

# Hydrothermal Synthesis of Graphene-ZnO Composites for Photodegradation of Methylene Blue under Sunlight Radiation

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## ABSTRACT

Graphene zinc oxide composites have been successfully synthesized via a hydrothermal reaction using graphite zinc chloride as starting materials. These prepared composites with different ratios of graphene and zinc oxides were characterized by X-ray diffraction (XRD), Raman and solid UV-Vis spectroscopies, and thermogravimetric analysis (TGA). The XRD and TGA analysis reveal that the intercalation of ZnO into graphene layer expands the  $d$  – spacing between graphene sheets and reduce the oxidation temperature. The results from Raman spectroscopy show that composites possess both characteristics of graphene and ZnO, and there is existence of interaction between ZnO and oxygenated functionalities on graphene sheets. In the photocatalytic reaction, the composite containing 10% in mass of ZnO exhibits the highest photocatalytic efficiency of 97.13% after 13 hours exposing to sun light.

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## Introduction

Graphene-based composites as photocatalysts have attracted considerably due to its potential applications in different fields. Since graphene possesses excellent electric conductivity and high surface area, it has been a suitable materials used as two-dimensional platform to accept and spread photogenerated electron-hole pairs from semiconductor upon light irradiation, therefore enhancing the photodegradation efficiency of semiconductors in photodegradation reaction [1, 2]. Recent years, different graphene semiconductor composites, especially metallic oxide semiconductors have reported that the attachment of metal oxide particles onto graphene layers could prevent the restack and aggregation of graphene sheets during reduction process. In addition, in the case of semiconductor metal oxides, the attachment of metal oxide particles can improve photocatalytic performance in the degradation of organic compounds as compared with metal oxide itself or pristine graphene [3]. The improvement of photocatalytic performance can be explained due to the special ability of graphene which can act as electron acceptor/shuttle photogenerated from semi-conductor metal oxide upon light irradiation. This makes the life span of photoexcited electron-hole pairs is prolonged thereby hindering the electron-hole recombination and enhancing photoactivity of materials. However, the recombination of photo-generated electron-hole pairs still exists in these composites, thus decreases their photocatalytic performance [4]. Further work on hybrid materials based on graphene should be done to overcome the above problem.

In this work, we report a one-step synthesis of graphene-ZnO composites through hydrothermal method from graphite and zinc chloride as precursors. The characterization of obtained materials using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), Thermalgravimetric analysis (TGA), ultraviolet-visible (UV-Vis) and raman spectroscopies, and photocatalytic activity of

the obtained materials assessed by degradation of Methylene Blue (MB) aqueous solution under UV-Vis radiation are also reported.

## Experiment Part

**Chemicals:** The graphite (GR) flake has been purchased from Sigma Aldrich. Distilled water was used, ZnCl<sub>2</sub> and all other chemicals were analytical grade reagents and used as received.

**Preparation of Graphene Oxide (GO):** GO was synthesized from GR by a modified Hummer's method [5]. In a 1000 mL beaker, 4.0 g GR and 2.0 g NaNO<sub>3</sub> were mixed with 100 mL concentrated H<sub>2</sub>SO<sub>4</sub> (98%). The mixture was stirred for 3.0 hours at ambient temperature. During stirring, 5.0 g KMnO<sub>4</sub> was slowly added to the suspension and the temperature was maintained at ambient temperature. After addition of KMnO<sub>4</sub>, the reaction mixture was then stirred at 30°C for 7.0 hours. Then, 250 mL dilute H<sub>2</sub>SO<sub>4</sub> (5%) was slowly added to the mixture with vigorous stirring. The diluted suspension was again stirred at 90°C for 4.0 hours. Finally, 50 mL 30% H<sub>2</sub>O<sub>2</sub> was added. The whole reaction mixture was washed by centrifuging with 5% H<sub>2</sub>SO<sub>4</sub> followed by distilled water for 6 to 8 times and filtered to obtain gray GO sheets.

**Hydrothermal Preparation of Graphene-ZnO:** Suspension of GO was prepared by mixing GO with distilled water under condition of vigorous stirring. After that, the aqueous solution of ZnCl<sub>2</sub> was slowly added to GO suspension followed by stirring for another 1.0 hour. Then equivalent amount of NaOH solution was added to the mixture under the continuously vigorous stirring condition. The mixture was finally transferred to 200 mL autoclave maintained at 200°C for 24.0 hours. The resulting composite was obtained by filtering following by washing with distilled H<sub>2</sub>O and drying at 120°C for 24 hours. The amount ZnCl<sub>2</sub> solution added to GO suspension was varied in order to produce composite samples with different Graphene/ZnO weight ratios of 95: 5, 90:10, 85: 15, 80: 20 and 65: 35. For convenience, composite

samples are denoted as GXZnO (X is weight percentages of ZnO in composite).

