

Photocatalytic Activity of GO/ZnWO₄ Nanocomposite Prepared by Co-precipitation under Visible Light

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Article history: Received 13 march 2017, Received in revised form 13 April 2017, Accepted 15 April 2017, Published 18 April 2017.

Abstract: Enhancement photocatalyst of reduced graphene oxide (GO/ZnWO₄) nanocomposite was prepared by Co-precipitation method. The photocatalytic activity of GO/ZnWO₄ was tested by photodegradation of Rhodamin B (RhB) under visible light irradiation. GO/ZnWO₄ nanocomposite revealed high improved of photocatalytic performance from crystal ZnWO₄ particles. The degradation of RhB was increased to 91.09 % in 60 min with the addition of GO as compared to pure ZnWO₄ was 18.22% in 120 min. The remarkable photocatalytic activity was attributed to the efficient photosensitized (the photosensitization of GO).

Keywords: Photocatalytic; ZnWO₄; Graphene oxide; Rhodamine B

1. Introduction

Dyes are widely used in different industries to colorize the products, such as in papers, cotton, foods, and pharmaceuticals etc. [1]. These industries released a large amount of dye waste water and which caused a serious environmental pollution [2]. Dyes are high chemical stability, complicated constitution and it is visible in flowing water even at a very low concentration, which inhibits photosynthetic process, by blocking out sunlight, what cause in retards the growth of aquatic biota [3],

[4]. There are several methods for the pollution remediation, for example, biological, physical and chemical [5]. Graphene has unique properties such as electrical, thermal [6], biological, chemical and mechanical properties etc. [7]. It found the composite of graphene with semiconductor enhanced the photoactivity [8]. In addition, it can absorb high a wide range of the spectrum of light and a facilitating the photocatalysis process in visible light [9]. The surface of GO has a large number of hydrophilic functional groups. ZnWO_4 was reported to be an excellent photocatalytic activity for splitting water and photodegradation of organic pollutants [10]. However, ZnWO_4 has a large band gap energy (3.75 eV) exhibit low photocatalytic activity [11], and high recombination ratios of photogenerated e^-/h^+ pairs. This makes it a weak response to visible light and restricted the practical application [12]. Many works dedicated to improving the photocatalytic properties of ZnWO_4 by reducing the recombination of electron-hole pairs and increasing the separation of charge carriers, which to make various heterostructure for example, anion doping, cation doping such as chlorine or fluorine, and coupling with other semiconductors such as ZnO , Bi_2WO_6 , C_3N_4 , Graphene, etc. [13][14]. Among of them, GO/ZnWO_4 nanocomposite photocatalyst exhibit high degradation of dyes under visible light irradiation [15].

The aim of this work is to investigate the effect GO content on the properties of the ZnWO_4 photocatalyst. The photocatalytic activity of GO/ZnWO_4 nanocomposite was determent by the degradation of RhB under visible light.

2. Experimental

2.1. Materials

Graphite powder (purity 99.999%), sodium nitrate (NaNO_3), sulphuric acid H_2SO_4 (98%), 10% hydrochloric acid (HCl), hydrogen peroxide (H_2O_2 , 30%), sodium tungstate2-hydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) Zinc nitrate 6-hydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and RhB was purchased from Sigma-Aldrich. All chemical materials were analytical grade without further treatment.

2.2. Preparation of the Catalysts

2.2.1. Synthesis graphene oxide (GO)

GO was prepared according to the Hummer's method from graphite 99.999% purity [16]. In a typical synthesis, 50 ml H_2SO_4 (98%) was added into a volumetric flask kept under at ice bath (0 - 5 °C). 1 g natural graphite powder and NaNO_3 (1 g) were added into the flask and stirred for 2 h. Then, 5 g KMnO_4 was added in an ice bath below 10 °C and stirred for 5 h. After that, remove the ice bath from the system and stirring the mixture for 24 h at room temperature. Then, the admixture was diluted by addition 350 ml water added step by step to the mixture until the temperature does not rise above

98°C, and become the color brown. After that, add 30 ml of H₂O₂ into solution, which turn to the bright yellow color. Then, the mixture was centrifuged (8000 rpm for 5 min). Then, the product washed with 250 mL of 10% HCl for two times, and 200 mL of water for cycles of centrifugal separation/washing/redispersion. The resulting precipitates were oven-dried overnight at 60 °C overnight.

