THE PHILIPPINE-AMERICAN Academy of Science & Engineering

Synthesis and Photocatalytic Activity of Zinc Oxide Microflowers via Electrochemical Process and UV-VIS Analysis

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ABSTRACT

We synthesized zinc oxide (ZnO) microflowers via electrochemical deposition and examined their photocatalytic activity. ZnO microstructures were verified using X-Ray Diffractometry and Scanning Electron Microscope (SEM). In order to determine the photocatalytic properties of the microstructures, the degradation of Methylene blue exposed under ultraviolet (UV) light was studied. Our results showed that zinc oxide microflowers degraded about 86 % of the dye within 12 hours. Such materials have great potential for applications in environmental restoration and energy harvesting.

KEYWORDS: zinc oxide; electrochemical deposition; UV-Vis; photocatalysis

1 INTRODUCTION

Pollution has been a worldwide problem since it poses hazards to different life forms. Organic dyes, like methylene blue, are one of the causes of water pollution. Environmental restoration includes degrading such pollutants.

Nanosized particles of semiconductor materials have gained much interest in recent years due to their desirable properties and applications in different areas such as photocatalysis. In photocatalysis, degradation of dyes are enhanced once light strikes the semiconductor. Many studies focus on zinc oxide (ZnO), a II-VI semiconductor. It has a large band gap of 3.37 eV at room temperature which makes it suitable for the said application (Jiangfeng et al, 2010; Dai et al, 2013; Kumar et al, 2013; Venkatesha et al, 2012).

There are many ways to synthesize ZnO. These methods include spray pyrolysis, electrochemical deposition, and chemical vapor deposition. ZnO nanostructures can be synthesized into a variety of morphologies including nanowires, nanorods, tetrapods, nanobelts, nanoflowers.

Electrochemical deposition is highly favored in the synthesis of semiconductor materials. This method exhibits large-area, low-cost, and generally low-temperature and soft processing of materials. It only includes a probe to where the anode and cathode are to be attached and then immersed into a solution operated with low voltage (Venkatesha et al, 2012).

The goal of our work is to synthesize ZnO microflowers using electrochemical deposition and determine the effect of varying precursor solution molarities in the degradation of methylene blue.

2 METHODOLOGY

2.1 Synthesis of ZnO

A silver (Ag) plate was used as a cathode while a 2 cm by 3 cm zinc plate served as an anode. These plates were washed with distilled water and ethanol, then soaked into 1 M hydrochloric acid (HCl) to activate the ions. In the experimental setup, the anode and cathode were immersed into different molarities of sodium nitrate ($NaNO_3$) solution. Molarities used were 0.150 M, 0.175 M and 0.200 M. All solutions were magnetically stirred at 500 rpm with an operating voltage was 7 V for 30 minutes.
The products of the reaction as predicted by the chemical equation (Venkatesha et al, 2012) are

At the anode:

$$Zn \rightarrow Zn^{2+} + 2e^- \quad (1)$$

At the cathode:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (2)$$

In Solution:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow \quad (3)$$

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-} \quad (4)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^- \quad (5)$$

The resulting solution was filtered immediately after the electrochemical process to avoid dissolution. The precipitate includes the solid product ZnO. To obtain its pure form, the precipitate was oven dried at 100°C for 5 hours.

2.2 Characterization of synthesized ZnO

The composition of the synthesized material was characterized using an X-ray Diffraction (XRD) machine, Rigaku Smartlab X-ray Diffractometer with Cu-Kα radiation (λ= 1.54 Å). Their morphologies were studied using a Scanning Electron Microscope (SEM), JEOL JSM-6010 LV.
To test the photocatalytic activity of the sample, one hundred milligrams of each sample was mixed with 5 ml of methylene blue. Samples were exposed to UV light for 12 hours and the degradation of methylene blue was determined using the UV-Vis spectrophotometer. UV-Vis graphs were observed after every three hours of irradiation.

