

## Preparation and Photocatalytic Properties of Graphene/TiO<sub>2</sub> Nanocomposites

Qing Zhu

Department of Chemical and pharmaceutical Engineering of Chengxian College in Southeast University,  
Nanjing 210088

**Keywords:** Graphene, Titanium dioxide, Photocatalytic properties

**Abstract:** In this paper, RGO/titanium dioxide nanocomposite is prepared by solvothermal method, and its photocatalytic properties are discussed. While graphene oxide is reduced to graphene, anatase titanium dioxide particles are grown on the surface of graphene. With the prolongation of solvothermal time, the active groups on the surface of graphene oxide decrease, and the reduction is more thorough. At the same time, the grain size of titanium dioxide tends to increase. Compared with the pure titanium dioxide, the photocatalytic activity of RGO/TiO<sub>2</sub> nanocomposite is obviously improved.

### 1. Introduction

In the face of increasingly serious organic pollution, titanium dioxide is considered as the most promising photocatalyst [1]. It has been widely used to help solve many serious environmental and pollution problems, and is expected to control environmental pollution and alleviate the energy crisis through the effective use of solar water cracking devices. In general, when the irradiated light energy is larger than the band gap width of titanium dioxide, electrons will be excited from valence band to conduction band, thus generating electron hole pairs. These electrons and holes migrate to the surface of titanium dioxide and react with the organic pollutants adsorbed on the surface of titanium dioxide. The organic pollutants are decomposed into inorganic ions, hydrogen dioxide and carbon dioxide. However, the rapid recombination of photogenerated electrons and holes seriously reduces the efficiency of the photocatalyst. As a large bandgap semiconductor, titanium dioxide can only absorb ultraviolet light in the ultraviolet region. Under the irradiation of visible light, the photocatalytic efficiency of titanium dioxide as a photocatalyst is very low. There are still many shortcomings in the use of titanium dioxide as a photocatalyst. The scientific community began to try different ways to improve its photocatalytic performance.

Graphene is a two-dimensional material with honeycomb structure, which is closely packed by carbon atoms. It has the characteristics of fast electron transfer rate and high heat rate. In recent years, graphene/oxide composites have been extensively studied because of its excellent properties, high specific surface area and high mechanical strength, and because graphene itself has a large number of active groups on its surface, it is easy to combine with oxide nanostructured materials to form composites. In recent years, graphene and its composites have been widely used in lithium-ion batteries, supercapacitors and photocatalysis. Because of the unique properties of graphene, graphene/titanium dioxide nanocomposites can extend the light absorption range, and have simple charge transport to separate photogenerated electrons and holes rapidly. Graphene/titanium dioxide nanocomposites are promising photocatalysts. In graphene-titanium dioxide composites, graphene can accelerate the transmission of photogenerated electrons of titanium dioxide, thus effectively inhibit the recombination of photogenerated electrons and holes of titanium dioxide, and significantly improve the photoelectric and photocatalytic properties of titanium dioxide [2].

Based on the functionalization of graphene, the photocatalytic activity of titanium dioxide under visible light was improved by adjusting the experimental conditions, which provided a new idea for the study of nano-materials of titanium dioxide.

## 2. Experiment

In this paper, RGO/TiO<sub>2</sub> nanocomposites were prepared by solvothermal method using graphene oxide GO and Ti(OBu)<sub>4</sub> as raw materials, and the photocatalytic properties of nanocomposite were investigated.