**Characterization:** Scanning electron microscope (SEM) was performed by a Hitachi S-4800 field emission scanning electron microscope at 5 kV. X-ray diffraction (XRD) patterns of the samples were measured on a Bruker-D5005 powder X-ray diffractometer using copper  $K\alpha$ -radiation with  $\lambda = 1.5406$  Å. Fourier transform infrared spectroscopy (FT-IR) was performed on NEXUS-670, Nicolet – USA. Raman spectroscopy was recorded using LAB RAM HR800, HORIBA-France. UV-Vis absorption spectra of solid forms were recorded by Jasco V670 spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a Shimadzu DTG-60H instrument at a heating rate of  $10^\circ/\text{min}$  under air flow.

**Photocatalytic activity:** the photocatalytic activity of the photocatalyst was confirmed by the degradation of Methylene Blue (MB) under visible radiation of sun light. Photocatalyst (5 mg) was dispersed into 80 ml MB solution with the concentration of 10 mg/L, and then the mixture was stirred for 5 min in the dark, after which the mixture was exposed to radiation of sun light (the temperature is about  $35^\circ\text{C}$ ). The samples were analyzed every 60 min using UV-visible spectrophotometer (LIUV-310S, Lambda). Experiments were carried out under sun light radiation from 10 am to 4 pm of the shiny day without cloud and with the temperature of around  $35^\circ\text{C}$ .

## Results And Discussion

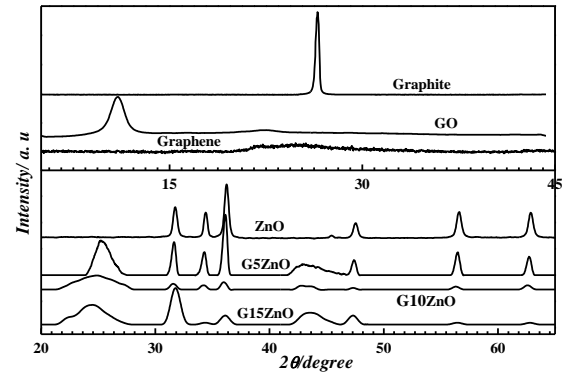
**Characterization of GXZnO composites:** Figure 1 shows the XRD patterns of graphite powder, graphene oxide, graphene, ZnO and GXZnO composites with different contents of ZnO ranging from 5 to 20%.

The XRD patterns of pure pristine graphite exhibits a sharp peak at about  $2\theta = 26.5^\circ$  correlating to an interlayer space of  $3.36$  Å. While, reflection angle of GO shifted to the lower value of about  $11^\circ$  correlated to interlayer distance of  $8.80$  Å. The increase in  $d$ -space of GO suggests that functional groups were formed after oxidation of graphite. For graphene, XRD pattern appears a broad reflection slightly shifted to lower value ( $\sim 25.7^\circ$ ) in comparison with reflection angle of graphite. This relative small shift reveals the presence of oxygen functional groups in graphene leading to slightly higher value of  $d$ -spacing compared with the case of GO [6].

As can be seen in figure 1, the XRD patterns of the GXZnO composites were different from the XRD pattern of pure ZnO, in which there are peaks characteristic for the standard wurtzite structure of ZnO with diffraction peaks at  $31.7, 34.4, 36.3, 47.6, 56.6$  and  $62.9^\circ$  [1, 7] indexed to (100), (002), (101), (102), (110) and (103) crystallographic planes of hexagonal ZnO (JPCDS 36-1451), and a peak characteristic for  $d$ -spacing between graphene sheet at  $25.3^\circ$ . These results demonstrate that the presence of graphene does not result in the development of new crystal orientations or changes favorable orientation of ZnO [7].