2.2.2. Synthesis of ZnWO₄

Zinc tungstate ZnWO₄ powder was prepared using precipitation method as a precursor's materials [17]. In a typical procedure 1.48 g of Zn(NO₃)₂·6H₂O dissolving in 50 ml water. 1.65 g of Na₂WO₄·2H₂O dissolved 50 ml in water and added drop wise into above solution with vigorous stirring for 4 h at room temperature and adjusts pH value to 7. Finally, the ZnWO₄ sediment white was washed, filtered four times with water, and dried in an oven for 5 h at 60°C. The obtained product was calcined at 700°C for 4 h in air.

2.2.3. Synthesis of GO/ZnWO₄ catalyst

ZnWO₄ and GO/ZnWO₄ with 5, 7, 15 and 20 % of GO content were synthesized as following: 1g of ZnWO₄ was dispersed in 50 ml of DI water and then GO was dispersed in DI water (20 ml) by sonication for 1h respectively. After that, the obtained brown solution of graphene was added into the ZnWO₄ suspension and dispersed by ultrasonication for 1h and stirred for 6 h. The resulting nanocomposite was collected and dried in an oven at 80°C overnight. A similar approach was used to synthesized other GO/ZnWO₄ catalyst by fixing the amount of ZnWO₄. Finally, the GO/ZnWO₄ annealed at 250°C in air. For comparison, pure ZnWO₄ was also synthesized by the same method.

2.3. Photocatalytic Activity of GO/ZnWO₄ Nanocomposite

The photocatalytic activity of GO/ZnWO₄ was determined by degradation of an aqueous solution of RhB. An accurately weighed quantity of 50 mg of GO/ZnWO₄ was added to bottle 50 mL, 10 ppm RhB solution, under ambient temperature with a magnetic stirrer. The pH of the solution was adapted by 0.1 M HNO₃ and NaOH. At specific time intervals, aliquots of suspension were collected 1 ml volume of the sample solution and the volume completed to 10 ml water and then the catalyst separated through centrifugation. The RhB concentration was measured using the UV-Visible spectrophotometer (Unicom 5625 UV/Vis Spectrophotometer, Perkin Elmer, USA, Lambda 2) at 554 nm. Also, the effects of pH, GO content, the initial concentration of RhB and weight of catalyst on the degradation of dye were studied.

The Percentage degradation of dye was calculated by the following equation [18]:

$$\text{Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

Where C_0 is the initial concentration of the RhB (mg/L), and C_t is the concentration of dye at any time (min).

3. Results and Discussions

3.1. Photocatalytic Degradation of RhB

3.1.1. Effects of GO content

Fig. 1 shows the effect of GO content on the photocatalytic degradation of RhB under visible light irradiation over GO/ZnWO₄ photocatalyst. It has been concluded that the addition of GO enhance the photocatalytic activities of ZnWO₄ as it enhances the light absorption due to promote e^-/h^+ separation during the reaction. Also, with increasing the amount of GO in ZnWO₄, the degradation of RhB occur faster and 10 wt% GO show the higher photoactivity. With increasing GO loading to 15 and 20wt% the degradation decreases. As shown in the Fig. 1 the best photocatalytic degradation was recorded with 10wt% GO/ZnWO₄.

