Electrochemical synthesis and photocatalytic properties of ZnO microflakes

Climson Ford B. Inso[*1], Ian Jasper A. Agulo[1] and Yoshitaka Matsushita[2]

[1]Micro and Nano Innovations Laboratory (miniLab)
Department of Physical Sciences, College of Science,
University of the Philippines Baguio, Governor Pack Road, Baguio City 2600, Philippines
[2]Chemical Analysis & X-Ray Diffraction, Materials Analysis Station, National Institute for
Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047 JAPAN

[*]E-mail: ford.physics@yahoo.com

ABSTRACT

Zinc oxide was synthesized using electrochemical deposition technique. An aqueous solution of sodium sulfate was electrolyzed using zinc metals as electrodes, under a constant power source of 4V. Scanning Electron Microscope showed that the synthesized samples were ZnO microflakes. Smaller microstructures were formed at larger precursor molarities. The photocatalytic properties of the synthesized products were tested using methylene blue under UV light irradiation. Approximately 88 % percent of the organic compound was degraded, which suggests the as – synthesized zinc oxide microflakes have comparable potential with ZnO microflowers in photocatalysis.

KEYWORDS: zinc oxide; electrochemical deposition; photocatalysis; microflakes

1   INTRODUCTION

Zinc oxide is a semiconductor which has numerous applications on various fields. In general, the applications depend on the morphology of the ZnO. For example, thin films and nanowires were proven to be suitable for solar cells applications (Zhu et al., 2014, Rani et al., 2014), while nanocones are better emitters, and in gas sensing applications (Rouhi et al., 2014, Hussain et al., 2014). The thicker nanorods are suitable for semiconductor electronics (Nam et al., 2014), while thin ZnO films can be used as antibacterial agents (Cuevas et al., 2013). Other structures such as microflowers, nanoarrows, nanospheres, and nanosheets are potent in photocatalytic applications (Venkatesha et al., 2012, Yadao, 2014, Murugan et al., 2014, Le et al., 2014, Xie et al., 2011).

Zinc oxide can be synthesized using various methods among which include electrochemical deposition (ECD) technique. ECD is a low – cost method of synthesis that has high growth rates (Hang et al., 2010) and can actually be performed at room temperature. It is a two – electrode system wherein the mechanism is typically based on the reduction of a precursor such as nitrate (Venkatesha et al., 2012, Yadao, 2014). This reaction gives off ions into the electrolyte solution, which will later participate in the formation of the desired compound. Different methods can be used to synthesize ZnO however, the authors chose to use ECD technique because of its numerous advantages.

Recent studies show that electrochemically synthesized ZnO using sodium nitrate as precursor, and different electrodes in the set – up, have been able to produce ZnO microflowers (Venkatesha et al., 2012, Yadao, 2014). These ZnO microflowers were proven to be an effective photocatalyst in the degradation of organic compounds such as methylene blue (Yadao, 2014). Very few articles have been reported about