### 2.1. Equipment and Raw Materials

Table 1. Equipment for the experiment

Instrument	Manufacturer	Model
Electronic Constant Temperature Water Bath	Shanghai Optical Instrument Factory	HW010L-2A
Electric Vacuum Drying Oven	Shanghai Kanaizi Lab Instruments Co., Ltd	ZK8LBB
Ultrasonic Cleaner	Kunshan Ultrasonic Instruments Co., Ltd	KQ-800KDE
High-Pressure Reaction Kettle	Customized	
X-Ray Diffractometer	Rigaku	D/MAX2500V
Field Emission Scanning Electron Microscopy	Rigaku	S-4800
Field Emission Transmission Electron Microscopy	Rigaku	SU 8020
Laser Confocal Raman Spectrometer	HORIBA Jobin Yvon	Lab RAM HR800

Table 2. Raw materials and the manufacturers

Name	Manufacturer	Model
Flaky graphite	Tianjin Kemiou Chemical Reagent Co., Ltd.	chemically pure
KMnO <sub>4</sub>	Nanjing Chemical Reagent Co., Ltd.	chemically pure
NaNO <sub>3</sub>	Tianjin Kemiou Chemical Reagent Co., Ltd.	chemically pure
H <sub>2</sub> SO <sub>4</sub>	Nanjing Chemical Reagent Co., Ltd.	chemically pure
H <sub>2</sub> O <sub>2</sub>	Nanjing Chemical Reagent Co., Ltd.	chemically pure
C <sub>14</sub> H <sub>14</sub> N <sub>3</sub> NaO <sub>3</sub> S	Tianjin Damao Chemical Reagent Factory	30%
H <sub>2</sub> O	Homemade	

### 2.2. Experiment Process

Graphene oxide is synthesized by Hummers method [3]. The concentration of graphene oxide solution used in this chapter is 4 mg/L. Three flasks of 250 mL are assembled in ice-water bath, 23 mL concentrated sulfuric acid is added, solid mixture of 0.5 g graphite powder and 0.5 g sodium nitrate is added under stirring, and then 3 g potassium permanganate is added slowly. The reaction temperature is controlled not more than 10 °C. After stirring reaction for 30 minutes, the temperature rises to about 35 °C. Continue stirring for 2 hours, slowly adding 40 mL deionized water, stirring for 30 minutes, then heating up to 90 °C, and adding 3 mL (mass fraction 30%) hydrogen peroxide to reduce the residual oxidant. After the reaction liquid turns bright yellow, it is filtered while hot, and washed with 5% HCl solution and deionized water until the PH of the filtrate is 6-7, which is the water solution of graphite oxide. The graphite oxide obtained from the above experiments was dispersed in 250 mL aqueous solution for 1 hour under ultrasonic conditions, and a stable dispersion solution, namely graphene oxide solution, was obtained. The obtained graphene oxide was filtered and dried at 60 °C in a vacuum drying chamber.

Graphene-supported titanium dioxide composites can be obtained by solvothermal method [4]. In order to study the effect of solvothermal reaction time on the structure of the composite, 20 mg GO was dispersed in 50 mL absolute ethanol, and GO was evenly dispersed in ethanol by ultrasound for 1 hour. Then, under stirring conditions, 3 mL Ti (OBu)<sub>4</sub> was slowly dripped into GO ethanol solution. After stirring for 0.5 hours, the mixture was transferred to polytetrafluoroethylene

inner gallbladder and stored in stainless steel reactor for different time at 180 °C. The product of solvothermal reaction was taken out and washed twice with ethanol and then twice with deionized water. The final product was dried at 60 °C in a vacuum drying chamber.

### 2.3. Tests of Sample Characterization and Photocatalytic

The crystal structure of the samples was determined by Japanese Physiology D/max-rB X-ray diffractometer. According to Scherrer formula, the particle size of the experimental sample is calculated:  $D = 0.89 \lambda / (\beta \cos \theta)$ ,  $\lambda$  is the wavelength of the incident X-ray,  $\beta$  is the half-width of the diffraction peak, and  $\theta$  is the diffraction angle. The micro-morphology of the samples was observed by Hitachi FE-SEM4800 field emission scanning electron microscope and SU8020 field emission scanning electron microscope. The morphology of the elements in the samples was analyzed by ThermoESCALAB250 X-ray photoelectron spectrometer. The light source was monochrome, the power was 150 W, the diameter of X-ray spot was 500  $\mu$ m, and the electronic binding energies of the elements were calibrated by C1s (284.8eV).