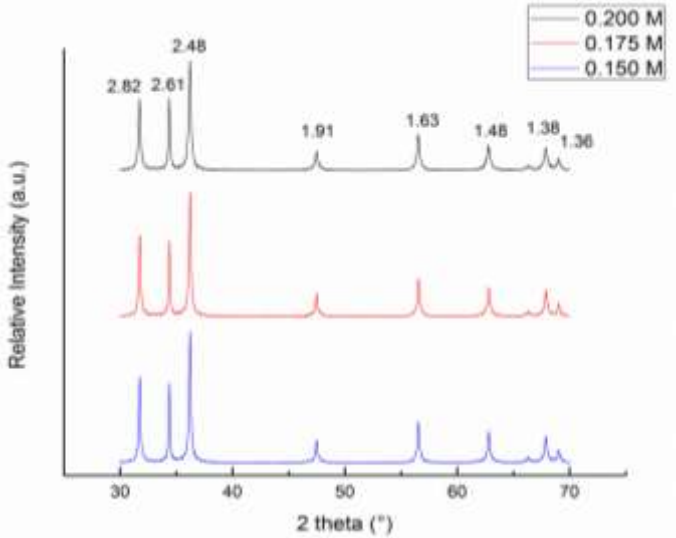

Figure 1: XRD pattern of produced ZnO for different molarities

3 RESULTS AND DISCUSSION

X-ray diffraction patterns for different molarities are shown in figure 1. The *d*-spacing of each peak (in Å) are indicated in the figure. The same magnitude of *d*-spacing for a specified peak was obtained for the different molarities. All values match a hexagonal-dihexagonal pyramidal zincite structure containing zinc and oxygen. This verifies that the synthesized sample is pure ZnO.

Figure 2 shows the synthesized ZnO structures observed under the SEM. All samples yielded ZnO microflowers but their sizes vary for every molarity. The 0.150 M samples showed the longest petal length while the 0.200 M sample showed the shortest. SEM measurements also reveal that the microflower size depends inversely to the molar concentration.