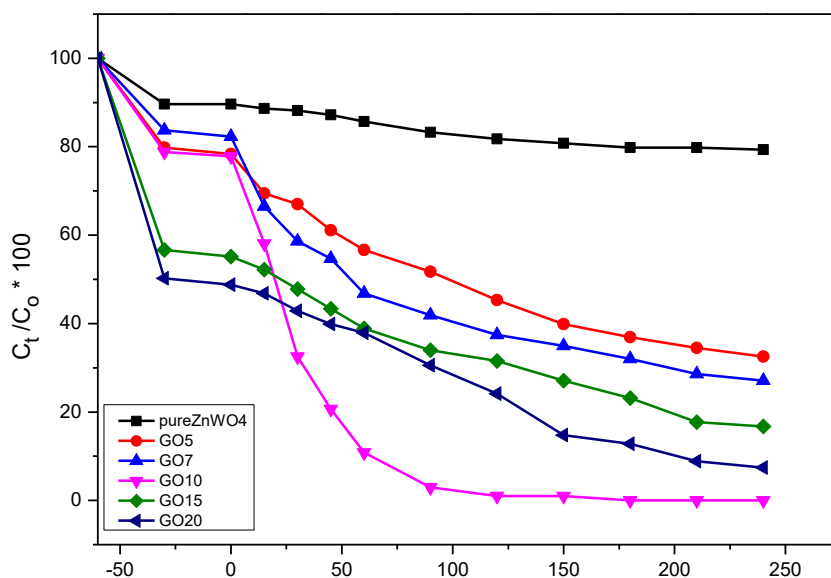


Fig. 1: Irradiation time for photocatalytic degradation of RhB by GO/ZnWO₄ calcined 250°C with different amount of GO loading

3.1.2. Effect of solution pH

The effect of pH on the photocatalytic degradation of RhB was studied. The pH values changed in the range from 4 to 12 at constant RhB concentration (10 ppm) and catalyst weight (50 mg). Fig. 2 indicated that the photodegradation activity of RhB increases with increasing in pH revealing the maximum rate of degradation at pH 8. In basic solutions, when the pH is increasing above 8, the photocatalytic degradation of RhB decreases, this indicated that pH of the solution was increased. In acidic conditions, the photodegradation of RhB increases. This may be due to the electrostatic

interactions between the positive catalyst surfaces and contains more surface acidic sites. Moreover, the charged radicals strongly depend on the pH of the solution and the positive charge on GO/ZnWO₄ surface increases which enhances the adsorption of dye molecules on the surface of the catalyst. Furthermore, acidic medium minimizes the e⁻/h⁺ recombination. The increase of pH renders GO/ZnWO₄ surface negatively charged and the repulsion could occur with dye molecules leading to low adsorption of molecules and thus decrease the photocatalytic degradation efficiency[19].

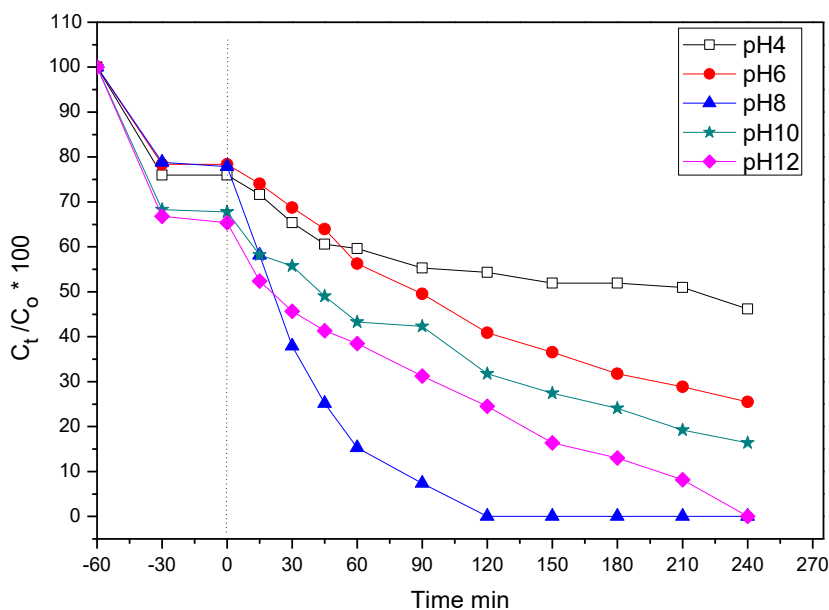


Fig. 2: Irradiation time for RhB under different pH by 10%RGO-ZnWO₄ calcined 250°C.

