

Preparation of ZnO-GO nanocomposites and their properties

Caifeng Jin¹, Yuqing Cheng¹, Wenbin Liu², and Yuguang Lv^{1,*}

¹ College of Pharmacy, Jiamusi University, Jiamusi, China

² School of materials science and Engineering, Jiamusi University, Jiamusi, China

Abstract. ZnO nanoparticles were prepared by hydrothermal method. The modified Hummer process was then used to prepare go. The ZnO-GO composites were then mixed to produce different ratios of ZnO-GO, characteristics and their photocatalytic properties were investigated using rhodamine B as the target degradation species. The results showed that the degradation rates of rhodamine B were 41.96% and 84.42% for the nano-ZnO and ZnO-GO 7% composites, respectively, when illuminated with xenon light for 360 min. The improved photocatalytic activity of composite materials is primarily due to the introduction of appropriate amount of GO, which could rapidly capture and transfer to the photogenerated electrons, and could load more ZnO and prevent the agglomeration of ZnO particles, increasing the specific surface area of ZnO and its activation point, as well as increasing the adsorption of pollutants on the ZnO surface and improving the photocatalytic efficiency.

Keywords: Nano-ZnO; Graphene oxide; Photocatalysis.

1 Introduction

As society develops and environmental problems such as waste pollution become increasingly prominent, a sewage treatment method is urgently needed. Semiconductor oxide photocatalytic oxidation technology is a relatively new type of technology for treating water pollution. As a photocatalyst, semiconductor oxides include TiO₂, ZnO, WO₃, SnO₂, etc. Among them, the redox capacity of titanium dioxide is very strong, chemically stable, non-toxic, and does not cause secondary pollution. Zinc oxide has a band gap closer to titanium dioxide, and zinc oxide synthesis with a low cost, is a metal oxide semiconductor material that can replace titanium dioxide for the effective degradation of the organic dye contaminant [1-2]. Nanoparticles will exhibit many excellent properties compared to normal ZnO, such as non-toxicity, piezoelectricity, fluorescence, and the ability to absorb and scatter ultraviolet light. The main ways to improve the photocatalytic activity of ZnO nanomaterials are: firstly, to control the ZnO growth structure; and secondly, to carry out surface modifications. At present, the problems encountered in the process of overcoming composite graphene are often solved by using surface modification, i.e. replacing graphene with graphene oxide. In this study, ZnO nanoparticles were firstly prepared by hydrothermal method; then graphene oxide (GO) was prepared by modified

*Corresponding author: yuguanglv@163.com

Hummers method; the two were then mixed to prepare ZnO-GO composites in different ratios, and their photocatalytic properties were investigated using rhodamine B as the target degradant^[3].

2 Catalyst material preparation

2.1 Preparation of ZnO-GO composites

The ZnO dispersion was obtained by adding 50 ml of anhydrous ethanol to a beaker and sonicating for 2 h. The graphene oxide ethanol suspension was added to the ZnO dispersion (50 ml of anhydrous ethanol was added to GO and sonicating for 2 h to obtain an ethanol suspension of graphene oxide) and stirred at elevated temperature for 24 h. The resulting product was washed by centrifugation and anhydrous ethanol. The product was then re-dispersed in 10 mL of anhydrous ethanol. Vacuum drying for 24 h to obtain ZnO-GO nanoparticles (ZnO-GO1%, ZnO-GO3%, ZnO-GO5%, ZnO-GO7%, ZnO-GO10% were produced respectively)