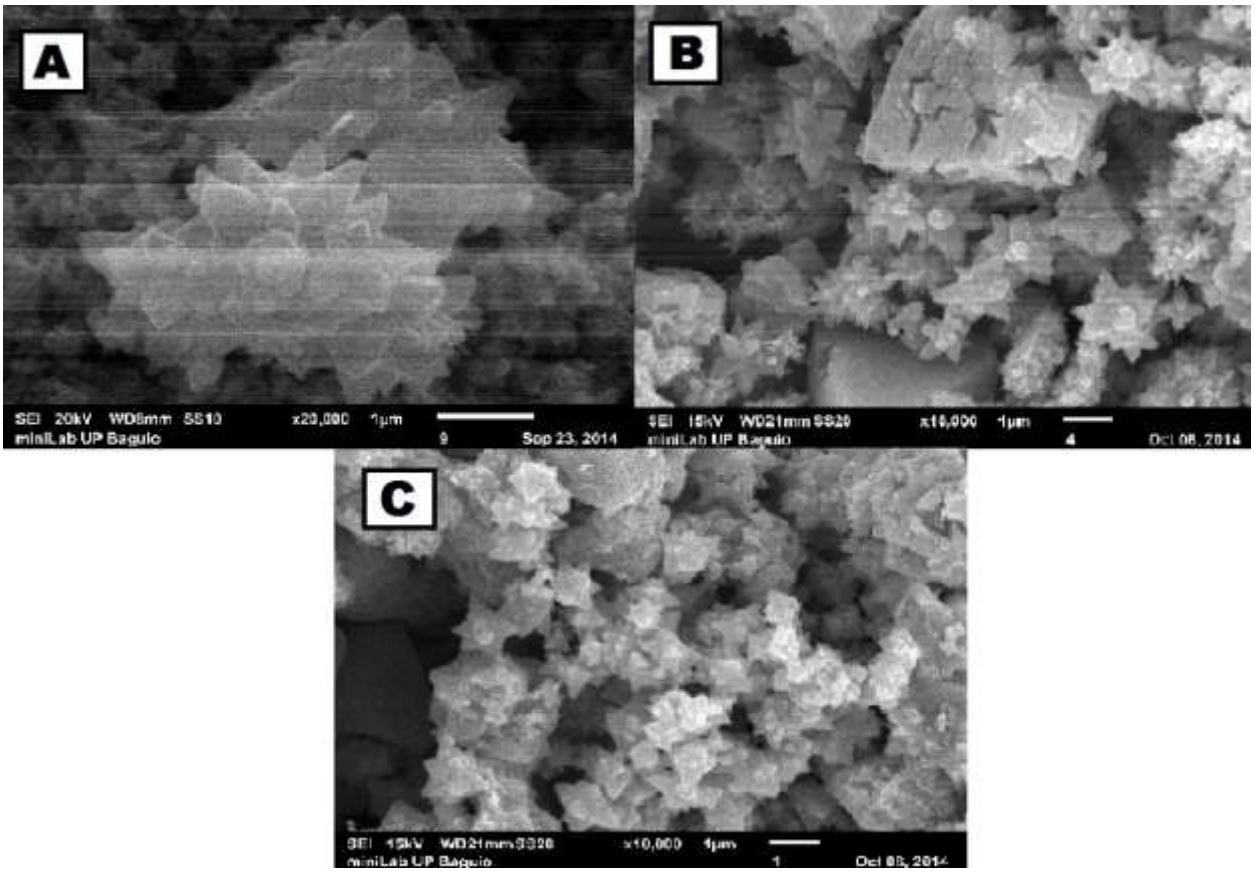

Figure 2: SEM images of ZnO on Silicon substrate using different molarities: (A) 0.150 M,(B) 0.175 M,(C) 0.200 M

Results of the UV-Vis measurements are shown in figure 3. A high rate of degradation implies high photocatalytic characteristic of the semiconductor material. Figure 4 shows the extent of degradation (A/Ao) of methlyene blue at λ=667 nm as a function of irradiation time. A is the variable absorbance while Ao is the initial absorbance of the sample. It was observed that ZnO at 0.200 M degraded methylene blue the most followed by 0.175 M and 0.150 M with the least amount of degradation.

