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## Synthesis of Reduced Graphene Oxide Wrapped TiO<sub>2</sub> Ball Composites for Enhanced Photodegradation of Methylene Blue

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**Abstract:** Reduced graphene oxide wrapped TiO<sub>2</sub> ball composite (RGO-TiO<sub>2</sub>) was synthesized via two step hydrothermal processes. SEM analysis indicated the formation of TiO<sub>2</sub> balls with an average diameter of 1.5 μm and the RGO sheets were wrapped on the surface. XRD characterization indicated the formation of anatase phased TiO<sub>2</sub> after the annealing treatment while UV-vis and FTIR spectroscopy confirmed that the graphene oxide in the resulting material was in the reduced form. The photocatalytic activity of the as-prepared RGO-TiO<sub>2</sub> composite was determined by the photodegradation of methylene blue under UV illumination. The RGO-TiO<sub>2</sub> composite showed much higher photocatalytic performance than pure TiO<sub>2</sub> balls. More specifically, the degradation rate constant of using RGO-TiO<sub>2</sub> composite was twice higher than pure TiO<sub>2</sub> balls. The main reason of enhanced photocatalytic property might be the increased adsorption capacity, and the strong electron transfer ability of RGO sheets in the composites as well as the retarded charge recombination rate contributed by the energy level of the two materials. In addition, RGO-TiO<sub>2</sub> composites also exhibited an excellent reusability. We believe that this TiO<sub>2</sub> based composite material can be effectively used as a highly active and stable photocatalyst to remove various pollutants.

**Keywords:** TiO<sub>2</sub>; Reduced graphene oxide; Methylene blue; Photodegradation

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## 1. Introduction

Semiconductors have been widely used as photocatalysts to cope with worldwide water pollution problems. Among the many types of semiconductors, titanium dioxide ( $\text{TiO}_2$ ) has been received lots attention due to its high photocatalytic activity as well as the low cost and nontoxicity [1,2]. However, the photocatalytic performance of  $\text{TiO}_2$  still restricted by the fast electro-hole pair recombination rate [3,4]. In order to improve the photocatalytic performance of  $\text{TiO}_2$ , many materials have been studied to coupling with  $\text{TiO}_2$  for suppressing the charge recombination rate. Recently, studies showed the introduction of carbon materials can effectively decrease the charge recombination rate, thus enhance the photocatalytic performance of  $\text{TiO}_2$  [5,6].

Among the carbon materials, graphene, a monolayer two-dimensional graphitic carbon system, has attracted much attention since it was isolated in 2004 [7]. The two-dimensional structure, large surface area, outstanding electronic and catalytic properties of graphene makes it become a suitable candidate for incorporating with  $\text{TiO}_2$ . In the last few years, both graphene and reduced graphene oxide (RGO) were used for designing  $\text{TiO}_2$  based photocatalysts and showed enhanced photocatalytic activity. For example, Lei and co-workers [8] were developed a RGO/ $\text{TiO}_2$  composite by UV treatment of GO mixed with Degussa P25  $\text{TiO}_2$ . The prepared composite was used to photocatalytically reduce decabromodiphenyl ether, and the degradation rate was twice as much in comparison to pure  $\text{TiO}_2$ . Gao et al. [9] synthesized a GO- $\text{TiO}_2$  composite by a layer-by-layer method to sequentially fabricate  $\text{TiO}_2$  and GO on a polysulfone base membrane. The modified membrane was utilized to photodegradation of methylene blue in both batch and filtration experiments. The results showed the photodegradation kinetics of GO- $\text{TiO}_2$  composite modified membrane has 60-80% higher than  $\text{TiO}_2$  modified membrane under UV illumination.

In the perspective, even though there are already a number of RGO- $\text{TiO}_2$  composites have been developed and investigated, but most of them are mainly focused on nano-sized  $\text{TiO}_2$ . It is well known that the nano-sized  $\text{TiO}_2$  is prone to aggregation and can hardly be separated from the aqueous system, which highly limits its practical applications. Thus, design a micro-sized  $\text{TiO}_2$ -graphene composite is much suitable for water treatment purpose. Herein, we reported the preparation of RGO wrapped  $\text{TiO}_2$  ball composite by two step hydrothermal processes. The as-prepared RGO- $\text{TiO}_2$  composite showed enhanced photocatalytic performance towards photodegradation of methylene blue (MB).

