Photocatalytic Properties of Zinc Oxide and Graphene Nanocomposites

Avery A. McLain

Physics, University of Wisconsin – La Crosse
La Crosse, Wisconsin, United States of America

Abstract

Zinc oxide (ZnO), as a semiconducting oxide, has potential as a photocatalyst due to some of the properties it possesses, including a large excitation energy, deep violet/borderline ultraviolet (UV) absorption at room temperature, and good photocatalytic activity. However, the main issue with using ZnO as a photocatalyst is that it has a rapid rate for the recombination of electron-hole pairs. Since the photoactivity of a catalyst is determined by its ability to create photogenerated electron-hole pairs, having a fast recombination rate can interfere with the reaction process. This issue could potentially be fixed by combining the ZnO with graphene, a carbon-based material. The conjugated structure of graphene enables the separation of charges in the photocatalytic process, so by combining ZnO and graphene the recombination rate could possibly be slowed while retaining the beneficial properties of both materials. This project analyzes the effects of ZnO/graphene nanocomposites on the degradation process of methylene blue dye. This dye breaks down when exposed to solar light, and so the photocatalytic properties of the nanocomposites can be studied by examining how they influence the speed of the reaction process.

1. Introduction

Semiconducting oxides are used as catalysts during heterogenous photocatalysis (Wang, Tsai, & Hsieh, 1998), and the most commonly used of these oxides is the compound titanium dioxide (TiO_2) due to its low production cost and good chemical stability. Photocatalysts have many useful applications due to their abilities to influence reactions involving solar light, including uses in harvesting solar energy and helping to power space probes and satellites as a less expensive alternative to consumable fuel. However, applications of TiO_2 involving solar energy are limited due to its high band gap (3.2eV) and low quantum efficiency (Wang et al, 2016). Zinc oxide (ZnO) been suggested as a potential alternative to TiO_2, because although they have similar band gap energies, ZnO has a higher absorption efficiency across a large part of the solar spectrum (Qui et al, 2007).

Some properties of ZnO include a broad direct band gap width (3.37eV), a large excitation binding energy (60 meV), and a deep violet/borderline ultraviolet (UV) absorption at room temperature (Choi, Kang, & Oh, 2012), in addition to many desirable electrical, mechanical, and optical properties (Caglar, Ilican, Caglar, & Yakuphanoglu, 2009) that make it comparable to TiO_2. It has also been shown to have good photocatalytic activity (Al-Fori, Dobrestsov, Myint, & Dutta, 2014).

The photoactivity of a catalyst is determined by its ability to form photogenerated electron-hole pairs. In the photocatalysis process, when the catalyst is photo-induced by light that has a photonic energy equivalent to or greater than the excitation energy, electrons from the filled valence band move up to an empty conduction band and leave behind holes in the valance band. These electron-hole pairs can then be used in secondary oxidation-reduction reactions (Ong, Ng, & Mohammad, 2018).

The main problem with ZnO as a photocatalyst is the rapid recombination rate of the photogenerated electron-hole pairs, which disturbs the reaction process. An additional problem with using ZnO is that, like TiO_2, its solar energy conversion performance is affected by its optical absorption ability, which is related to its large band gap energy (Ong, Ng, & Mohammad, 2018). To increase the effectiveness of ZnO as a photocatalyst, a technique should be developed to extend its light absorption range or to slow the rate of the electron-hole recombination.

One potential solution to this problem would be to combine ZnO with a carbon-based material such as graphene. The interest in using a carbon-based material for this application is because of their unique pore structure, electronic properties, absorptive properties, and acidity. Graphene is favored over other carbon-based materials because it has an ideal sp^2 hybrid carbon nanostructure and surface area (Hosseini & Babaei, 2017). The conjugated structure of graphene allows for the separation of charges during the photocatalytic reaction process, so a combination of ZnO and graphene could potentially have a slower recombination rate than that of ZnO alone (Giem, 2009).

For this project, the photocatalytic properties of the ZnO/graphene nanocomposites were studied by examining their effect on the degradation of methylene blue (MB) dye, which breaks down when exposed to solar light. The objectives were to examine the photocatalytic properties of ZnO and graphene nanocomposites formed by ultrasonic homogenization, to compare these properties to those of ZnO or graphene alone, and to measure changes in the concentration of MB dye relative to the exposure time for UV irradiation in order to gain information about the degradation process of MB with the ZnO/graphene nanocomposites as photocatalysts.

