The Effect of CTAB addition in ZnO Nanorods Optical Properties

A H Ramelan\(^1\), S Wahyuningsih\(^1\), FN Aini\(^1\), L N M Z Saputri\(^1\)

\(^1\) Inorganic Materials Research Group, Universitas Sebelas Maret, Indonesia
Email : aramelan@mipa.uns.ac.id

Abstract
ZnO nanorods have been successfully synthesized using precursor of zinc nitrate tetrahydrate and \textit{cetyltrimethylammonium bromide} (CTAB) as the surfactant. The composition adopted is specified by the ratio of Zn(NO\(_3\))\(_2\)·4H\(_2\)O:CTAB = 1:0, 1:1, 1:2, and 1:3 (w/w) using hydrothermal method at temperature of 180 °C for 24 hours. The resulted ZnO nanorods were characterized by X-Ray Diffraction (XRD), Transmission electron microscopy (TEM) and UV-Vis Spectrophotometer. The presence of CTAB addition was found to increase the crystal size. The TEM characterization results showed the formation of homogeneous rods in nano scale. Modified ZnO nanorods improved optical properties, attaining a band gap energy of ~2.9 eV. The transmittance increases and the reflectance decreases with increasing CTAB.

1. Introduction
ZnO material is a semiconductor material that has high transmittance and reflection\(^[1]\) that was developed as Anti-Reflection Coating (ARC) material. The developed one-dimensional nanostructures such as nanorod improved optical, electronic to that bulk structured materials. The properties of zinc oxide are strongly depend on its structure, including the morphology, aspect ratio, size, orientation and density of crystal. Moreover, these structural characteristics play an important role in many applications. Therefore, development of a shape controlled zinc oxide synthesis method is indispensable for exploring the potential of this material as a smart and functional material\(^[2]\). Though many methods have been proposed to synthesize 1D structure. Recently, large-scale and low-cost synthesis of ZnO nanomaterials with 1-D structure, such as nanorods, have been achieved using a hydrothermal method\(^[3,4]\). This brings a good chance to study its optical properties.

CTAB is a cationic surfactant. When CTAB was dissolved in water or ethanol, it will be ionized into CTA\(^+\) and Br\(^-\). ZnO, as a polar crystal, has a polar axis and possesses a positive face and a negative face on the crystal due to the asymmetrical distribution of Zn and O atoms along its polar axis, and the positive face (0 0 0 1) was occupied by Zn atoms while the negative face (0 0 0 1) was distributed by O atoms. So CTA\(^+\) and Br\(^-\) will affect the crystal size and morphology of ZnO by electrostatic attraction\(^[5]\), where crystal size dan morphology will affect in ZnO optical properties. In this paper, the effects of CTAB on the crystal size and morphologies of hydrothermal synthesis of ZnO nanorods were investigated.
2. Materials And Sample Preparation

2.1 Materials
Zinc nitrate tetrahydrate (Zn(NO$_3$)$_2$.4H$_2$O) Aldrich) and ammonium hydroxide (NH$_4$OH, Aldrich), deionized water were used as the starting materials. N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB) was used as the surfactant.

2.2 Synthesis of ZnO nanorods
ZnO nanorods were synthesized by hydrothermal method. 0.1M Zn(NO$_3$)$_2$.4H$_2$O was dissolved in 100 mL of deionized water and stirred magnetically for about an hour at room temperature. Ammonium hydroxide was added into solution until pH of the solution was maintained as 7, followed by vigorous stirring for an hour. A white precipitate (Zn(OH)$_2$ was produced which was collected by centrifugation and washed thoroughly with deionized water. Then the precipitate was transferred into 100 mL water containing CTAB. The stoichiometric ratio of Zn(NO$_3$)$_2$.4H$_2$O and CTAB was taken as 1:0; 1:1; 1:2; and 1:3 (w/w). The solution was transferred into a Teflon-line coated and then heated in a electrical oven at a constant temperature of 180 °C for 24 h. After completion of the reaction, it was cooled to room temperature and powder sample was collected by centrifugation. Powder sample was thoroughly washed with deionized water and ethanol. Finally, sample was dried at 80 °C for 12 h.