## 2. Experimental

### 2.1 Materials

Poly(diallyl dimethyl ammonium chloride) (PDAA, 20 wt.%,  $M_w = 100\,000$ - $200\,000$  g/mol), titanium butoxide, acetic acid and MB were purchased from Sigma-Aldrich. Graphene oxide (GO) powder was purchased from JCNANO, INC. All other chemicals used were analytical grade reagents without further purification. Milli-Q water ( $18.2\text{ M}\Omega\text{ cm}$ ) was used throughout the experiments.

## 2.2 Synthesis of RGO-TiO<sub>2</sub> composites.

The synthesis of TiO<sub>2</sub> balls was based on a hydrothermal method reported by Liu et al. [10] with some modifications. Briefly, 1 mL titanium butoxide was added into 10 mL acetic acid and stirring for 0.5 h. The mixture then transfer to a 20 mL Teflon-lined stainless steel autoclave. The autoclave was heated to 140°C and maintained for 10 h in an oven and naturally cooled down to the room temperature. The sediment was collected and centrifuged few times (5000 rpm, 10 min) followed by a water wash to remove the excess acetic acid. The result solid was then heated to 300°C in a furnace for 3 h to form crystallised TiO<sub>2</sub>.

In order to synthesis of RGO-TiO<sub>2</sub> composite, PDDA was invoked as binding material. In a typical synthesis process, 1 mL PDDA was added into a 5 mL dispersion contains 50 mg TiO<sub>2</sub>. The dispersion was kept stirring for 1 h to achieve PDDA functionalized TiO<sub>2</sub>. The excess PDDA was removed by three times centrifugation followed by water wash. Then, 1 mL GO (1 mg/mL) was added into a 5 mL dispersion contains 50 mg PDDA functionalized TiO<sub>2</sub>. The mixture was stirring for 1 h and transfer to a 20 mL Teflon-lined stainless steel autoclave. The autoclave was heated to 120°C and maintained for 2 h to reduce GO. The final RGO-TiO<sub>2</sub> composite was collected by centrifugations and dried overnight at 80°C.

## 2.3 Characterization

FTIR was performed using a Nicolet iS5 (Thermo Scientific, USA). UV-vis spectra were carried out in the wavelength range from 190 to 800 nm. Surface morphology of samples were analyzed by a field emission scanning electron microscope (FeSEM, ZEISS SUPRA 40VP combined with EDX, Germany). The crystal structure of samples was collected from 5° to 90° in 2θ by a XRD with Cu Kα radiation (D8-Advanced, Bruker, Germany).

## 2.4 Photocatalytic degradation of MB:

The photocatalytic activities of different samples were determined by degradation of MB in solution using a UV lamp as light source (100 W Oliphant Bros, Pty. Ltd, Australian). In a typically process, 20 mg photocatalysts were added into a quartz tube containing 50 mL MB solution (20 mg/L). Prior to the illumination, the suspension was magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium. At given time intervals, 2 mL of suspension was sampled and centrifuged, the supernatant was collected for absorption analysis on a UV-vis spectrophotometer. The absorbance of MB at 664 nm was used for measuring the residual dye concentration.

# 3. Results and Discussion

## 3.1 Characterization of RGO-TiO<sub>2</sub> composites

In order to confirm the reduction of GO during the hydrothermal treatment, the RGO-TiO<sub>2</sub> composite was sonicated for 0.5 h and centrifugated to collect the free RGO dispersion. Fig 1a shows the UV-vis spectra of GO and RGO dispersions. It can be observed that the GO dispersion exhibits a characteristic

absorption peak at 227 nm corresponds to the  $\pi \rightarrow \pi^*$  transition of the C=C bonds. The RGO dispersion displays two main absorption peaks at 200 nm and 259 nm, which corresponding to the absorption of free PDDA [11] and the excitation of  $\pi$ -plasmon of graphitic bond [12], receptivity. This red shift from 227 to 259 nm indicates the successful achievement of RGO through the hydrothermal reaction.