We used Shimadzu UV-1800 ultraviolet-visible spectrophotometer to detect the photocatalytic activity of the samples. The photocatalytic performance of the composite was evaluated by the degradation efficiency of methyl orange MO under illumination using 300W high pressure mercury lamp as light source. With deionized water as blank sample, 20 mg photocatalyst was added to methyl orange solution with 50 mL concentration of 30 mg/L and placed in the photocatalyst. Before illumination, the samples were stirred in the dark box of the photocatalyst for 1 hour to achieve the equilibrium of adsorption and desorption. After the illumination started, 3 mL of the sample was extracted every 10 minutes, and the supernatant was separated by centrifugation. The absorbance of the solution at  $\lambda = 464$  nm was determined by UV-1800 ultraviolet-visible spectrophotometer. According to Bill-Lambert's law, in  $C/C_0 = A/A_0$ , the concentration of methyl orange in the solution adsorbed by dark box and after photodegradation was  $C_0$  and  $C$  respectively; in  $A_0$  and  $A$ , the solution adsorbed by dark box and after photodegradation was adsorbed by dark box respectively.

## 3. Results and Discussion

### 3.1. Characterizations of Composite

The XRD spectra of the samples at 4G-T-6h show the characteristic peaks of anatase-type titanium dioxide, but the diffraction intensity is weak and the diffraction peaks are not sharp, indicating that the crystallization is incomplete. With the increase of GO content, the diffraction peaks of the samples at 10G-T-6h, 20G-T-6h and 40G-T-6h are all the characteristic peaks of anatase, and the intensity of the diffraction peaks increases gradually, the crystallization of titanium dioxide in the composite becomes more complete, and GO exists. It promoted the crystallization of titanium dioxide. During solvothermal reaction, the oxygen-containing active groups on GO surface are reduced to water under high temperature and pressure. Water is an indispensable factor for the hydrolysis of  $\text{Ti}(\text{OBU})_4$  into titanium dioxide. Therefore, the higher the initial GO content, the better the crystallization of titanium dioxide anatase in the structure of RGO/nano-titanium dioxide composite. With the prolongation of reaction time, the nanocrystalline size of titanium dioxide increases from 9.2 nm of 20G-T-3h sample to 12.7 nm of 20G-T-12h sample, and the anatase grain grows gradually. In addition, at the same solvothermal time, the increase of GO content also increases the grain size of titanium dioxide in RGO/titanium dioxide nanocomposites. The XRD patterns of graphene/nano  $\text{TiO}_2$  composites was shown in Figure 1.

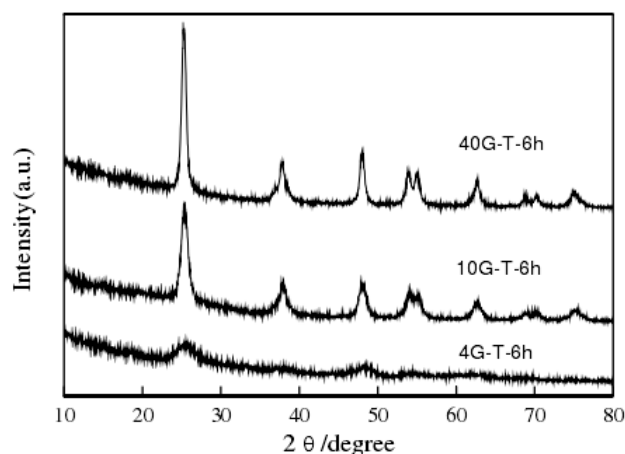


Figure 1. XRD patterns of graphene/nano TiO<sub>2</sub> composites obtained at different GO ratios