2.3 Sample Characterization
The crystal structure of the powder was studied by powder X-ray diffractometer using monochromatic nickel filtered CuKα (λ=1.5416 Å) radiation. The particles morphology was investigated by transmission electron microscopy (TEM-JEM-2010, JEOL). The optical absorption spectrum of the sample was taken in the range between 200-800 nm using double beam UV-Vis spectrophotometer.

3. Results And Discussion
During hydrothermal process following chemical reactions may have been involved [6].

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \]........................................................................................................(1)

\[ \text{Zn(OH)}_2 \leftrightarrow \text{ZnO} + \text{H}_2\text{O} \]..........................................................................................................(2)

\[ \text{Zn(OH)}_2 + 2\text{OH}^- \leftrightarrow [\text{Zn(OH)}_4]^{2-} \].............................................................................................(3)

\[ \text{CTAB} \leftrightarrow \text{CTA}^+ + \text{Br}^- \]...............................................................................................................(4)

\[ [\text{Zn(OH)}_4]^{2-} + \text{CTA}^+ \leftrightarrow \text{CTA}^+ + [\text{Zn(OH)}_4]^{2-} \]............................................................................(5)

\[ \text{CTA}^+ - [\text{Zn(OH)}_4]^{2-} \leftrightarrow \text{ZnO} + \text{H}_2\text{O} + \text{CTA}^+ \]...........................................................................(6)

Sun et al [4] has suggested that CTAB not only accelerate the reaction of the growth units but also leads to their oriented growth due to the presence of CTAB reduce the surface tension of the solution which is decreasing the endothermic energy to form a new phase.

The diffractogram of ZnO nanorods shown in Figure 1, the XRD peak position shows that ZnO hexagonal wurzite with lattice constants a = 3.253Å and c = 5.215Å corresponding to the ICSD (No. 67848). Dominant peak is present at 2θ = 36.52° (101). The increasing of CTAB addition performed sharp and clear peaks indicating the formation of materials with high crystallinity and intensity that indicated the addition of CTAB enhanced the alignment of nanorods [7].
Figure 1. ZnO diffractogram pattern with variations of addition CTAB surfactant (a) ICSD Standard No.67848; (b) ZnO without addition of surfactant; (c) 1:1 surfactant addition; (d) 1:2 surfactant addition; (e) 1:3 surfactant addition

Crystallite size for ZnO nanorods was calculated using Debye-Scherer formula given in Eq. 1 [8]. Increased calcination temperature has an impact on increasing crystallite size.

$$D = \frac{k\lambda}{B \cos \theta}$$  \hspace{1cm} (1)

Where B is full width at half maximum (FWHM), k is constant of proportionality, λ is the X-ray wavelength and θ is the Bragg’s diffraction angle. Crystal size of ZnO material shown in Table 1.

Table 1. Average crystal size of ZnO nanorods

| Precursor Zn(NO$_3$)$_2$·4H$_2$O:CTAB (w/w) | B (deg) | 2θ (deg) | Cos θ | D (nm) |
|-------------------------------------------|--------|----------|-------|--------|
| 1:0                                       | 0,355  | 36,610   | 0,949 | 23,632 |
| 1:1                                       | 0,278  | 36,012   | 0,951 | 30,061 |
| 1:2                                       | 0,272  | 35,970   | 0,951 | 30,755 |
| 1:3                                       | 0,236  | 36,010   | 0,951 | 35,387 |

The more CTAB added, the larger crystal size was formed. This is because the more CTAB that added would encourage the nanorods materials formation. TEM imaging results of ZnO nanorods are shown in Fig. 2, indicating that rods have been formed with a tapered end or cone.
The optical studies are performed to evaluate the potentially useful optical quality of the nanorods. UV-Vis absorption spectrum of the ZnO nanorods prepared under hydrothermal conditions is shown in Fig. 3. ZnO nanorods absorption peak ranges from 310-330 nm that indicated the material properties was transparent. This properties has advantages such as the optical properties will be increased due to a lot of light was absorbed. The band gap of ZnO nanorods in rasio 1:3 (w/w) is about ~2.9 eV. The increasing crystal size results in less bandgap energy due to quantum confinement effect phenomenon in nanomaterials [9]. This decreasing of bandgap energy becomes an indication of the increase in crystallinity caused by the gathering of ZnO nuclei to form a cluster and eventually become a solid and regular crystallite grain of larger size [10].