The reduction process was further evidenced by FTIR analysis. As shown in Fig 1b, the GO spectrum shows several peaks at  $2946\text{ cm}^{-1}$ ,  $1734\text{ cm}^{-1}$ ,  $1398\text{ cm}^{-1}$  and  $1047\text{ cm}^{-1}$ , which belong to the stretching vibration of  $\text{CH}_2$ , C=O stretching of COOH groups, C—OH stretching vibrations and C—O vibrations from alkoxy groups, respectively. After hydrothermal reaction, these peaks are dramatically decreased or even vanished, indicating the successful reduction of RGO.

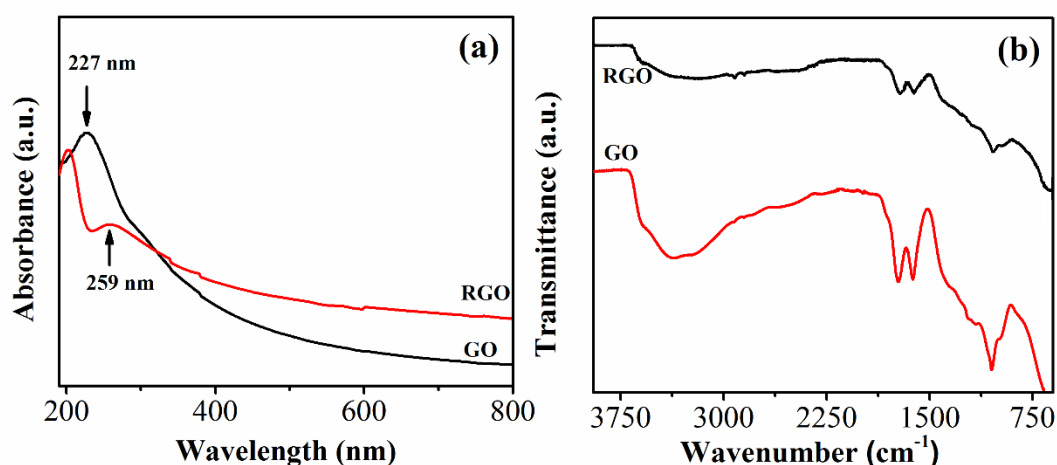


Fig. 1. (a): UV-vis spectra of GO and RGO. (b): FTIR spectra of GO and RGO.

The top-view SEM images of  $\text{TiO}_2$  ball and RGO- $\text{TiO}_2$  composite are shown in Fig. 2a-c. The pure  $\text{TiO}_2$  ball shows a rough surface with approximately  $1.5\ \mu\text{m}$  in diameters (Fig. 2a). This rough surface morphology produces a larger surface area to absorb dye molecules even the size of the particle is in the micro range. After loading with RGO sheets, the composite resembles a hydrangea-like shape. Under higher magnification view, it can be clearly observed that the surface of  $\text{TiO}_2$  ball represent nano-ribbon “petals”, which indicating the  $\text{TiO}_2$  was wrapped with RGO sheets. The crystalline phase of RGO- $\text{TiO}_2$  composite was examined by XRD. A series of characteristic peaks is noted in the XRD pattern at  $2\ \theta$  of  $24.9^\circ$ ,  $35.6^\circ$ ,  $47.8^\circ$ ,  $54.0^\circ$ ,  $54.0^\circ$  and  $62.4^\circ$  which related to the (101), (004), (200), (105), (211) and (204) planes of anatase  $\text{TiO}_2$ . Moreover, the broad peak located around  $25.0^\circ$  illustrates the presence of exfoliated RGO.

### 3.2 Photodegradation of MB

According to the literatures, the typical work functions of  $\text{TiO}_2$  and graphene are 4.40 eV and 4.42 eV, receptivity [13]. Thus, under UV irradiation, the electrons produced from CB of  $\text{TiO}_2$  can be transferred RGO, which could effectively separation of electrons and hinder the charge recombination. In this case, the photocatalytic activities of the as-prepared samples were investigated by the

photodegradation of MB under UV illumination. As shown in Fig. 3a, the MB itself could slightly decomposed under UV light. After 90 min illumination, 8% of MB was degraded. It was also noted that the RGO sheets showed a higher adsorption capability but feeble photocatalytic ability. Moreover, the photodegradation rate of  $\text{TiO}_2$  ball was outperformed by the RGO- $\text{TiO}_2$  composite. For the quantitative measurement of the difference in photocatalytic performances, the first order degradation rate constant ( $K_{\text{app}}$ ) was calculated. As shown in Fig. 3b, the  $K_{\text{app}}$  of RGO- $\text{TiO}_2$  (0.04002/min) was found to be almost double than that of  $\text{TiO}_2$  (0.02036/min), implying the introduction of RGO can highly accelerate the photodegradation rate.