the ECD synthesis of ZnO microflakes and its photocatalytic properties. This paper however, reports the photocatalytic property of electrochemically – synthesized zinc oxide wherein two electrodes of the same material were used and sodium sulfate was used as precursor. ZnO microflakes were produced. Methylene blue was used as the model for degradation. Ultraviolet – Visible Spectroscopy was used to confirm its photocatalytic characteristics. Scanning electron microscope was used to describe the structural morphologies of the synthesized ZnO samples while the crystalline structure was characterized by x-ray diffraction (Rigaku SmartLab 9 kW).
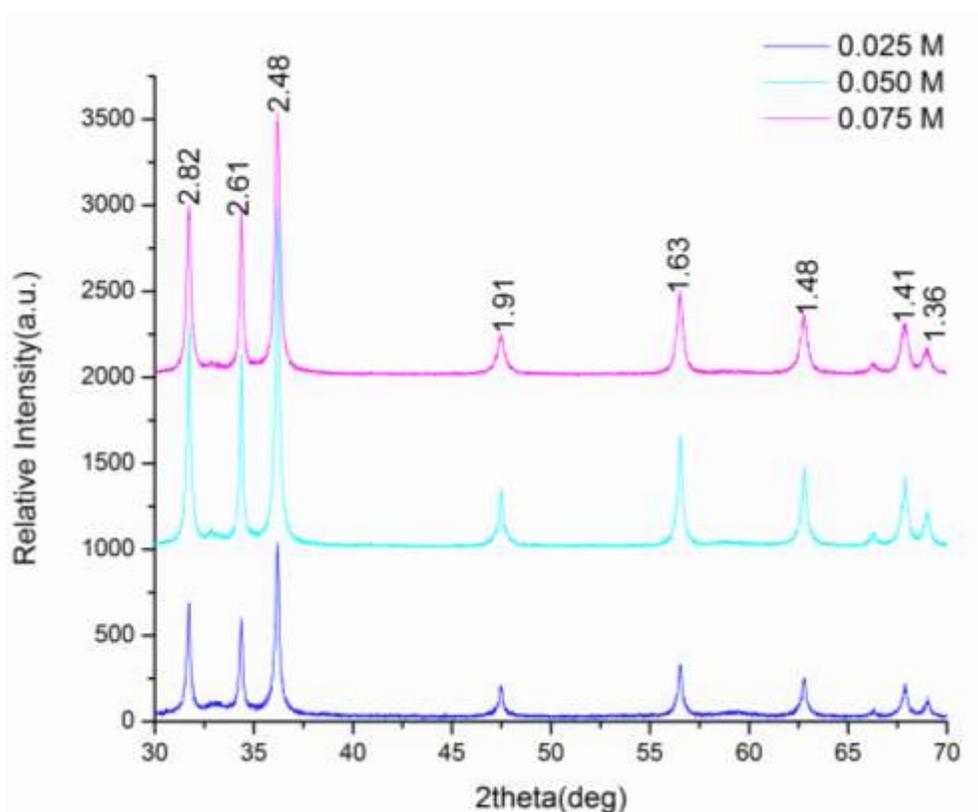

Figure 1: XRD pattern for samples prepared at different precursor molarities with their corresponding *d*-spacing

2   EXPERIMENTAL PROCEDURE

The electrochemical deposition set – up involves a two – electrode system wherein two zinc metals (2 cm by 3 cm) obtained from a commercially available battery served as the electrodes. In a typical ECD process, the anode and the cathode used are of different materials. The microstructures formed in those cases were microflowers (Venkatesha et al., 2012, Yadao, 2014). This work is unique since the same type of material served as electrodes and ZnO microflakes were produced.

The surfaces of both electrodes were washed with distilled water and ethanol. Immersing them in 0.1 M of HCl activated their ions. These electrodes were placed approximately 1.6 cm apart. Deionized water was used in preparing different concentrations (0.025 M – 0.075 M) of Na_2SO_4, which were magnetically stirred at about 500 rpm for 30 minutes under a constant 4V power source. The precipitates were then filtered and dried at an average temperature of 87°C ± 11°C for at least 5 hours.

One hundred milligrams of the synthesized ZnO samples were added in a 5 ml 20 micro molar solution of methylene blue ($C_{16}H_{18}N_3SCl$). The solutions were irradiated for 12 hours under a UV light source. Using a UV – VIS spectrometer, their absorbance was measured every 3 hours.

3   RESULTS AND DISCUSSION

The electrochemical synthesis of ZnO is governed by a series of chemical reactions occurring on the electrodes as well as in the electrolyte solution. The anode gives off Zn^{2+} ions into the solution. At the surface of the cathode, the SO_4^{2-} ions undergo reduction producing OH^- ions. Both Zn^{2+} ions and OH^- ions combine to form $Zn(OH)_2$. As the reaction goes on more Zn^{2+} ions and OH^- ions are accumulated, creating $Zn(OH)_4^{2-}$. Finally, the decomposition of $Zn(OH)_4^{2-}$ gives off ZnO as a byproduct.