Similar research on the photocatalytic properties of ZnO/graphene nanocomposites was done by A. R. Nanakkal and L. K. Alexander at the University of Calicut in India, where they studied the properties of nanocomposites fabricated using an electrochemical method (Nanakkal & Alexander, 2017). Other related studies include the research done by Gayathri et al on ZnO/graphene nanocomposites synthesized using a simple chemical precipitation method (Gayathri, Jayabel, Kottaisamy, & Ramakrishnan, 2014), and the research of Seyed A. Hosseini and Shabnam Babaei at Urmia University in Iran, on nanocomposites fabricated by ultrasonication using ethanol, methanol, and chloroform, precipitation, and freeze-drying (Hosseini & Babaei, 2017).

2. Materials and Methods

For this experiment, ZnO powder and graphene nanoplatelets were purchased from Alfa Aesar. The nanocomposites of ZnO/graphene were formed using two different methods: one type was created using ultrasonic homogenization and the other type was formed by chemically reacting the ZnO and graphene in a furnace. The nanocomposite formed using the second method was created by Dr. Dan Little from the University of Wisconsin – La Crosse's department of chemistry. This nanocomposite is a synthesized material made from graphene and zinc(II) oxalate with a 10:1 mole ratio of carbon to zinc. At high temperatures the zinc(II) oxalate decomposes into ZnO and CO_2 so this nanocomposite was created in an attempt to cause the ZnO to chemically insert itself into the structure of graphene, instead of just mixing them.

Separately, ZnO, graphene, and both types of nanocomposites of ZnO/graphene were mixed with

0.05g/L methylene blue dye (MB) and 50mL H_2O. Each of these dispersions were sonicated for 15 minutes at 15% power. They were then placed under a solar simulator for 1.5 hours, and a portion of each dispersion was removed every 15 minutes. These portions were centrifuged at 4000 rpm for 20 minutes to remove any excess particles and separate out the liquid, and then the liquid was analyzed in a UV-Vis Spectrometer in order to collect absorbance data. This data was plotted in SciDaVis to show the changes in MB concentration relative to exposure time, and to compare the differences between the photocatalytic abilities of the nanocomposites in each of the different dispersions.
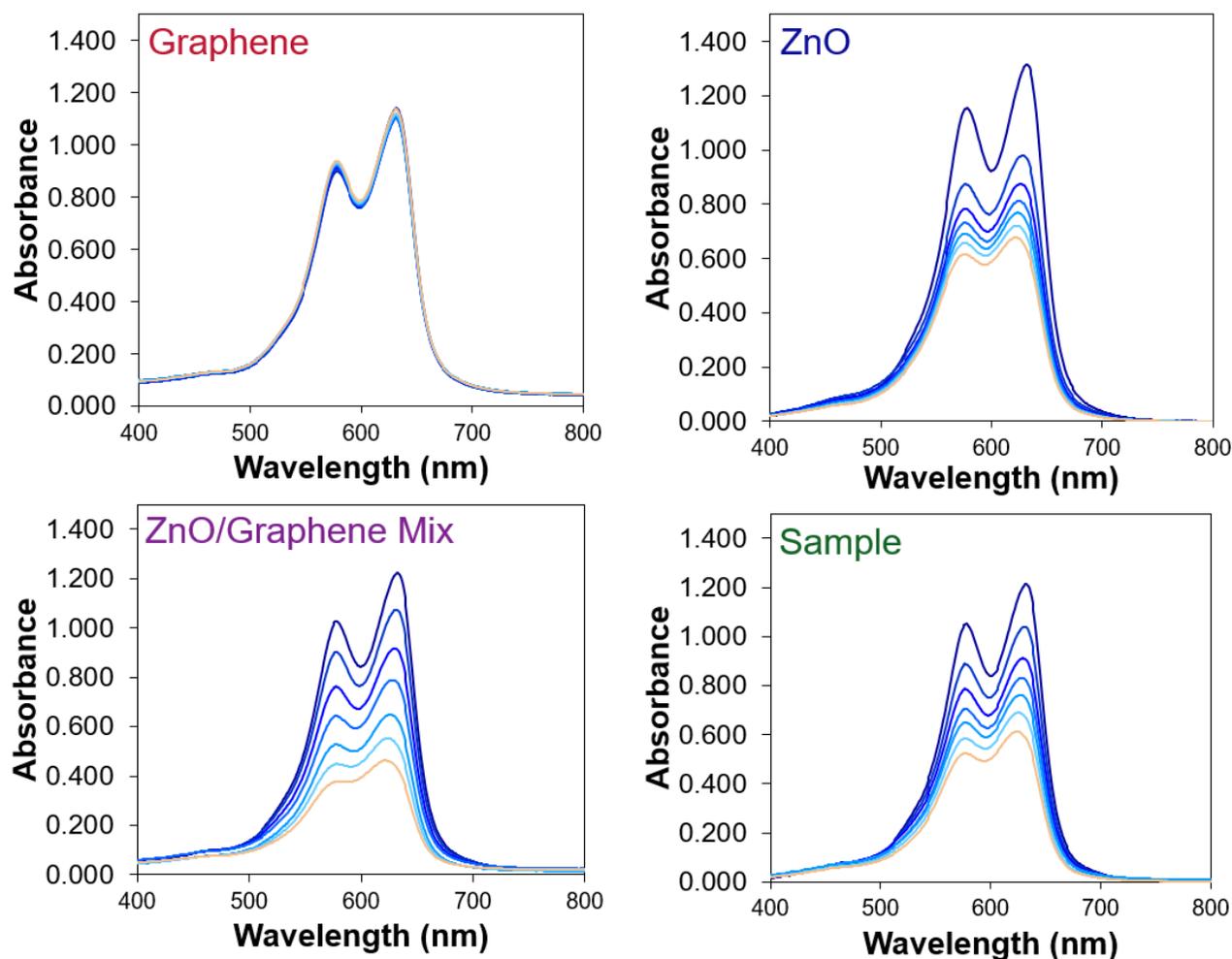
3. Key Results

