., Ltd, and all experimental water used was deionized water.

**Synthesis of NG/TiO$_2$ Composites**

**Preparation of nano TiO$_2$.** The preparation of anatase nano-TiO$_2$ was done by the hydrothermal method. 30 mL HF (160 mmol/L), 50 mL H$_2$O and 192 mg Ti (SO$_4$)$_2$ were added to a plastic beaker. The HF was added first to water because Ti(SO$_4$)$_2$ would be hydrolyzed. Next, the prepared solution was sonicated for 15 min and magnetically stirred for 15 min, then the reaction solution was transferred to a 100 mL Teflon-lined reactor, and incubated at 180 °C for 12 hours. Finally, the product was centrifuged, washed with anhydrous ethanol and deionized water to remove impurities, the sample was dried in a vacuum oven at 60 °C for 12 hours. The obtained white powder was the anatase type nano-TiO$_2$ powder.

**Preparation of nano NG.** A modified Hummers method was used for graphene oxide (GO) preparation. 30 mL of the GO dispersion was added to the beaker, and then urea was added in a mass ratio of GO to urea being 1:5. After magnetic stirring for 30 minutes, the solution was transferred to a Teflon-lined reaction vessel, kept at 160 °C for 3 hours, allowed to cool naturally, then centrifuged several times, and lyophilized to give the final product as NG.

**Preparation of nano NG/TiO$_2$.** 60 mg TiO$_2$ powder, different mass of NG (1%, 3%, 5%, 7%, 9% by mass of TiO$_2$) and 50 ml deionized water were added to the test tube. After ultrasonic treatment for 3 hours, the mixed solution was poured into 100 ml PTFE lined reactor and kept at 180°C for 12 hours. Then, the product was centrifuged, washed with anhydrous ethanol and deionized water for several times to remove impurities, and the sample was dried in a vacuum oven at 60°C for 12 hours. The obtained powder was an NG/TiO$_2$ composite material.

**Characterization**

X-ray diffraction (XRD, Bruker AXS D8 Advance) with Cu target and Ka radiation ($\lambda=0.15406$ nm) was used for phase identification of the samples in the range of 10° - 80°. The morphology of the samples was examined by transmission electron microscope (TEM, Tecnai G² F20). The absorption range and absorption properties of the sample were measured by ultraviolet-visible diffuse reflectance spectroscopy (UV-VIS DRS, PerkinElmer Lambda 650).

**Photocatalytic Activity**

0.1 g of composite materials having a different NG doping ratio were added to 100 mL of a 10 mg/L MB solution, and the mixture was stirred for 1 hour in the dark. In order to study the photocatalytic degradation ability of composite materials, catalytic reactions were carried out under ultraviolet light and sunlight respectively. The ultraviolet light source is a 250 W high-pressure mercury lamp (365nm ultraviolet light), which is 15 cm away from the mixture and was sampled every 10 min. After centrifugation, the supernatant was taken, and the absorbance was measured by a UV-visible spectrophotometer to calculate the photocatalytic efficiency. The solar photocatalysis test was carried out in sunny outdoor for 3 hours, and samples were taken every 30 minutes. Calculation of photocatalytic efficiency based on formula (1).

$$\eta = \frac{C_{d0} - C_{dt}}{C_{d0}} \times 100\%$$

$C_{d0}$ is the initial concentration of MB; $C_{dt}$ is the concentration of MB when the reaction time is $t$.

**Results and Discussion**

**XRD**

Figure 1 shows the XRD of TiO$_2$ and NG/TiO$_2$ composites. It can be seen from Figure 1 that the
characteristic diffraction peaks at 2θ = 25.51 °, 38.02 °, 48.15 °, 54.04 °, 55.20 °, 62.87 °, 68.95 °, 70.36 ° and 75.21 ° correspond to (101), (004), (200), (105), (211), (204), (116), (220) and (215) crystal planes (jcpds 21-1272) in anatase TiO₂, respectively. The results show that anatase crystal is the main type of TiO₂ and NG/TiO₂ composites. The diffraction peaks of NG/TiO₂ composite are significantly weaker than that of TiO₂, which is due to the interaction between NG and TiO₂. In the NG/TiO₂ composite, the (002) characteristic diffraction peak of graphene did not appear near 2θ = 26° because this diffraction peak overlaps with the (101) crystal plane diffraction peak of the anatase phase TiO₂.

Figure 1. XRD patterns of TiO₂ and NG/TiO₂.

TEM

Figure 2. TEM image (a) and SAED images (b) of 5wt% NG/TiO₂.

