

Preparation and Photocatalysis Property of Exfoliated Graphite by In-situ Inserting Nano-TiO₂

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Abstract The composite of exfoliated graphite/nano-TiO₂ (EG/TiO₂) is prepared by using the in-situ inserting method, and its photocatalysis properties was studied by investigating the decomposition of the dichlorvos under different conditions. The results suggest that the composite has good photocatalysis properties for the decomposition of dichlorvos, and it can be reproduced after baking at 700 °C.

Keywords Graphite · Intercalation · Photocatalysis · Nano-TiO₂

Some composites of carbon nano-TiO₂, such as carbon coating of photoactive anatase-type TiO₂ [1], carbon-TiO₂ photocatalyst [2], TiO₂-mounted activated carbon [3], and other modified nano-TiO₂ particles [4, 5], has drawn much attention due to their good photocatalytic activity for the decomposition of organic compounds. However, there are still some difficulties at present for the composites applying as environmental protective material because its preparation is inconvenient on a large scale. The exfoliated graphite (EG) prepared by using the nature graphite (NG) has been made in our lab and this material has a property of strong decomposition for organic compounds [6]. In this

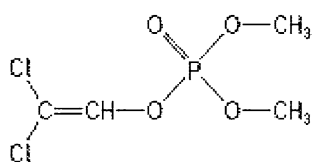
work, the composite of exfoliated graphite/nano-TiO₂ (EG/TiO₂) was prepared by using the in-situ inserting method. The composite has photocatalysis function for organic compounds and can be reproduced after baking at 700 °C. Its photocatalytic activity was evaluated by studying the decomposition of dichlorvos (produced in Linxi, Shandong, China) and the molecular structure of dichlorvos is shown in Scheme 1.

The EG/TiO₂ composite was prepared as follows: 5.0 g natural flake graphite, 1.5 g sulfuric acid (98%), 5.0 g acetic acid anhydride, 0.4 g potassium dichromate, 0.5 g hydrogen peroxide and 3.0 g tetra-*n*-butyl titanate were added into a flask, and stirred for 50 min at 45 °C, and then a graphite intercalation compounds (GIC) was obtained [7]. When heating the GIC from 700 to 1100 °C, the EG/TiO₂ was obtained, and the exfoliating volume of EG/TiO₂ was 280 mL/g with the surface area of 41.29 m²/g. When the EG/TiO₂ was put into the dichlorvos stirring without ultraviolet irradiations, the adsorption equilibrium was achieved about 12 h, and the saturation adsorption weight of EG/TiO₂ for dichlorvos was 15.00 g/g (1.00 g of EG/TiO₂ can absorb 15.00 g of dichlorvos). Comparing with 13.50 g/g of the saturation adsorption weight by the exfoliated graphite for dichlorvos, the result of EG/TiO₂ is better than the exfoliated graphite.

UV-2000 ultraviolet spectrophotometer (Shimadzu Co. Japan) was applied to analyze the extraction solution of GIC [7]. Figure 1 shows the UV spectra of the extraction solution of GIC, and it has an absorption peak at 204.0 nm which is attributed to the acetic acid standard peak. In the water solvent, acetic anhydride molecule can hydrolyze into the acetic acid molecule, so it proves that the absorption peak of 204.0 nm is the peak of acetic anhydride and the NG had been intercalated by the organic compounds.

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Scheme 1 Molecular structure of dichlorvos