3.1.3. Effect of initial concentration of RhB

The initial of RhB concentrations C₀ were varied from 10 ppm to 50 ppm with 50 mg of GO/ZnWO₄. Fig.3 shows that the effect of initial concentration of RhB on photocatalytic degradation rate. It was observed that as the RhB concentration increases, the photodegradation rate decreases. This may be due to at lower concentration there are more available active sites for adsorption of RhB molecules on the surface RGO/ZnWO₄ photocatalyst. At higher concentration, more molecules of RhB adsorbed on the surface GO/ZnWO₄ photocatalyst, which has prevent the photogeneration of •OH, causing the decrease of photodegradation of RhB. So, longer time is required to complete the degradation of RhB when contrasted with a low concentration of the RhB [20][21].

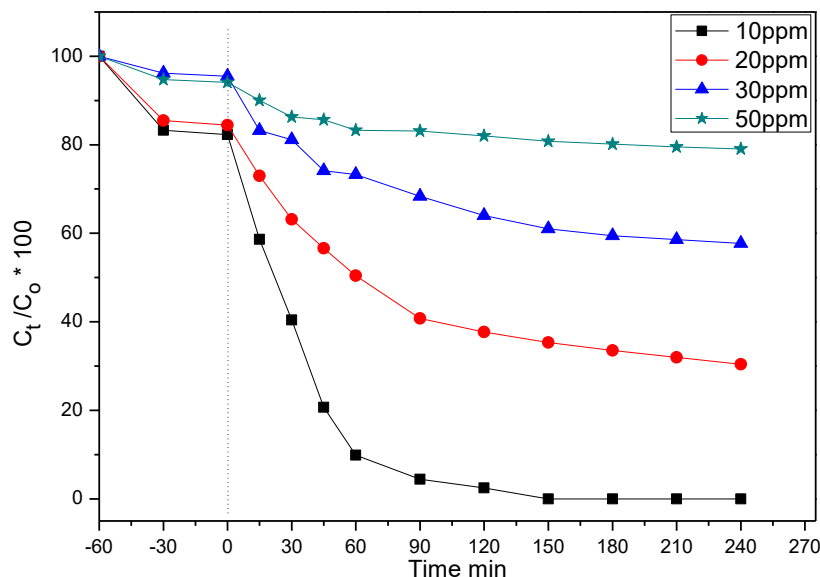


Fig. 3: Irradiation time for photocatalytic degradation of RhB by RGO/ZnWO₄ at different initial concentration

3.1.4. Effect of the catalyst weight

Fig. 4 shows the effect of catalyst weight on the photodegradation of RhB. It can be seen that with increasing the catalyst weight from 25-75 mg the degradation efficiency increases. This may be due to the increasing in the active sites on the photocatalyst [22]. However, with increasing the catalyst weight above 100 -150 mg the photoactivity decreases. The reason for this decrease may result due to the aggregation of GO/ZnWO₄ nanoparticles leading a decrease in the number of active sites on the GO/ZnWO₄ surface.

