Structural-characterization-of-hydrothermally-synthesized-MnO-nanorods

by Agus Subagio

Submission date: 12-Nov-2019 07:21PM (UTC+0700)
Submission ID: 1212186731
File name: hesized-MnO-nanorods2017Journal-of-Physics-Conference-Series.pdf (1.37M)
Word count: 1868
Character count: 9575

Structural characterization of hydrothermally synthesized MnO_2 nanorods

Structural characterization of hydrothermally synthesized MnO_2 nanorods

D Q A'yuni[1], I Alkian[1], F K Sya'diyah[1], Kadarisman[1], A Darari[1], V Gunawan[1] and A Subagio[1]

[1]Department of Physics, Faculty of Science and Mathematics, Diponegoro University Jl. Prof. Soedarto, Tembalang, Semarang City, 50275, Indonesia

E-mail: dewiqurrota@st.fisika.undip.ac.id

Abstract. We prepared the hydrothermal method to synthesize MnO_2 nanorods with controlled structure. $KMnO_4$ and HCl with the various molar ratio (1:2,1:6,1:8) reacted at 160°C for three hours to form MnO_2 nanorods. The study found that changing the molar ratio can control the structure and morphology of MnO_2. The result revealed that MnO_2 formed in nanorod microstructures with different crystallographic structure and phase composition of each molar ratio. The diffraction peaks observed at 2θ values of 28.9°, 37.8°, 40.9°, 49.7° and 60.5° respectively indexed to (110), (101), (200), (411) and (521) plane reflections of a tetragonal phase of β-MnO_2 and α-MnO_2. The characterization of the morphology showed that the diameters of nanorod microstructures of MnO_2 ranging from 30 to 145 nm with length ranging from 0.5 to 3 μm. These MnO_2 nanorods product would be potentially used in energy storage devices.

1. Introduction

MnO_2 was one of the most attractive materials because of its applications, such as catalysts, lithium-ion batteries and Mg batteries, electrochemical supercapacitors, ionic or molecular sieves, for its advantages of low cost, earth abundance, environmentally friendly, and superior performance in energy capacity [1,2]. The physical properties of MnO_2 relied on the crystalline phase and morphology of MnO_2 nanostructures [2,3]. The previous studies investigated the morphology and crystal structure of MnO_2 in the different morphology, including nanorods [1,3,4], nanoflower [5,6], nano urchin [3,7], nanowires [8,9], nanoneedles [10]. Nanorods were one of the most interesting morphologies because it can control self-aggregation effectually [11]. The various method has been developed to synthesize MnO_2 with controlled morphologies, including thermal, refluxing, hydrothermal, sol-gel, electrochemical, solid-state reaction [12]. The hydrothermal method was attractive because it is a cheap, environmentally friendly method to prepare materials in different nanostructures [13]. For example, Li et al. [3] studied the electrochemical properties on supercapacitor with the different morphology of MnO_2 including nanorod, hollow urchin, and smooth ball, and nanorod structure displayed the best electrochemical capacity.

In this study, we demonstrate a hydrothermal method to synthesize MnO_2 nanorods with controlled structure. We changed the molar ratio of Mn precursor solution to HCl to control the structure of MnO_2. To calculating the crystallite sizes of MnO_2, we used the Scherrer equation given below [14]:

$$D = \frac{K\,\lambda}{\beta \sin \theta} \qquad (1)$$

where λ is X-Ray wavelength (nm), β is the peak width of the diffraction peak profile at half maximum height (rad) and K is a constant related to crystallite shape. Furthermore, the products of MnO_2 nanorods potentially would be used in energy storage and other devices which are need storage of electron.

2. Experimental

2.1. Synthesis MnO_2 Nanorods

MnO_2 were synthesized by using $KMnO_4$ and HCl with the different molar ratio (1:2, 1:6, 1:8). All chemicals were analytical grade reagents from Merck, Germany. 0.395 g $KMnO_4$ was dissolved completely in deionized water + HCl at room temperature. The solution was kept continuous stirring to form a clear solution. The mixture was transferred into a 20 mL Teflon-lined autoclave. The autoclave was heated at 160 °C for three hours (**Figure 1.**) in an oven and then cooled down to room temperature naturally.

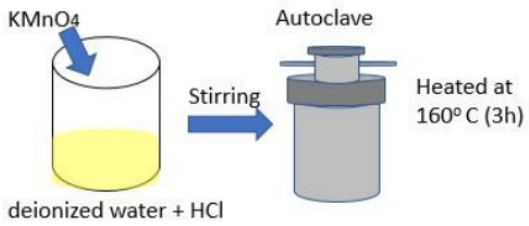

Figure 1. Schematic of hydrothermally synthesized MnO_2 nanorods

2.2. Characterization

The samples were characterized by X-ray diffraction spectroscopy (XRD, Philip Analytical X-Ray B. V) with Cu Kα radiation (λ=1.5418 Å) at 40 kV, and Scanning Electron Microscopy (SEM) to study the morphology of MnO_2 nanorods.