3 Results and Discussion

3.1 Structural and morphological characterisation

Figure 1(a) shows the XRD pattern of the morphology of the ZnO nanoparticles prepared by the hydrothermal method. All diffraction peaks match the standard data for the fibrillated ZnO structure of the ZnO hexagonal crystal system (JPCDS 36-1451). The sharp shape of the diffraction peaks in the figure indicates that the obtained ZnO crystals are well crystalline. The XRD patterns of both are highly compatible and the absence of their characteristic diffraction peaks in the XRD patterns indicates that the synthesised samples are both of high purity and no impurities are produced. No diffraction peaks of graphene were observed in the XRD patterns due to the small proportion of graphene oxide in the catalyst. The XRD patterns of the composites (c) show that the doping of different amounts of graphene oxide resulted in lower intensity and wider peak shape of ZnO compared to pure ZnO, and a decrease in crystallinity of the composite samples. The effect on the crystallinity of ZnO gradually increases as the amount of graphene oxide doping increases^[5]. In addition, the SEM and TEM photographs given in Figure 2 show that the ZnO particles are attached to the surface layer of graphene oxide, and the graphene oxide doping obviously prevents the agglomeration of ZnO nanoparticles.

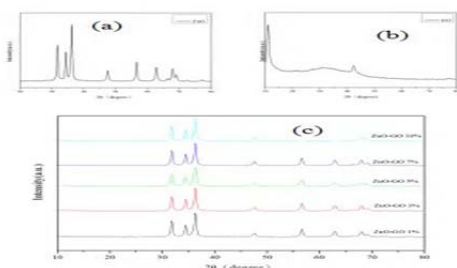


Fig. 1. XRD spectra of ZnO (a), GO (b), ZnO-GO composites (c).

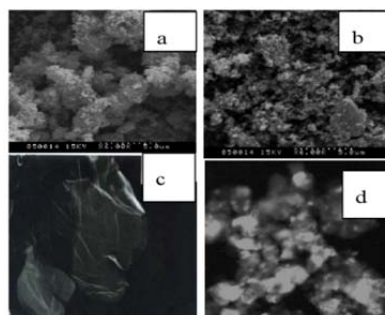


Fig. 2. Scanning electron micro-graphs of ZnO nanoparticles (a) and ZnO-GO1%(b),GO(c), ZnO-GO1% (d) transmission electron micrographs.

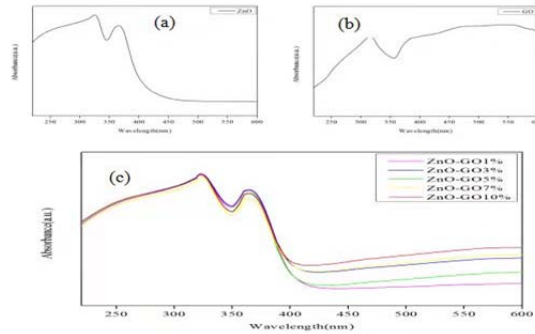


Fig. 3. UV-Vis spectra of ZnO (A), GO (B), and ZnO-GO composites with different concentrations (C).

Figure 3 shows the UV-Vis absorption spectra of different amounts of graphene oxide doped ZnO, from which it can be seen that all samples have strong absorption at 385 nm, corresponding to the intrinsic band width of ZnO nanoparticles. The absorption intensity of the graphene oxide doped photocatalysts was significantly enhanced in the visible range, indicating that the addition of graphene oxide altered the light absorption properties of ZnO.

4 Degradation of rhodamine B by ZnO-GO composite photocatalyst

4.1 Photocatalytic methods

50 mg of photocatalyst and 100 mL of rhodamine B solution at a concentration of 10 mg/L were weighed separately in a 100 mL double beaker. The solution was magnetically stirred in the dark for a certain period. A xenon light source and condensation unit were then switched on for visible light-catalyzed degradation. Approximately 5 mL of the reaction solution is extracted at regular intervals, the catalyst is removed by centrifugation and the supernatant is measured by UV-Vis spectrophotometer at a maximum absorption wavelength of 554 nm to determine the residual concentration of the catalytic degradation and to calculate the degradation rate $\eta\%$ ^[6]. The formula was calculated as:

$$\eta\% = 1 - C_t/C_0 \times 100\% = 1 - A_t/A_0 \times 100\% \quad (1)$$

t-reaction time (min).

C_t -concentration of pollutant at time t (mg/L).

C_0 -equilibrium concentration of pollutant after dark adsorption-desorption equilibrium (mg/L).

