

Fabrication of TiO₂/GO Composites by Feasible Ultrasonic Method with Improved Photocatalytic Activity

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Abstract. Firstly, the graphite oxide was fabricated with the modified Hummers' method, and then it was dispersed in an aqueous solution along with TiO₂ nanoparticles. The graphite oxide was peeled off by ultrasonic method and graphene oxide (GO) was obtained. The abundant functional groups on the GO surface make the TiO₂ nanoparticles attach to the GO chips, and finally get the TiO₂/GO composites. The results show that TiO₂ and GO are independent of each other in the TiO₂/GO composites and no doping or solid solution is formed. The photocatalytic efficiency of TiO₂/GO composite is improved compared with that of pure TiO₂. With increasing the contents of GO in TiO₂/GO composites, the photocatalytic activity of TiO₂/GO also increased.

Introduction

With the economic and social development, environmental issues have been more and more serious. Especially water pollution has seriously affected the survival and health of human beings [1]. Physical adsorption and the photocatalytic technology have been widely used to treat contaminants. Especially, the photocatalytic technology with the advantages of low energy consumption, controllable reaction conditions and no secondary pollution is getting more and more attention [2]. Photocatalytic technology can directly oxidized organic compounds into small molecules by the active groups originated from electron-hole separation under ultraviolet light irradiation [3]. Titanium dioxide is one of the most widely used semiconductor photocatalysts due to its stable properties, low cost, environmental friendly, non-toxic and harmless [4,5]. However, the photocatalytic efficiency is low because the electron-hole of TiO₂ is easily recombined during the migration to the surface [6,7]. In recent years, graphene has attracted much attention due to its superior conductivity, and its carrier mobility at room temperature is $200000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, far exceeding that of electrons in general conductors [8,9]. The binding of TiO₂ and graphene can make the photogenerated electrons of TiO₂ transfer to graphene, which can effectively improve the separation efficiency of photoelectrons and holes of TiO₂, reduce the recombination of carriers and improve the activity of the catalyst. The current research is focus on dispersing TiO₂, ZnO and other nano-particles onto the graphene layer [10]. However, the preparation of TiO₂/graphene composites is complicated due to the poor dispensability of graphene in water and the weak binding force with TiO₂. Compared with graphene, graphene oxide (GO) contains a large amount of organic functional groups, and the binding force between TiO₂ and graphene (GO) is better. GO is a good electron acceptor [11], and electrons can be transferred to the GO surface rapidly, so the electron-hole pair recombination can be inhibited [12]. Therefore, the TiO₂/GO photocatalyst is widely reported to have higher photocatalytic activity.

GO could be prepared by peeling off graphite oxide by ultrasonic, long stirring and high-speed centrifugation. Hummers method has been the most common method for the preparation of GO [13]. The traditional preparation of TiO₂/GO photocatalyst is preparing the GO nanosheets firstly, and then loading the TiO₂ particles onto GO sheets. In this composite photocatalyst, graphene is a continuous phase and TiO₂ is the dispersed phase, so the majority of the composition of graphene. However, since the graphene does not have photocatalytic performance, this would make the improvement of the

catalytic efficiency unsatisfactory. In this study, graphite oxide was first prepared by an modified Hummers method [14]. The graphite oxide was stripped by a high power ultrasonic system, and the TiO₂ particles were dispersed and compounded on the GO sheets. Since the surface of the GO layer contains a large amount of hydroxyl, carboxyl and epoxy groups, it can combine with the hydroxyl groups on the surface of nano-TiO₂, and finally form the TiO₂/GO large-particle cluster. In this structure, the TiO₂ component occupies the major part and is located outside the catalyst. It can take full advantage of the excellent catalytic properties of TiO₂, and can transfer the photogenerated electrons into the inner GO sheets, further reducing the recombination of photo-generated electron-hole and improving the catalytic efficiency.