Figure 1 shows the XRD spectra of the as – synthesized materials. XRD patterns of the products synthesized at different precursor molarities match well with the characteristic peaks of ZnO (JCPDS No. 36 – 1451). The major peaks at 2θ values of 31.7°, 34.4°, 36.2°, 47.5°, 56.5°, 62.8°, 66.3°, 67.9°, and 69.0° can be indexed as *100*, *002*, *101*, *102*, *110*, *103*, *200*, *112*, and *201*, respectively. The *d*-spacing measured primarily at 2θ values of 31.7°, 34.4°, 36.2° were 2.82 Å, 2.61 Å and 2.48 Å, respectively. This suggests that the synthesized products were of wurtzite structure. It was also observed that varying the precursor molarity shows no significant change in the purity of the samples as well as in their crystalline structure.
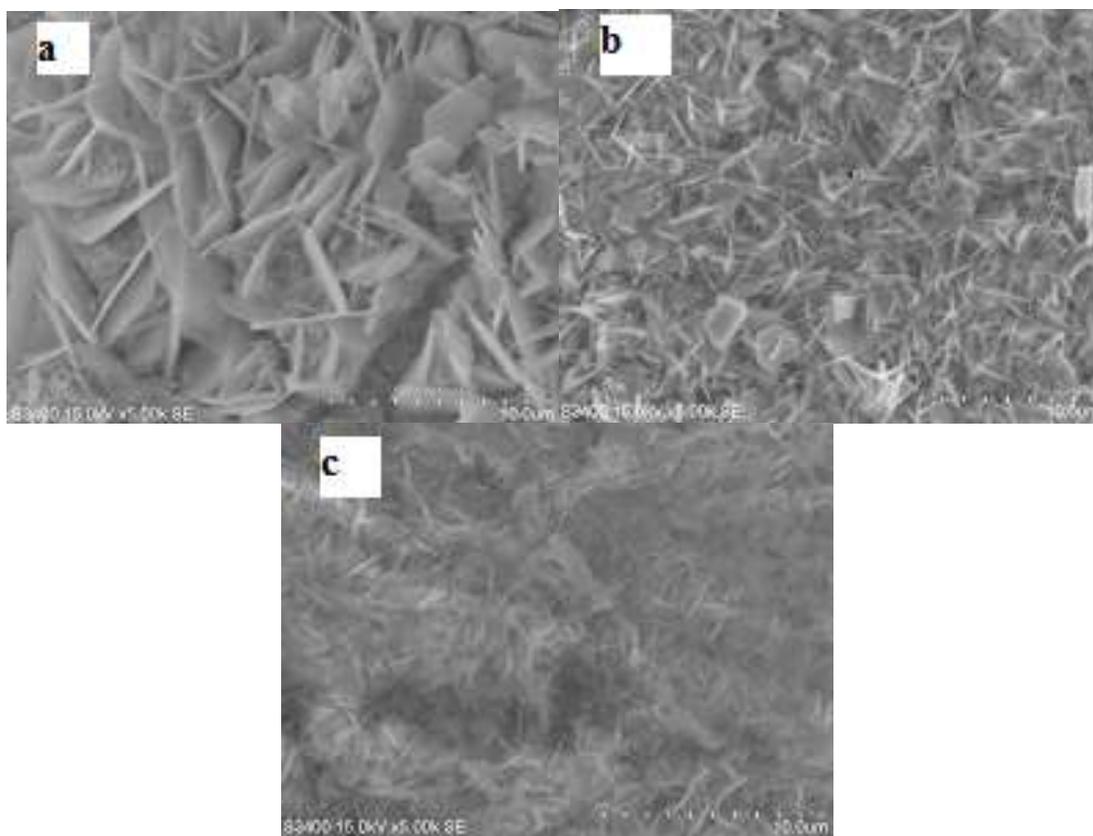

Figure 2: SEM images of ZnO samples magnified 5000 times and synthesized using different precursor molarties a) 0.025 M b) 0.050 M c) 0.075M.