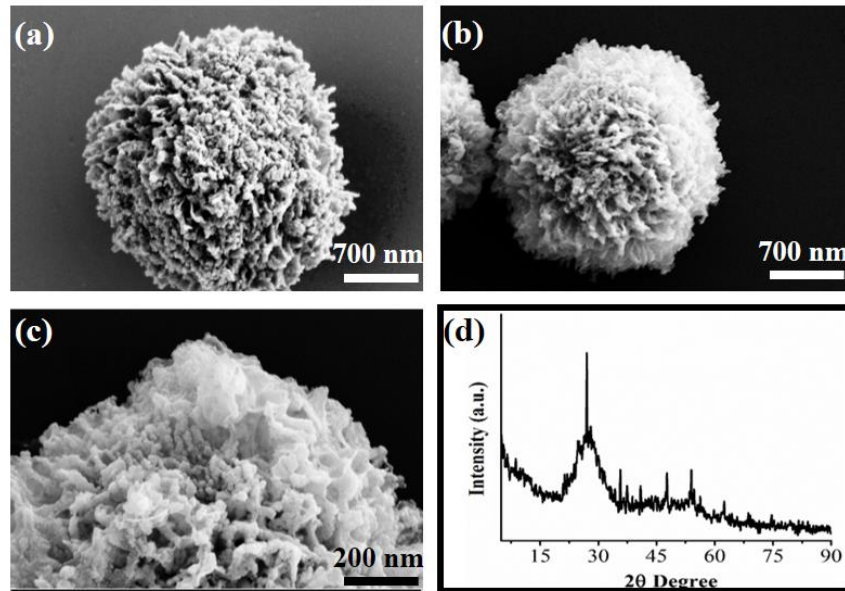


Fig. 2. SEM images of (a):  $\text{TiO}_2$  ball and (b,c): RGO- $\text{TiO}_2$  composite. (d): XRD pattern of RGO- $\text{TiO}_2$  composite.

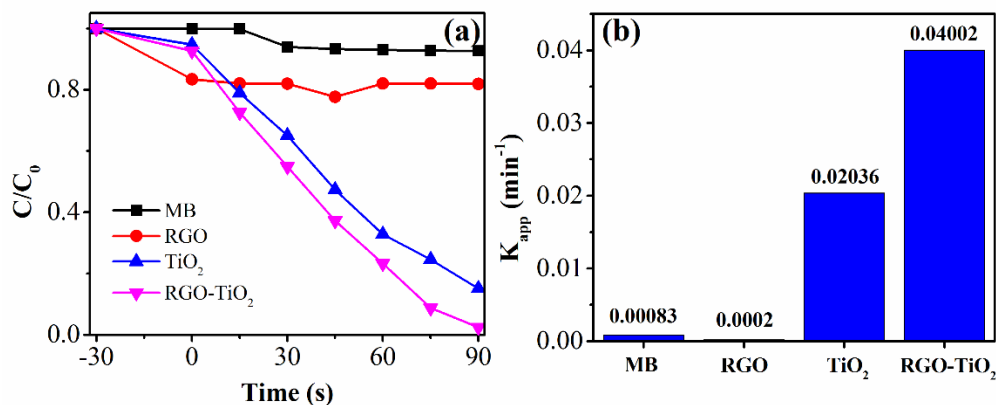


Fig. 3. (a): Comparison of MB photodegradation in the presence of different photocatalysts. (b): The rate constant of different photocatalysts in degradation of MB.

## Conclusion

Using two step hydrothermal reactions, RGO wrapped  $\text{TiO}_2$  ball composite was synthesized. According to the UV-vis spectroscopy and FTIR results, the RGO was formed from GO during the second step of hydrothermal treatment. The photocatalytic activity tests demonstrated that the

incorporation of RGO with TiO<sub>2</sub> could highly enhance the photocatalytic performance towards degradation of MB under UV illumination.

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### Conflicts of Interest

The authors declare no conflict of interest

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