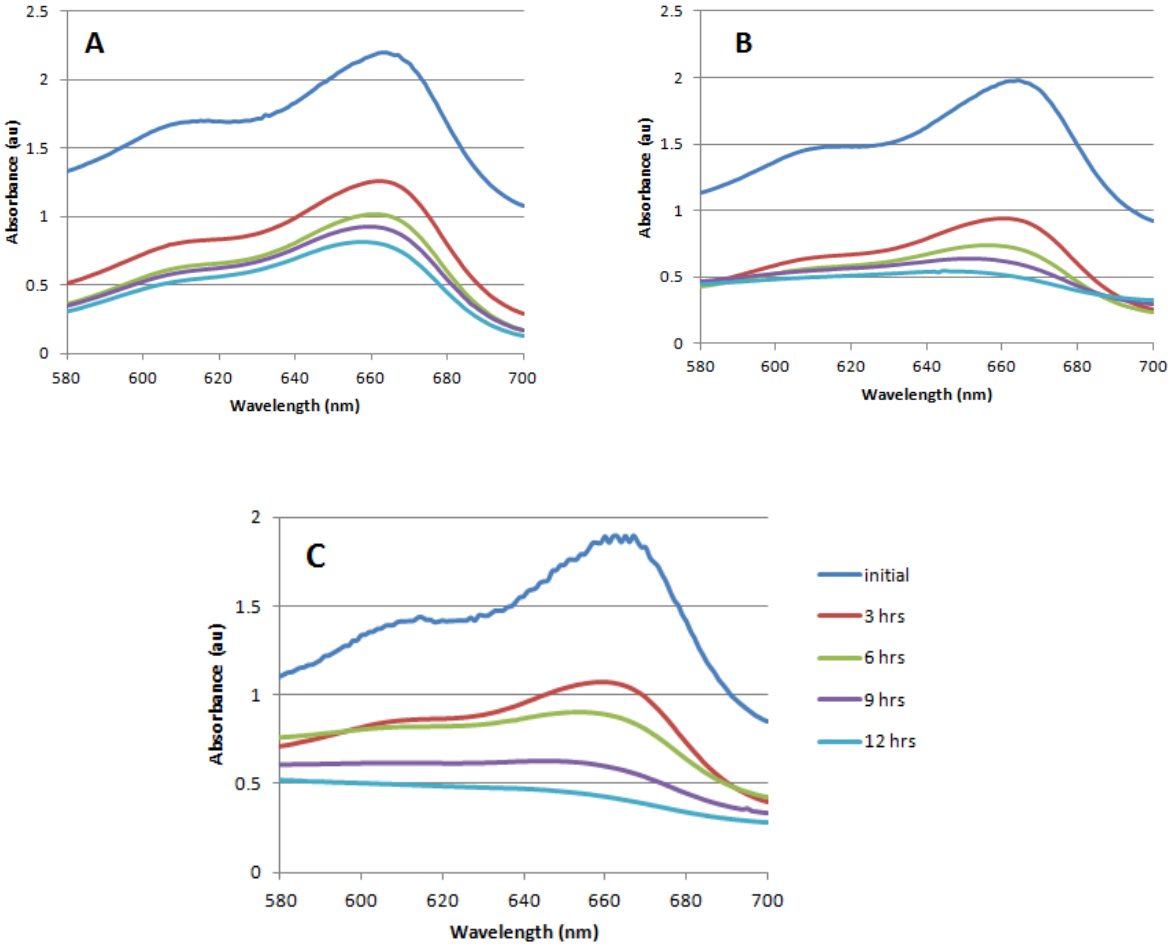

Figure 3: Absorbance for varying UV exposure time for different precursor molarities: (A) 0.150 M, (B) 0.175 M. (C) 0.200 M

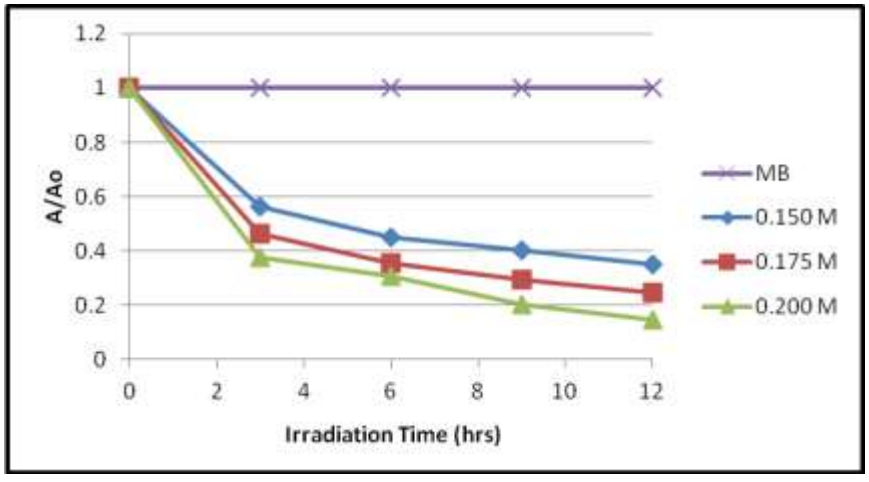

Figure 4: Extent of degradation of Methylene Blue (A/Ao) as a function of irradiation time

For quantitative analysis, the remaining dye concentration was computed using the formula

$$Remaining\ dye\ concentration = \frac{A}{A_0}\, x\, 100\% \quad (6)$$

Table 1 shows the computed values for remaining dye concentration after 12 hours of irradiation. The sample using the least molarity also degraded the least amount of dye molecules.
ZnO particles with larger surface area to volume ratio have greater levels of reactivity (Yadao, 2014). The particle size and surface area to volume ratio are inversely related. This is the reason why the 0.200 M sample, the sample with the shortest petal length, degraded most of the methylene blue.

Table 1 Remaining dye concentration after 12 hours of irradiation for different Molarities

Sample	Remaining dye concentration (%)
0.150 M	34.91
0.175 M	24.62
0.200 M	14.52

4 CONCLUSION

ZnO microflowers were successfully synthesized using electrochemical process. Varying the molarities of the precursor solution affects the morphology of the samples. The 0.200 M sample, which has the smallest petal length, degraded almost 86% of the dye. All samples denote a great potential for environmental restoration and energy harvesting since all of them degraded more than 50% of the dye.

5 ACKNOWLEDGEMENTS

We would like to thank Mr. Richard Dean Yadao, and Mr. Jasper Madalipay for the pointers and extra supervision.

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