Figure 2 shows the SEM images of the samples. All of the images obtained were described as ZnO microflakes. All of the images obtained exhibit similar kind of morphology, but with varying microstructure sizes. Results suggest that increasing the precursor molarity decreases the size of the microstructures formed. Figure 3 shows the plot for degradation of methylene blue (MB) as a function of irradiation time. The remaining MB concentration was calculated using the following equation:

$$MB\ concentration = \frac{A}{A_0} \qquad\qquad (1)$$

where A_0 is the initial maximum absorbance at $\lambda = 664$ nm, and A is the maximum absorbance measured every three hours. The overall shift for 12 hours of UV irradiation in which the maximum absorbance occurred was about one nanometer. It can be seen from figure 3 that microflakes synthesized at higher precursor molarities degraded greater amounts of MB. Synthesized ZnO using 0.050 M and 0.075 M degraded almost 88 percent of the MB solution while the one synthesized at 0.025 M only degraded 71 percent of the solution. This is consistent with the SEM images. Smaller particles (which are synthesized at 0.050 M and 0.075 M) generally have greater surface area – to volume ratios. This explains why the smaller microflakes showed faster degradation rates. Larger surface areas can accommodate more molecules, which leads to a faster decomposition rate. Hence, smaller ZnO microflakes have better efficiency in MB degradation. ZnO microflowers in Yadao's work (2014) only degraded 84 percent. Based on these facts, ZnO microflakes are arguably larger compared ZnO microflowers. Further analysis of its surface area in comparison with that of the microflower is needed in order to understand why the degradation is faster for such microflakes.
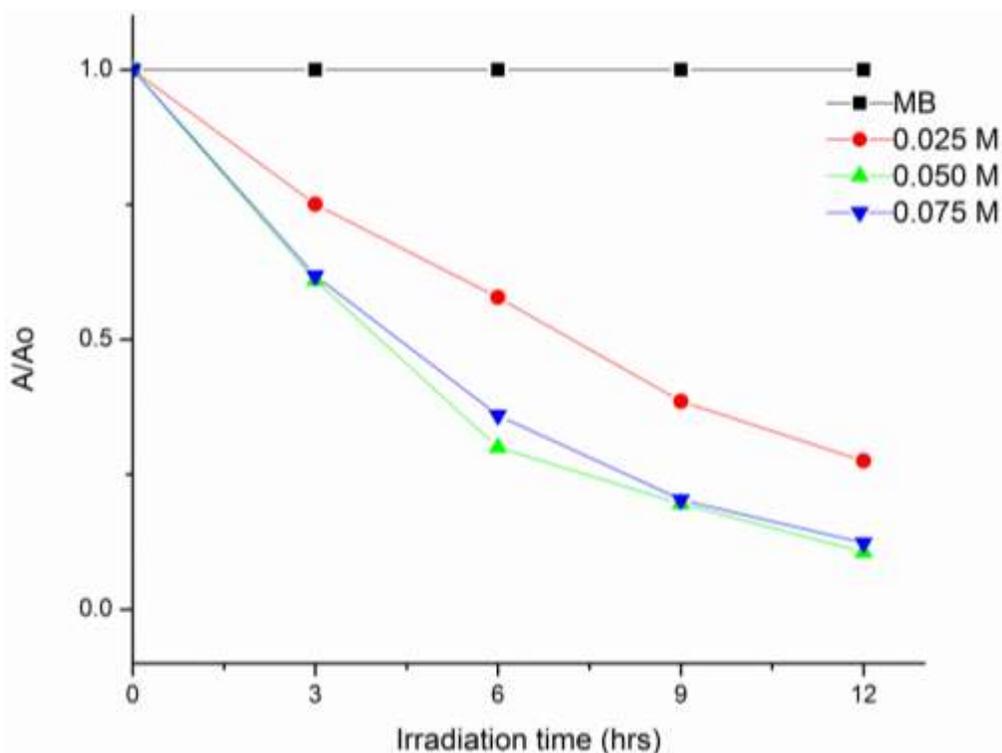