By deconvolution fitting, besides the symmetrical C-C peak of SP<sup>2</sup> hybridization at 284.8eV, GO also has a large number of oxygen-containing active groups such as epoxy C-O-C (286.8eV) and carboxyl O=C-OH (288.9eV). This is because the graphite oxide obtained by oxidation of flake graphite to a certain extent has many functional groups on the flake layer, which makes some other peaks appear in XPS spectrum. In the composite structure prepared with GO as raw material, the peak strength of other active groups such as epoxy group decreased sharply in C1s of 20G-T-3h, 20G-T-6h and 20G-T-12h samples except for the symmetrical C-C peak of SP<sup>2</sup> hybridization. With the prolongation of solvothermal reaction time, the oxygen-containing active groups on graphene surface gradually decreased, indicating that GO was reduced more thoroughly. At the same time, a peak at 282.3eV appeared in the C 1sXPS spectra of samples at 20G-T-6h and 20G-T-12h, which could be attributed to the C-Ti bond. Graphene is a kind of carbon material.

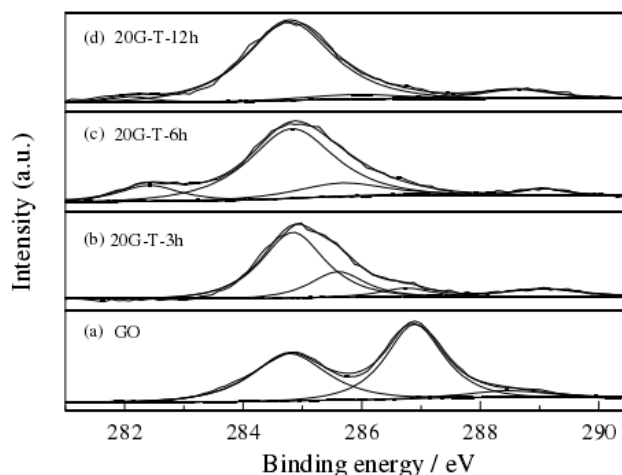


Figure 2. XPS patterns of the pristine GO and RGO/ TiO<sub>2</sub> nanocomposites prepared with different reaction times

Raman spectroscopy, as an effective analytical method, can be well applied to characterize the hybridization of sp<sup>2</sup> and sp<sup>3</sup> on graphene surface to study the disordered arrangement and defects of carbon atoms on graphene surface. The Raman vibration peak of carbon atom sp<sup>2</sup> plane is located at 1598cm<sup>-1</sup>, commonly called G-band. By comparing the peak intensity ratio of D-band to G-band, the disorder degree of carbon atoms in graphene plane can be indirectly expressed. As shown in Figure 3, the strength ratio of D-band to G-band of GO is 0.97. After 6 hours of solvothermal reaction, the strength ratio of D-band to G-band in Raman spectra of sample 20G-T-6h increases to 1.02, indicating that the hybrid plane of graphene sp<sup>2</sup> is relatively smaller. Combined with the previous XPS analysis results, GO was reduced to graphene by solvothermal reaction, while the area of graphene sheet became smaller, resulting in the increase of sp<sup>3</sup> hybrid carbon atoms at the edge of graphene.

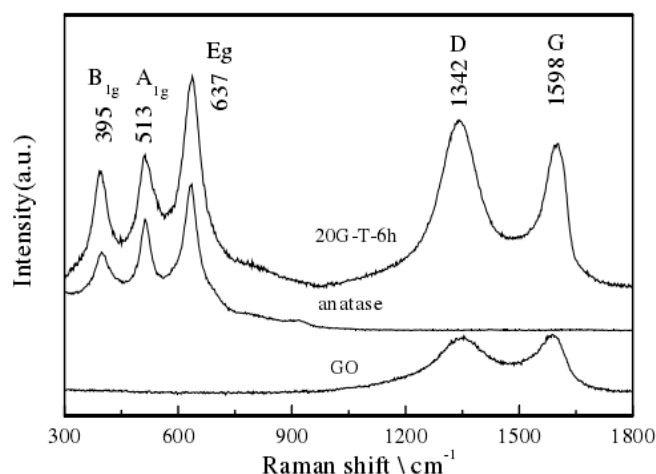


Figure 3. Raman patterns of GO, anatase and graphene/  $\text{TiO}_2$  nanocomposites