Experimental

Materials

Graphite powder, sulfuric acid, sodium nitrate, potassium permanganate, hydrochloric acid and hydrogen peroxide (30%) and methylene blue were purchased from Sinopharm Shanghai Chemical Reagent Co., Ltd. Titanium dioxide was purchased in Shanghai Aladdin Reagent Co., Ltd.

sample preparation method

The graphite oxide used in this paper was prepared by the modified Hummers method [14]. The obtained graphite oxide is dried in a vacuum drying oven at a drying temperature of 60 °C. A certain amount of graphite oxide was added into deionized water. The solution was sonicated for 4s and paused for 4s with the ultrasonic power was 100 w, which last for 30 min, to obtain the GO dispersion. A certain amount of TiO₂ nanoparticles were added into the GO dispersion. The mixed solution was sonicated for 4s and paused for 4s with the ultrasonic power was 100 w, which last for 30 min. The suspension was centrifuged and dried at 60 °C to obtain the TiO₂/GO composite materials. The experimental parameters are shown in Table 1.

Table 1 Experimental parameter

| TiO ₂ : GO | GO* | TiO ₂ * | Ultrasonic time ** |
|-----------------------|------|--------------------|--------------------|
| 3:1 | 330 | 1000 | 30 |
| 2:1 | 500 | 1000 | 30 |
| 1:1 | 1000 | 1000 | 30 |

Note: * The unit is milligram (mg); ** The unit is minute (min).

Characterization

The morphologies of the samples were characterized with a field emission scanning electron microscope (FESEM, Hitachi S-4800). X-ray diffraction (XRD) was carried out on a Rigaku-D/max 2550 PC (Japan) diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The samples were characterized with a Fourier transform infrared (FTIR) spectrometer (Nicolet 8700, Bruker Optik GmbH, Ettlingen, Germany) using KBr pellets.

Photocatalytic degradation of methylene blue

The photocatalytic efficiency of the prepared sample was calculated by measuring the concentration of residual MB in the aqueous solution by using methylene blue (MB) as the degradation object. The maximum absorption wavelength of MB is 665 nm. The specific experimental procedure is as follows: A certain amount of photocatalyst is added to 50 mL, the initial concentration of 30 mg/L MB solution. The suspension was left in the dark for 30 min and then the suspension was irradiated for 2 h with a 300 w mercury lamp. During the course of the reaction, 3 mL of the solution was taken out with a syringe every 20 minutes and filtered with a filter. The change in the concentration in each degraded solution was monitored on a PerkinElmer Lambda 35 spectrophotometer by measuring the absorbance of MB at 655 nm after the separation of each catalyst.

Results and discussion

Fig. 1 shows the SEM images the TiO₂/GO composites. The GO surface has been covered by TiO₂ nanoparticles, forming a large cluster structure (Fig. 1a). The particle size of TiO₂ is about 50 nm, and there are lots of holes in the TiO₂/GO composites (Fig. 1b), which is conducive to the adsorption of the pollutant molecules onto the catalyst, enhancing the catalytic efficiency. The inset in Fig. 1b is GO, which has a clear two-dimensional sheet structure with a size of about 5 μm. It has rough surface with much wrinkles. The size of the composites are nearly the same with that of the GO sheets because the size of TiO₂ is in nanometer scale and the TiO₂ layer covered is not thick.