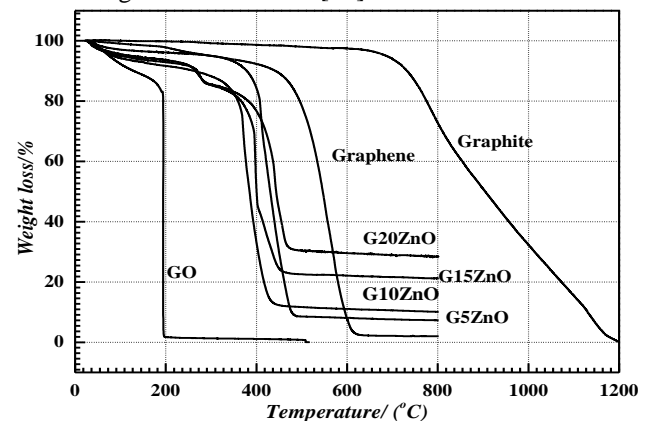
**Thermo-Gravimetric Analysis (TGA):** The composition of the GXZnO composites were further studied by thermogravimetric analysis. Plots in Figure 3 are the TGA curves of graphite and GO, graphene and GXZnO composites obtained with heating rate of  $10^\circ/\text{min}$  and under air flow. As

expected, graphite was highly stable up to  $700^\circ\text{C}$ , while almost mass of GO was lost rapidly at the temperature of under  $200^\circ\text{C}$ .



**Figure 1. X-ray diffraction patterns of pristine graphite, GO, graphene, ZnO and GXZnO composites.**

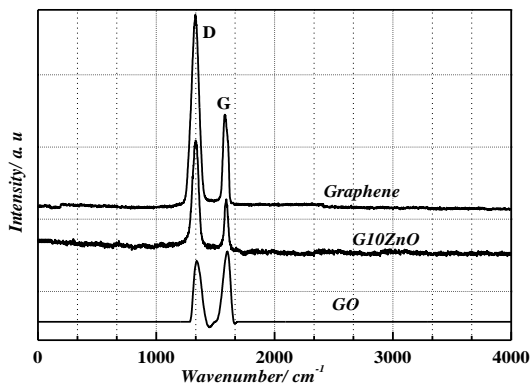
This can be explained due to pyrolysis of labile oxygen-containing functional groups yielding a vigorous release of steam, CO and  $\text{CO}_2$  gases, and therefore leading to the large mass loss [8, 9]. In contrast with GO, TGA curve of graphene shows the significantly improved thermal stability indicating the removal of oxygen-containing functional groups in GO sheets during reduction of GO [10].



**Figure 2. Thermogravimetric analysis of pristine graphite, GO, graphene, ZnO and GXZnO composites.**

As shown in Figure 2, TGA curve of all the composites reveals the improvement in thermal stability of composites in comparison to GO. At the temperature under  $200^\circ\text{C}$ , only small amount of composites is lost due to the de-intercalation of  $\text{H}_2\text{O}$  from graphene [11]. At the temperature ranging from  $350^\circ\text{C}$  to  $500^\circ\text{C}$ , the oxidation of graphene in composites occurs vigorously, and therefore, almost of the graphene in composites lost in this range of temperature. Compared with graphene, composites are less stable and burned vigorously at the temperature lower than in the case of graphene. This result can be explained due to the intercalation of ZnO particles into the space of graphene sheets leading to the expansion of graphene sheets and the ease of burning. This result can also be in good agreement with XRD result.

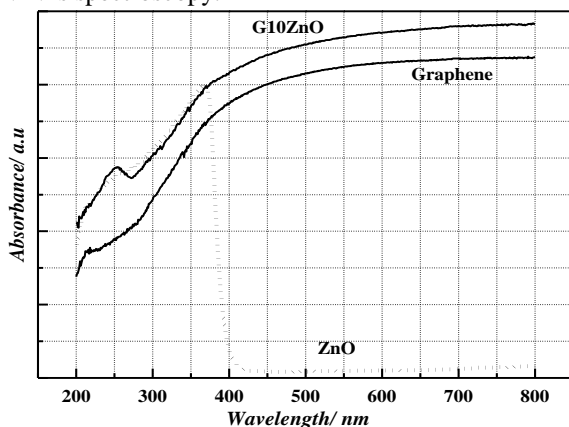
**Raman spectroscopy:** In order to prove the formation of graphene in composites from reduction of GO and interaction between ZnO and oxygenated functionalities on graphene sheets, Raman spectrum of GO, graphene and G10ZnO was used to study further their characteristics.