A_t - the absorbance of the contaminant at time t.

A_0 -absorbance of the pollutant after dark adsorption-desorption equilibrium.

4.2 Photocatalytic properties

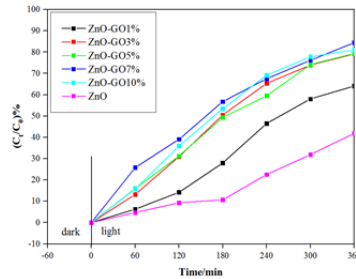


Fig. 4. Effect of different GO concentrations on the photocatalytic performance of the catalyst.

The photocatalytic activity of rhodamine B was tested by desorption of the sample under UV light. The reaction was preceded by adsorption in a dark box for 30 min and after reaching adsorption equilibrium, the UV light source was switched on. Figure 4 shows the photocatalytic activity of the different samples^[7]. It can be seen that the ZnO nanopowder has a certain degradation effect on rhodamine B, with a degradation rate of 41.96% at 360min of light exposure. From the photodegradation curves of the ZnO-GO composites for rhodamine B, more GO content does not necessarily mean that the photocatalytic performance of the composites is good, probably because too much GO content in the composites will instead affect the absorption of UV light by ZnO, thus affecting the photoexcitation and catalytic activity of the ZnO particles. The proper introduction of GO can make the composite adsorb organic dyes well and can promote the effective separation of ZnO photogenerated carriers and reduce the composite rate. This shows that the ratio of ZnO and GO in the composite has a very strong influence on photocatalysis. Among them, ZnO-GO 7% has the best photocatalytic performance, with a degradation rate of 84.42% at 360 min of light.

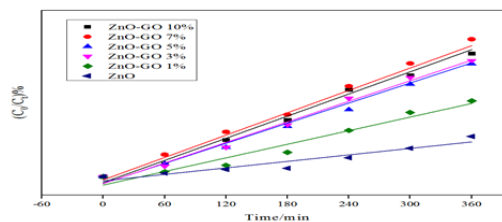


Fig. 5. $\ln(C_0/C_t)$ -t linear fit curves for catalyst samples with different GO concentrations.

Table 1. Linear correlation coefficients between reaction rate constants and regression equations for different catalysts.

Sample name	Regression equation	K	R ²
ZnO	$y=0.0995x-0.1077$	0.00147	0.928
ZnO-GO1%	$y=0.2975x-0.1769$	0.00307	0.9951
ZnO-GO3%	$y=0.2906x-0.1733$	0.00464	0.9887
ZnO-GO5%	$y=0.2069x-0.2134$	0.00500	0.9791
ZnO-GO7%	$y=0.3114x-0.0813$	0.00504	0.9909
ZnO-GO10%	$y=0.316x-0.1506$	0.00453	0.9895

Figure 5 shows the linear fitting curve of $\ln(C_0/C_t)$ -t for ZnO-GO 7%. It can be seen that $\ln(C_0/C_t)$ -t shows a good linear correlation, indicating that the photocatalytic degradation of

rhodamine B is an apparent primary reaction. The rate constants and linear correlation coefficients of the regression equations are shown in Table 1, which shows that ZnO-GO 7% had the best catalytic effect with the highest rate constant of 0.00504. The kinetic fitting results are consistent with the degradation efficiency results in Figure 4. The linear correlation coefficients of the regression equations were all greater than or close to 0.99, indicating a good regression effect.

5 Conclusion

ZnO nanoparticles were obtained by simple hydrothermal method, and GO and ZnO were obtained by modified Hummer method, and ZnO-GO composites with different GO concentrations were prepared by mixing ZnO nanoparticles with GO. Here we study the efficiency of rhodamine B as a pollutant for photocatalytic degradation by using a xenon lamp greater than 400 nm as the unique light source. The experimental results showed that ZnO-GO 7% had the best catalytic effect with 84.42% degradation rate when the light time was 360min. The composite material is simple to prepare and has certain practical application value.

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