Figure 2(a) is a TEM image of 5wt% NG/TiO₂ composite, in which the edge of NG is curled, and the TiO₂ particles are evenly distributed on the surface of NG. Figure2(b) is a 5wt% NG/TiO₂ selected area electron diffraction photo. The SAED pattern shows a clear concentric ring structure distribution, which proves that there are well-developed TiO₂ nanoparticles crystal on the NG surface of the composite. In Figure2(b), the diffraction spots of hexagonal structure correspond to (100) crystal surface of graphene cell, and the electron diffraction rings correspond to (101), (004), (200) and (105) crystal surface of anatase TiO₂ from inside to outside, which is consistent with the XRD test results.
UV-VIS DRS

Figure 3. UV-Visible diffuse reflectance spectra of TiO$_2$ and NG/TiO$_2$ (a); optical bandgap determination of TiO$_2$ and NG/TiO$_2$ (b).

It can be seen from the UV-Visible diffuse reflectance spectrum (Figure 5a) that the pure TiO$_2$ has a light absorption range of less than 400 nm and can only absorb ultraviolet light. This is due to the transfer of electrons from the valence band ($\sigma^2$ p) to the conduction band (Ti $3d$). Compared with pure TiO$_2$, the light absorption boundary of the NG/TiO$_2$ composite material is red-shifted, and the absorption range of the photocatalyst is expanded to the visible light region. TiO$_2$ is grown on the in-situ nitrogen-doped graphene layer by Ti-O-C bond, and the C 2p and O 2p atomic orbitals are hybridized under high temperature and high pressure$^{[10]}$. This leads to an increase in the edge of the valence band, which reduces the width of the band gap$^{[11]}$. The band gap energy of TiO$_2$, 3 wt % NG/TiO$_2$, 5 wt % NG/TiO$_2$, and 7 wt % NG/TiO$_2$ can be calculated by the formula $E_g = 1240/\lambda$, and are approximately 3.18 eV, 2.98 eV, 2.92 eV and 2.96 eV. (Figure 5b).

BET

Figure 4. Nitrogen adsorption desorption isotherms (a) and pore size distribution (b) of 5wt% NG/TiO$_2$.

It can be seen from the Fig(a) that when $P/P_0 < 0.4$, the adsorption capacity of the composite to N$_2$ is small, and then the adsorption capacity of the composite to N$_2$ begins to increase significantly, which shows that the adsorption desorption isotherm of the composite is isotherm IV, with typical mesoporous structure$^{[12]}$. The specific surface area of the sample is 33.53 m$^2$/g. The pore size distribution is mainly between 3.45 nm and 4.05 nm, mainly 3.95 nm mesoporous, which is in line with the definition of mesoporous materials of IUPAC$^{[13]}$. 
Photocatalytic Activity

Figure 5 shows the photocatalytic efficiency curves of the composites with different amounts of NG under UV (a) and sunlight (b) conditions. It can be seen from Figure 5 (a) that the photocatalytic efficiency of the composite increases after the introduction of go compared with that of pure TiO\textsubscript{2}, and with the increase of NG content, the catalytic performance of different photocatalyst samples increases first and then decreases, and 5wt% NG/TiO\textsubscript{2} shows the best photocatalytic activity: under UV light, the degradation efficiency of MB reached 96.30% after 30 min degradation. Under the condition of sunlight (Figure 5 (b)), the overall efficiency of the composite photocatalyst is higher than that under the condition of UV, which is due to the fact that compared with the ultraviolet light source with 365 nm as the main part of the high-pressure mercury lamp, the sunlight is a full spectrum light source with ultraviolet and visible light of various bands. The introduction of graphene reduces the band gap width, making the composite photocatalyst visible light region has a certain response ability. Among them, the degradation efficiency of 5wt% NG/TiO\textsubscript{2} to methyl orange reached 97.67% after 30min. The introduction of graphene reduces the band gap and makes the composite photocatalyst have a certain response ability in the visible region. The degradation rate of MB by 5wt% NG/TiO\textsubscript{2} was 99.87% after 30min.

Conclusions

NG/TiO\textsubscript{2} composites were successfully synthesized by the hydrothermal method with HF as the surface etchant and urea as the nitrogen source of NG. TiO\textsubscript{2} was uniformly loaded on the ng surface with good morphology. By adding different amounts of NG, the recombination of photogenerated electron hole pairs is effectively suppressed, and the response ability of the composite to visible light is improved. The pore size distribution of the composite is mainly between 3.45 nm and 4.05 nm, and the main pore size is 3.95 nm. The photocatalysis test shows that NG/TiO\textsubscript{2} composite has better adsorption and photocatalysis performance than pure TiO\textsubscript{2}. Among them, the photocatalytic activity of 5wt% NG/TiO\textsubscript{2} is the best. The degradation rate of methylene blue reaches 96.30% after 30 minutes under ultraviolet light, and 99.87% after 180 minutes under sunlight. Therefore, NG/TiO\textsubscript{2} composite is a new photocatalytic material with ideal industrial application prospect.

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