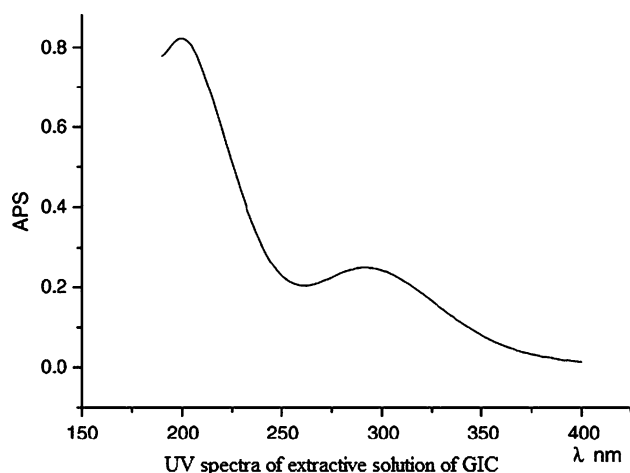


Fig. 1 UV spectra of the extraction solution of GIC

D8-ADVANCE X-ray diffractometer (Germany), using Cu K α radiation with 40 kV and 40 mA in steps of 0.02°/0.3 s, was used to measure XRD patterns of NG and GIC (Fig. 2). As seen from Fig. 2a, the nature graphite has a sharp reflection peak at $2\theta = 26.2^\circ$ which is attached to 001 profile of the nature graphite. The peak appears in GIC is also at about $2\theta = 26.2^\circ$ in Fig. 2b. Thereby, the oxidation dealing does not change the scale structure of the nature graphite [8]. However, there is a peak that is lower than 26.2° in Fig. 2b, so it is confirmed the surface of GIC is not evenner than that of NG and the graphite layers in GIC have been opened.

Figure 3a,b show the scanning electron microscopy (SEM) photographs of EG/TiO₂. As seen from Fig. 3a, some microstructure liking worm suggests that the graphite

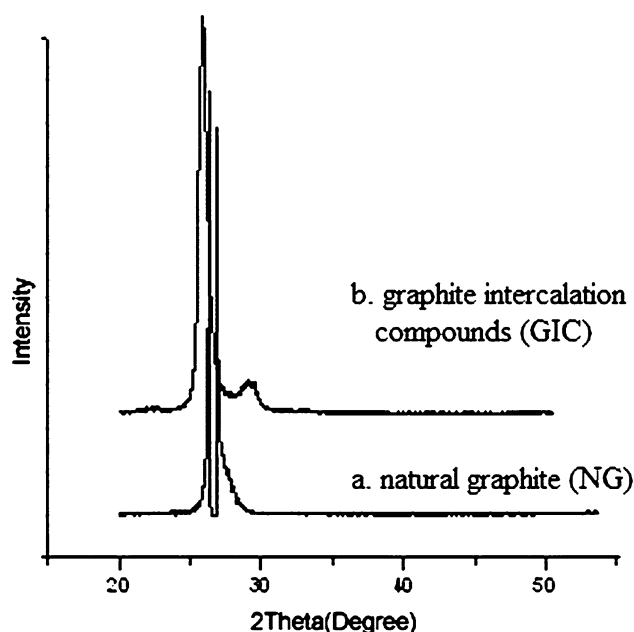


Fig. 2 XRD patterns of NG and GIC

layers had been opened mostly. Each exfoliated graphite particle has a “bean pod” structure (Fig. 3a) [9], and each of the pods represents a domain where the nano-TiO₂ in-situ inserting into the graphite. An enlarged SEM photograph is shown in Fig. 3b, there are some small white particles between the graphite layers. These particles are observed by transmission electron microscopy (TEM), and the picture shows that they are small balls of nano-TiO₂ with the size of about 50 nm (Fig. 3c).

The structure-type of nano-TiO₂ in EG/TiO₂ would be changed while heating them at different temperatures. The data of XRD showed that the type of nano-TiO₂ is a single phase of anatase-type (A) at 700 °C, almost rutile-type (R) at 1,100 °C and complex type at 1,000 °C [1].

The dichlorvos was used to evaluate the photocatalytic activity and stability of EG/TiO₂. Dichlorvos was dissolved in water with a concentration of 1:5,000 (the ratio of volume). The 0.05 g of EG/TiO₂ was dispersed into 25 mL