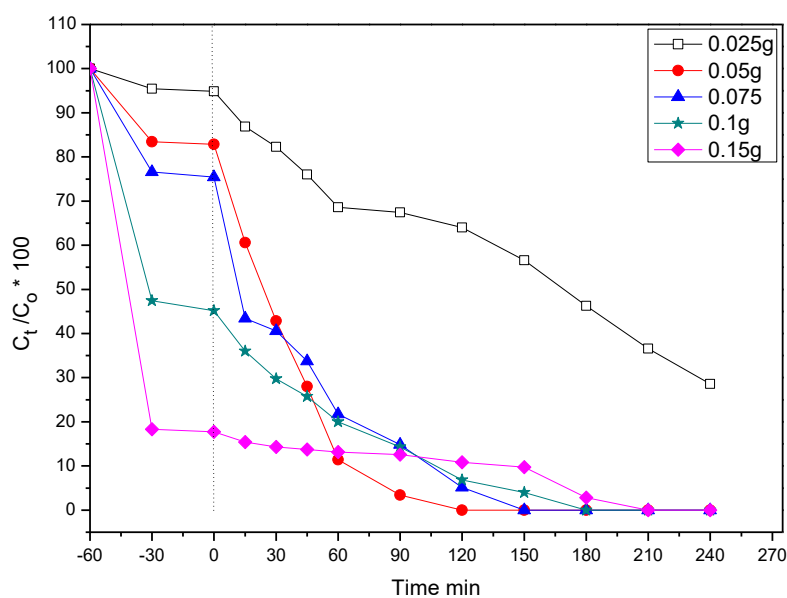


Fig. 4: Irradiation time for photocatalytic degradation of RhB by GO/ZnWO₄ using different catalyst weight

3.1.5. Effect of reuse

The reusability of the photocatalyst is necessary to evaluate the long-term stability of the GO/ZnWO₄ nanocomposite. Fig. 5 shows four reuse times of GO/ZnWO₄ and the removal efficiency were maintained at around 62% of RhB in the fourth times, the photocatalyst does not exhibit a significant loss in the photoactivity. This meaning that the obtained GO/ZnWO₄ catalysts are excellent stability. Therefore, these results indicate that the GO/ZnWO₄ composite have a potential application in waste water treatment.

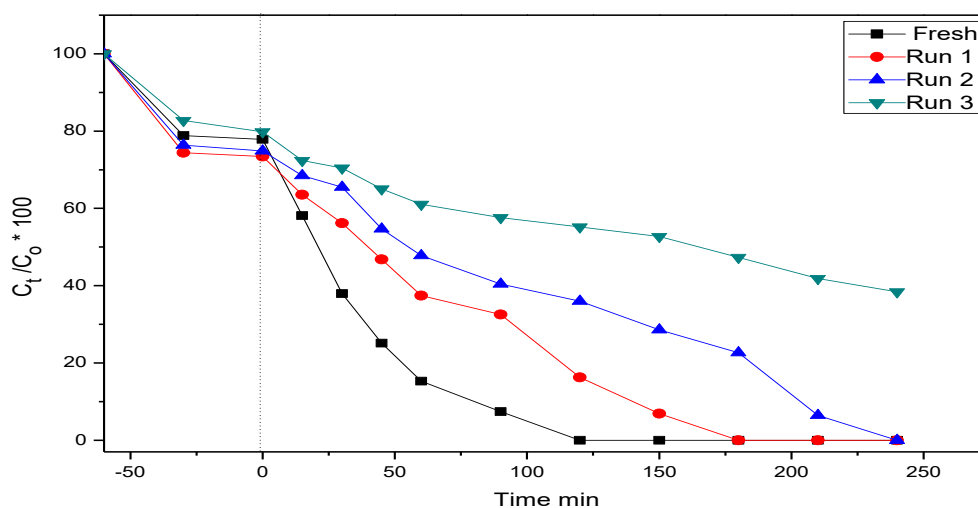


Fig. 5. Photodegradation reuse for RhB over GO/ZnWO₄ nanocomposite

4. Conclusion

The GO/ZnWO₄ nanocomposite was synthesized via Co-precipitation method. GO/ZnWO₄ nanocomposites show higher photocatalytic efficiency of RhB than pure ZnWO₄ particles. The degradation of RhB was increased to 91.09 % in 60 min with the addition of GO as compared to pure ZnWO₄ which only about 18.22%. 10% GO/ZnWO₄ showed the higher photocatalytic activity compare with other GO content. The reusability of the GO/ZnWO₄ photocatalyst is excellent.

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