**Figure 3. Raman Spectra of GO, graphene and G10ZnO composite.**

As can be seen from the spectra in Figure 3, two intensity peaks at  $1344$  and  $1600\text{ cm}^{-1}$  are dominated in spectrum of GO. These peaks are referred to D band corresponding to the breathing mode of  $\kappa$ -point phonons of  $A_{1g}$  symmetry and G bands assigned to  $E_{2g}$  phonon of  $sp^2$  bonds of carbon atoms, respectively. Similarly to spectrum of GO, spectrum of graphene and G10ZnO also consists of D and G bands. However, the D/G intensity ratio ( $I_D/I_G = 1.70$  for Graphene and  $2.08$  for G10ZnO composite, respectively) is much higher than that of GO ( $I_D/I_G = 0.87$ ), which indicates a decrease in the average size of  $sp^2$  domains upon reduction of graphene oxide to form graphene and an increase in edge planes as well as the degree of disorder in the synthesized graphene sheets [12]. In addition, in spectrum of G10ZnO, the peak assigned to G band is slightly shifted to higher wavenumber. This shift indicates the chemical interaction between ZnO and oxygenated functional group on graphene sheets [7, 13].

**UV-Vis spectroscopy:** UV-Vis spectra of graphene, ZnO and G10ZnO composite are shown in Figure 4. The pure ZnO mainly absorbs irradiation in the region of UV, while graphene and G10ZnO composites absorb both UV and visible regions. There is no shift of absorbance peak, which can be seen in G10ZnO composite in comparison to the pure semiconductor oxides, i. e., The effect of the intercalation of zinc oxide into graphene layers is not strong enough to be seen in UV-Vis spectroscopy.

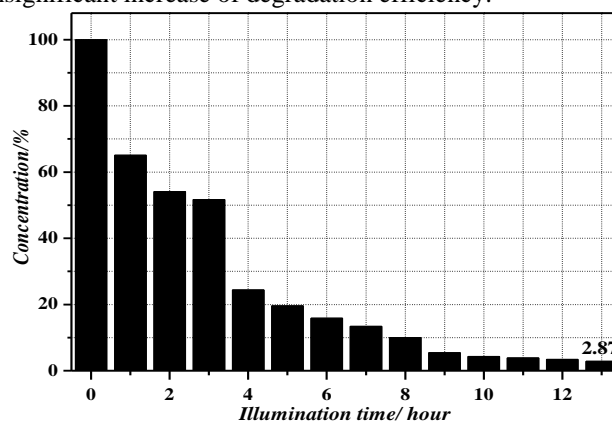


**Figure 4. UV-Vis spectra of GO, graphene and G10ZnO composite.**

**Photoalytic reactivity:** The photocatalytic activity of GXZnO composites was studied with number of experiments carrying out on the degradation reaction of Methylene Blue (MB) under sun light irradiation, where GXZnO composites were used as photocatalysts. The determination of MB concentration was carried out using LIUV 310S UV-Vis spectrometer, LAMBDA at  $665\text{ nm}$ .

**Effect of ZnO content on degradation efficiency:** experiments were carried out as following:  $5\text{ mg}$  of each GXZnO ( $X = 5, 10, 15$  and  $20\text{ wt}\%$ ) material was mixed thoroughly in dark with  $80\text{ mL}$  of  $10\text{ mg/L}$  MB solution. pH of the solution was established by itself with value of around  $6.5$ . The mixture was then transferred to  $250\text{ mL}$  Erlenmeyer flask with stopper and exposed to the sun light irradiation for  $15$  hours in the sunny day with outside temperature of about  $35^\circ\text{C}$ . The illumination usually lasts from  $10\text{ am}$  to  $4\text{ pm}$ . The obtained results show that all GXZnO composites have high degradation efficiency ( $>96\%$ ). The G10ZnO reaches the highest efficiency of  $97.13\%$  and G20ZnO has the lowest efficiency of  $96.90\%$ . Therefore, hence experiments will be carried out with G10ZnO composite.

**Effect of Illumination time on degradation efficiency:** As result shown in Figure 6, the optimized exposure time for degradation reaction of  $10\text{ mg/L}$  MB solution is  $13$  hours with the degradation efficiency of  $97.13\%$  because after  $13$  hours of illumination, the efficiency increases insignificantly. This result can be explained due to at low concentration the possibility of collision between photo-generated electron-hole pairs and MB molecules is very small leading to the insignificant increase of degradation efficiency.



**Figure 5. Time dependence of degradation efficiency.**

## CONCLUSION

In this paper, we present the preparation and characterization of graphene zinc oxide composites from graphene oxide and zinc chloride as precursors using hydrothermal method. The results XRD, Raman spectroscopy show that composites possess both characteristics of graphene and ZnO, and there is existence of interaction between ZnO and oxygenated functionalities on graphene sheets. The photodegradation study shows that the composite composed of  $10\%$  ZnO possesses the highest photodegradation efficiency of  $97.13\%$  after  $13$  hours exposing to sun light irradiation.

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