Fig. 3 SEM and TEM photographs of EG/TiO₂

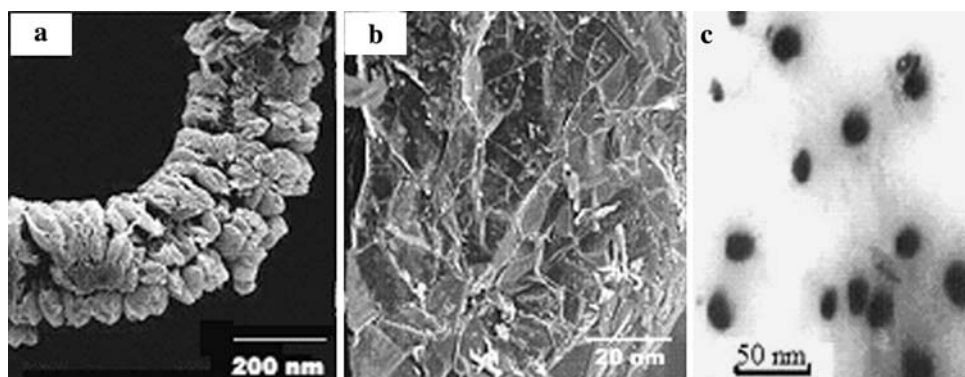


Table 1 The decomposition ratio of dichlorvos and the irradiation time

Irradiation time (h)	2	3	4	5	6	7	8	9	10
Degradation rate (%)	21	26	33	42	50	57	66	77	85

of dichlorvos solution in the beakers of 50 mL. The mixture was stirred without the ultraviolet irradiations and another compared mixture was stirred under ultraviolet irradiations of 253 nm for 10 h, respectively. The decomposition ratio of dichlorvos could be obtained by measuring the absorbance by UV–visual spectrophotometer (China). The decomposition ratios of dichlorvos and irradiation time are elucidated in Table 1.

As seen from Table 1, the decomposition ratio of dichlorvos is a function of the irradiation time and it increased gradually along with the irradiation time. This result also illuminates that EG/TiO₂ is stable as a photocatalysts in the process of ultraviolet irradiations of 253 nm. After the decomposition, EG/TiO₂ was separated from the solution, washed in ultrasonic cleaning bath, dried and activated at 700 °C. Subsequently, it was reused twice for the decomposition experiment, and the decomposition ratio of dichlorvos was 81% at the first time and 77% at the second time. This result also suggests that EG/TiO₂ have good stability and photocatalytic activity. However, the decomposition ratio for dichlorvos decreases of 4% once after washing and activating (or baking), the reason might be that some TiO₂ particles fall off from EG/TiO₂ during the washing process under ultrasonic irradiation leading to a reduce of the decomposition ratio. When the dichlorvos solution was decomposed for 12 h, the gas chromatograph (Agilent Technologies 6890 N Network GC System, America) and COD determining apparatus (5B-3C COD Apparatus, China) was used to measure the concentration of the dichlorvos. It is found that little dichlorvos molecules are in the solution and COD was smaller than 5 mg/L.

In order to evaluate the life-time of EG/TiO₂, the dichlorvos concentration was increased from 1:5,000 to 3:5,000, and then the above experiments were repeated. It is found that the decomposition ratio could reach 100% after 36 h, suggesting that the life-time of EG/TiO₂ is 36 h at least.

Moreover, the decomposition ratio can reached 100% at 12 h when using the composite that baked at 700 °C, and

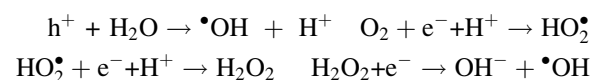
higher than using other EG/TiO₂ which were baked at 1,000 and 1,100 °C. These results show that the decomposition ratio of EG/TiO₂ for dichlorvos is correlated with the type of nano-TiO₂, that is, anatase-type (A) is better than rutile-type (R).

The decomposition mechanism of dichlorvos by EG/TiO₂ under ultraviolet irradiation may be as follows:

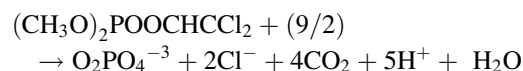
Under this condition, the valence-band's electrons of the nano-TiO₂ are excited to the conductor-band, and then the electron-cavity pair with strong chemical activity is come into being [10]:



These electron-cavity pairs transfer to the surface and can join in a series of the redox reaction. The following reactions take place in the H₂O/O₂ system:



The $\bullet\text{OH}$ is a nonselective strong oxidant, and then dichlorvos can be oxidized by it and finally be decomposed to CO₂, H₂O and inorganic acids:



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