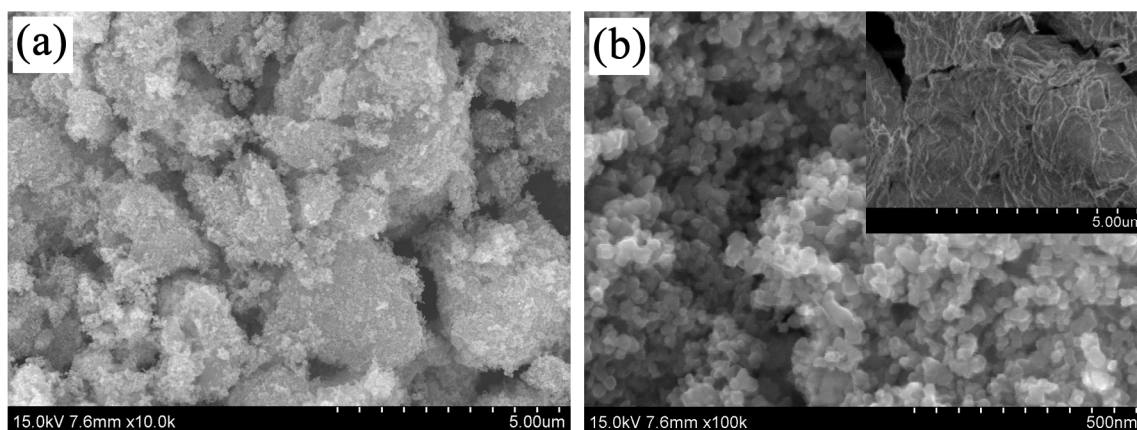


Fig. 1 SEM images of (a) TiO₂/GO composites and (b) TiO₂ nanoparticles on the composites. The inset in Fig. 1b is GO.

Fig. 2 shows the XRD patterns of GO, TiO₂ and different ratios of TiO₂/GO composites. It can be seen that the characteristic diffraction peaks of graphite oxide appear near 2θ of 10°. By the formula $2d\sin\theta = n\lambda$, GO crystal spacing d was calculation to be 0.82 nm, compared with 0.335 nm graphite [15]. In the strong oxidation, the oxygen-containing group and the water molecule were interposed in the gap of the GO, so that GO layer spacing is greater than graphite. TiO₂ and composites show similar XRD patterns with 2θ at 25°, 27°, 38°, 48°, 53°, 55°, 62°, 69°, 70° and 75°, indicating that TiO₂ and composite materials containing anatase and rutile phase [16]. The crystal form of TiO₂ in the composite was not destroyed by ultrasound.

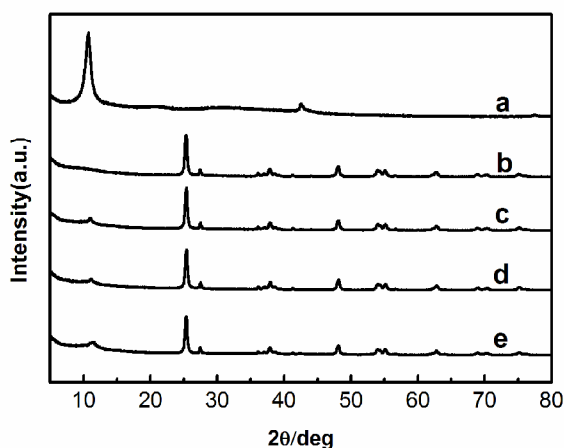


Fig. 2 XRD patterns of GO (a), TiO₂ (b) and TiO₂/GO composites with the TiO₂:GO ratio of 3:1(c), 2:1(d) and 1:1(e).

Fig. 3 shows the infrared absorption spectra of GO, TiO₂ and different ratios of TiO₂/GO composites. Various oxygen-containing functional groups are contained in the oxidized graphite. For example, The peak at 3400 ~ 3450 cm⁻¹ is the stretching vibration peak of OH bond in water and hydroxyl group in the surface. The peak at 1731 cm⁻¹ is the stretching vibration peak of carboxyl group (-COOH). The peaks at 1624 cm⁻¹ (C = C), 1225 cm⁻¹ (C-OH) and 1050 cm⁻¹ (the stretching vibration peak of CO in epoxy group) were also observed [17]. Due to the presence of these polar groups, GO

has good hydrophilicity. From the IR spectrum of TiO_2 , it can be seen that TiO_2 has absorption peaks at 3400 cm^{-1} and 1628 cm^{-1} , which may be due to the presence of water molecules and surface hydroxyl groups adsorbed in the TiO_2 sample. At the same time, (Ti-O-Ti) stretching vibration peak [18]. At the same time, it can be seen from the figure that TiO_2/GO composite contains both TiO_2 and GO absorption peak, and the impact of the content of TiO_2 and GO to the absorption peak is not significant.