There is a increase of % T of ZnO nanorods material with increasing of CTAB due to the increasing number of CTAB that caused ZnO nanorods was distributed evenly to increase optical scattering (Figure 4).
Figure 4. Transmittance spectra of the samples with CTAB additions of (a) 1:0; (b) 1:1; (c) 1:2; (d) 1:3 (w/w)

There is a decrease in% R of material ZnO with increasing of CTAB due to the increasing number of CTAB that caused ZnO nanorods was distributed evenly to increase optical scattering (Figure 5).

Figure 5. Reflectance spectra of the samples with CTAB additions of (a) 1:0; (b) 1:1; (c) 1:2; (d) 1:3 (w/w)

Relatively larger crystal size tends to decrease the reflectance. This is due to the larger absorption of photons following the Lambert-Beer's law. Smaller size, has shorter photon's internal path and hence more effective surface reflection [11].

4. Conclusion
ZnO nanorods was synthesized by a cost-effective hydrothermal route with addition of CTAB surfactant. The diffraction peak (101) was found stronger and narrower than the other peaks, which indicates a preferential orientation along the c-axis. The addition of CTAB caused increasing crystal
size that leads to nanorods. Absorbance of ZnO nanorods material indicated that the material absorbs in the UV region. The large crystal size caused a decrease in reflectance, so ZnO nanorod can applied as an anti-reflection (ARC).

Acknowledgments
The authors would like to acknowledge the International Research Collaboration and Scientific Publications Program, Ministry of Research, Technology and Higher Education, Republic of Indonesia, for supporting this research and to the Integrated Mathematics and Natural Science Laboratory of Sebelas Maret University for supporting and providing the facilities for this research.

References
[1] M.H. Aslan, A.Y. Oral, E. Menşur, A.Giil and E.Başaran. 2004. *Sol. Energy Mater Sol. Cells.* **82**(4) 543-552
[2] S. Cho, S-H Jung and K-H. Lee 2008 *J. Phys. Chem.* **112** 12769-12776
[3] N. Yamazoe, G. Sakai, K. Shimanoe 2003 *Catal. Surveys Asia* **1** 63–75
[4] X.M. Sun, X. Chen, Z.X. Deng, Y.D. Li, A 2002 *Mater. Chem. Phys.* **78** 99–104
[5] Y-X. Wang, J. Sun, X. Y. Fan and X. Yu 2011 *Ceram. Int.* **37** 3431-3436
[6] S.D. Shinde, G.E.Patil, D.D.Kajale, D.V.Ahire, V.B.Gaikward and G.H. Jain. 2012 *Int. J. Smart Sensing Intell. Sys.* **5**(1) 57-70
[7] U.N.Maiti, S.Nandy, S.Karan, B. Malik and K.K.Chattopadhyay 2005 *Appl. Surf. Sci.* **254**, 7266-7271(2005).
[8] A. Gupta, H.S. Bhatti, D. Kumar, N.K.Vema, and R.P.Tandon 2006 *Digest Int. J. Nanomat Biostruct* **1** 1-9
[9] G.Pellegrini, G.Mattei and P.Mazzoldi 2005 *J. Appl. Phys.* **97**(7) 6-8
[10] A.HYuwono, B.Liu, J.Xue, J.Wang, H.I.Elim, W.Ji and T.J.White 2004 *J. Mat. Chem.* **14**(20) 2978-2987
[11] B. T. Jheng, P.T Liu, M.C.Wang and M.C.Wu 2013 *Appl. Phys. Lett.* **103**(5) 052904