Figure 3: Extent of photocatalytic degradation of methylene blue vs. irradiation time

4   CONCLUSION

Zinc oxide microflakes were successfully synthesized via electrochemical deposition technique. Results indicate that ZnO microflakes are potential photocatalysts and are arguably better compared to ZnO microflowers. The sizes and morphology of the ZnO samples can be controlled by varying the precursor molarity Na_2SO_4. All of the samples displayed significant results but smaller microflakes had faster rates of degradation. Further analysis of its surface area in comparison with that of the microflower is needed in order to understand why the degradation is faster for such microflakes.

5   ACKNOWLEDGEMENTS

REFERENCES

Y.F. Zhu, D.H. Fan, Y.W. Dong, G.H. Zhou. (2014) "Morphology – controllable ZnO structures: Ethanol assisted synthesis, growth mechanism and solar cell applications", *Supperlattices and Microstructures* 74, pp 261 – 272.

A. Amala Rani, Suhashini Ernest. (2014) "Structural, morphological, optical and compositional characterization of spray deposited Ga doped ZnO thin film for Dye-Sensitized Solar Cell application", *Supperlattices and Microstructures* 75, pp 398 – 408.

J. Rouhi, M. Alimanesh, R. Dalvand, C.H.R. Ooi, S. Mahmud, M.R. Mahmood. (2014) "Optical properties of well-aligned ZnO nanostructure arrays synthesized by anelectric field-assisted aqueous solution method", *Ceramics International* 40, pp 11193 – 11198.

S. Hussain, T. Liu, M. Kashif, S. Cao, W. Zeng, S. Xu, K. Naseer, U. Hashim. (2014) "A simple preparation of ZnO nanocones and exposure to formaldehyde", *Materials Letters* 128, pp 35 – 38.

G.H. Nam, S.H. Baek, I.K. Park. (2014) "Growth of ZnO nanorods on graphite substrate and its application for Schottky diode", *Journal of Alloys and Compounds* 613, pp 37 – 41.

A.G. Cuevas, K. Balangcod, T. Balangcod, A. Jasmin. (2013) "Surface morphology, optical properties and antibacterial activity of zinc oxide films synthesized via spray pyrolysis", *Procedia Engineering* 68, pp 537 – 543.

T.G. Venkatesha, Y.A. Nayaka, R.Viswanatha, C.C. Vidyasagar, B.K. Chethana. (2012) "Electrochemical synthesis and photocatalytic behavior of flower shaped ZnO microstructures", *Powder Technology* 225, pp 232 – 238.

R.D. Yadao. (2014) Electrochemical Synthesis of Zinc Oxide Microflowers and its Photocatalytic Activity", Undergraduate Thesis in B.S. Physics, March2014, Department of Physical Sciences, College of Science, University of the Philippines Baguio.

R. Murugan, T. Woods, P. Fleming, D. Sullivan, S. Ramakrishna, P.R. Babu. (2014) "Synthesis and photocatalytic application of ZnO nanoarrows", *Materials Letters* 128, pp 404 – 407.

T.H. Le, A.T. Bui, T.K. Le. (2014) "The effect of Fe doping on the suppression of photocatalytic activity of ZnO nanopowder for the application in sunscreens", *Powder Technology* 268, pp 173 – 176.

J. Xie, H. Wang, M. Duan, L. Zhang. (2011) "Synthesis and photocatalysis properties of ZnO structures with different morphologies via hydrothermal method", *Applied Surface Science* 257, pp 6358 – 6363.

H.Y. Hang, S.H. Lee, T.W. Kim. (2014) "Effect of zinc nitrate concentration on the structural and the optical properties of ZnO nanostructures", *Applied Surface Science 256*, pp 6117 – 6120.