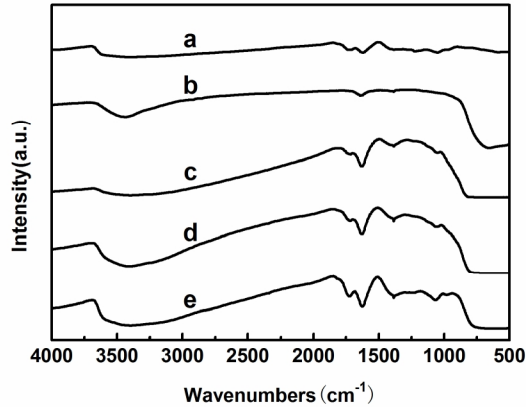


Fig. 3 FT-IR spectra of GO (a), TiO_2 (b) and TiO_2/GO composites with the TiO_2/GO ratio of 3:1(c), 2:1(d) and 1:1(e).

In order to compare the photocatalytic activity of TiO_2/GO composites and TiO_2 , 10 mg TiO_2/GO composite catalyst and TiO_2 photocatalyst were added into the MB solution, and the suspension was first avoided in the concentration of 30 mg/L. After the adsorption-desorption equilibrium without light for 20 min, the degradation performance of MB solution was investigated by irradiation with mercury lamp for 2h. The results are shown in Fig. 4. The photocatalytic activity of TiO_2/GO composite catalyst is higher than that of TiO_2 , and the photocatalytic activity is enhanced with the increase of the proportion of GO in the composite catalyst. The reason is that the adsorption ability of GO is stronger than that of TiO_2/GO . When more GO is added, the composite catalyst can adsorb more MB molecules to the surface of the catalyst. When irradiated by an ultraviolet light, the MB molecules which have been adsorbed to the catalyst surface can be rapidly degraded, thereby greatly increasing the photocatalytic efficiency. At the same time, GO can quickly transfer electrons and holes from ultraviolet excitation, and inhibit the recombination of electron - hole pairs in the interior, thus improving the photocatalytic efficiency.

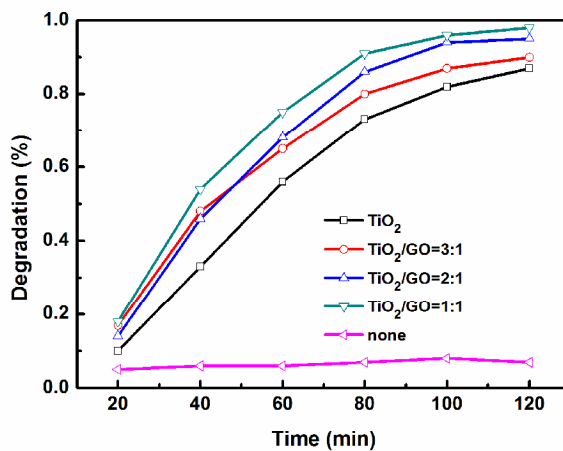


Fig. 4 The photocatalytic degradation of MB over different samples

Conclusion

In this experiment, TiO₂/GO composite was prepared by ultrasonic method. The method is simple and efficient, so that the catalyst can be used in practical application. The results show that the TiO₂ nanoparticles attach to the surface of GO, forming a larger cluster structure, and the size of clusters is related to the size of GO. The results of XRD and FTIR show that TiO₂ and GO are independent of each other in the TiO₂/GO composites, and no doping or solid solution is formed. GO surface containing a large number of functional groups, is conducive to the contact of TiO₂ and GO. The photocatalytic efficiency of TiO₂/GO composite photocatalyst is obviously higher than that of pure TiO₂ photocatalyst. With the increase of the ratio of GO in TiO₂/GO composites, the photocatalytic activity of GO increases. In short, TiO₂/GO composites have been successfully synthesized by ultrasonic method. The method is simple and feasible, and the photocatalytic efficiency is high. It has the possibility of mass production and practical application prospects.

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