### 3.2. Photocatalytic Properties of Composite

The photocatalytic degradation efficiency of methyl orange was gradually enhanced by 4-T-6h, 10-G-T-6h, 20-G-T-6h and 40-G-T-6h. That is to say, with the increase of graphene content, the photocatalytic activity of the composites increases gradually. It should be pointed out that graphene has little photocatalytic activity, and the photocatalytic activity of the sample at 4G-T-6h is weaker than that of the titanium dioxide produced. This is due to the incomplete crystallization of anatase of titanium dioxide in the sample at 4G-T-6h, which affects the photocatalytic activity. In addition, the photocatalytic activities of 10G-T-6h, 20G-T-6h and 40G-T-6h were better than those of P25. The photocatalytic enhancement of RGO/ $\text{TiO}_2$  nanocomposites can be attributed to two aspects: graphene has excellent conductivity, photogenerated electrons and holes produced by anatase titanium dioxide under ultraviolet light can be effectively separated, carrier recombination can be inhibited, carrier lifetime can be prolonged, and photocatalytic activity can be enhanced. The organic molecules of methyl orange in solution can be well adsorbed and enriched on the graphene surface.

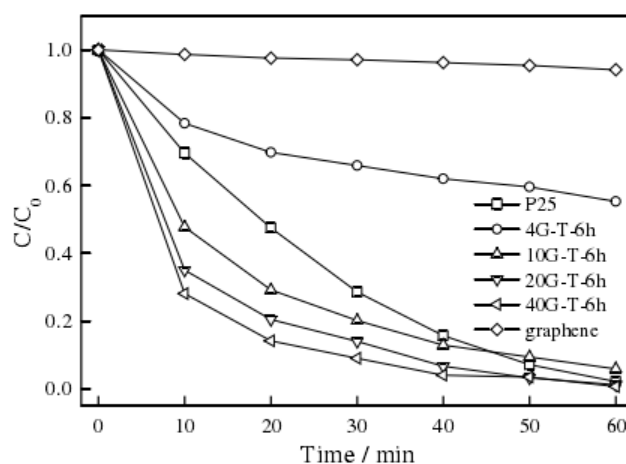


Figure 4. Photocatalytic activity of graphene/ $\text{TiO}_2$  nanocomposites, P25 and graphene

### 4. Conclusion

Graphene/titanium dioxide nanocomposite can be prepared by solvothermal method. The experimental results show that the photocatalytic performance of graphene/titanium dioxide nanocomposite is much better than that of pure titanium dioxide, which has great potential in many aspects of photocatalytic field. However, in order to make use of the graphene/titanium dioxide

nanocomposite in real life, the problem of what are the key factors affecting the photocatalytic efficiency of graphene/titanium dioxide nanocomposites still need to be studied theoretically.

## References

- [1] Gao Hang, Du Pengwei, Sheng Pengtao, et al. Preparation and photocatalyst properties of graphene quantum dots/TiO<sub>2</sub> nanowire composite material [J]. Chemical Research and Application, 2017, 29(11): 1738-1742.
- [2] Guan Enhao, Yue Hongyan, Gao Xin, et al. Preparation and application of TiO<sub>2</sub> nanowire (tube)-graphene [J]. New Chemical Materials, 2018, 46(9): 13-16.
- [3] Chen Ping, Liu Ting, Yao Kaibo, et al. Preparation and photoelectric property of TiO<sub>2</sub> composite nanoparticles modified by graphene quantum dots [J]. New Chemical Materials, 2018, 46(8): 79-84.
- [4] Qi Qi, Wang Yuqiao, Wang Shasha, et al. Preparation of Reduced Graphene Oxide/TiO<sub>2</sub> Nanocomposites and Their Photocatalytic Properties [J]. Acta Physico-Chimica Sinica, 2015, 31(12): 2332-2340.