Figure 1: The absorbance data collected during the dispersions' 1.5-hour exposure to the solar simulator

The top two graphs show how graphene and ZnO alone affected the degradation process for MB, using 0.0057 g/L graphene and 0.043g/L ZnO respectively. The bottom graphs show the nanocomposite formed by mixing the graphene and ZnO and then sonicating them together (left)

and a sample of the nanocomposite synthesized in the lab using a furnace (right). Both contain the same amounts of ZnO and graphene as used for the individual tests.
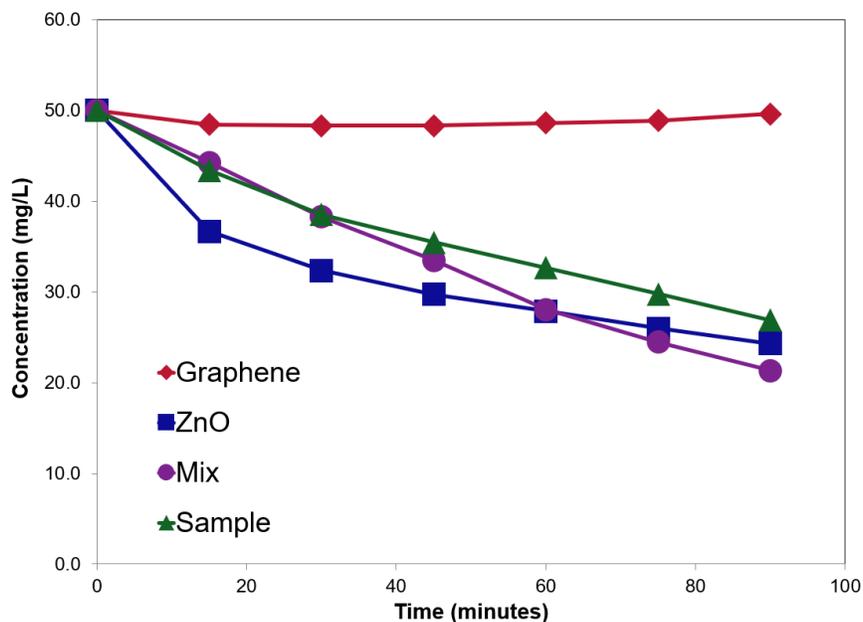

Figure 2: A comparison of the rates of change of the concentrations of MB dye during the 1.5-hour solar exposure, for each of the different materials used as photocatalysts

In order to better compare the different capabilities of each of the materials used as photocatalysts, the changes in the amount of MB over time were calculated for each material, and then plotted together to show how each material affected the degradation of MB during the exposure period.

4. Discussion

The different rates at which the MB degraded shows the different ways in which each of the materials used impacted the degradation process and demonstrates the potential of each material as a photocatalyst. As expected. Graphene alone does not have the potential to be an effective photocatalyst. ZnO, the nanocomposite formed by sonicating a mixture of ZnO/graphene, and a sample of the nanocomposite created in a furnace all degraded a similar amount of MB at the end of the 1.5-hour exposure period, as illustrated by Figure 2. However, an interesting thing to note about this is that even though these materials had degraded comparable amounts of MB by the end of the exposure period, each material had a different rate of change over the 1.5 hours. ZnO alone had a sharp initial decrease in the amount of MB, but then the rate of change became less steep after that. The mix and the sample both start with similar rates of changes, but then around the 30-minute mark the rate of the sample decreases while the rate of the mix stays the same. This helps to show how different methods of fabrication can affect the properties of the nanocomposite that is formed, and further study of the different methods of fabricating ZnO/graphene nanocomposites could help determine which fabrication method is best for making more efficient photocatalysts.

This connects to the other research mentioned earlier of other scientists studying the photocatalytic properties of their nanocomposites, which were created using a variety of methods including an electrochemical method and chemical precipitation.

5. Acknowledgements

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