3. Results and Discussion

Analysis role of the molar ratio of $KMnO_4$ to HCl, we made three different samples with the molar ratio of 1:2, 1:6, and 1:8. The reaction was carried out at the temperature of 160 °C for 3 h. The morphology of samples was characterized by SEM. **Figure 2.** shows the morphology of MnO_2 nanorods at the different molar ratio. The results show nanorod microstructures with aggregation with length ranging from 0.5-3 μm. However, the product of molar ratio 1:2 shows more spherical nanostructure than nanorod structure (**Figure 2.** (a)). **Figure 2.** (b) and (c) shows nanorod and nanowire structures with more nanorods in the molar ratio of 1:8. The products of nanorod structures consist with the diameter ranging from 30-145 nm. It is likely that a larger amount of HCl will produce more nanorod structures with the same reaction time. Based on the reaction process, the reaction on the formation of MnO_2 using $KMnO_4$ and HCl is according to the following reaction [1]:

$$KMnO_4 + H_2O + HCl \rightarrow MnO_2.H_2O + KCl + H_2O$$

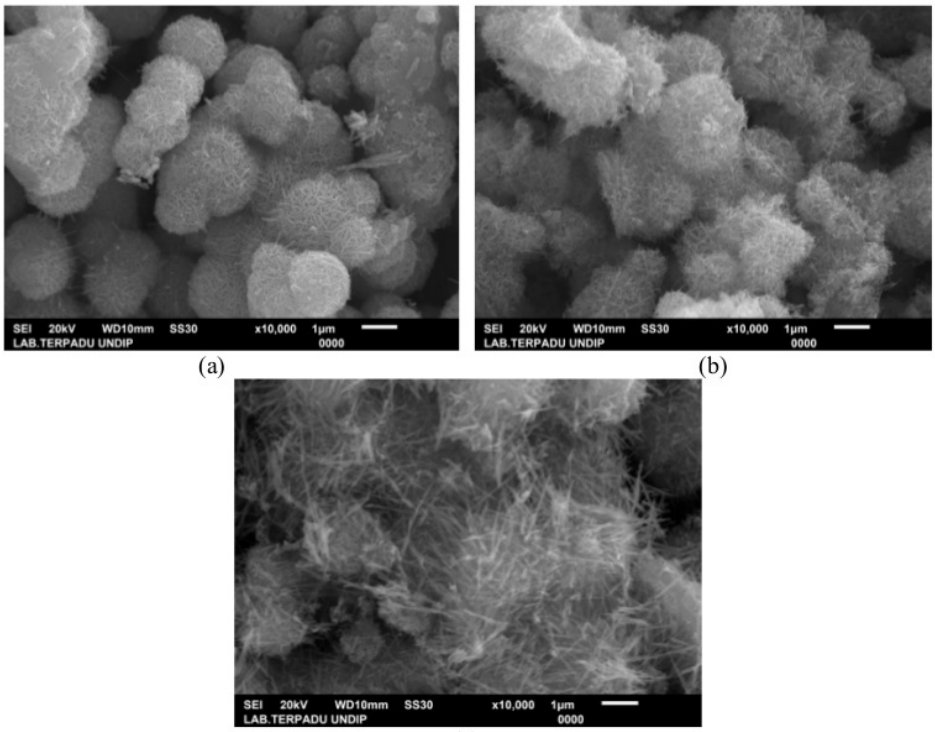

Figure 2.SEM images of MnO_2 nanorods at the different molar ratio: (a) 1:2, (b) 1:6, (c) 1:8

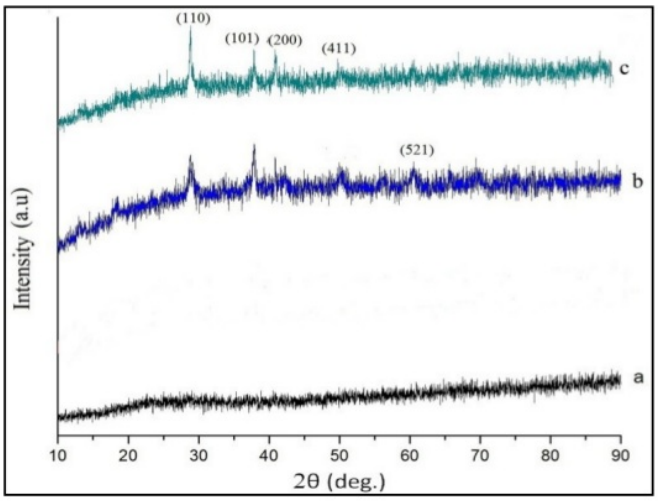

Figure 3. XRD patterns of MnO_2 nanorods at the different molar ratio: (a) 1:2, (b)1:6, (c) 1:8

The powder X-Ray diffraction (XRD) pattern was shown in **Figure 2.** for the samples synthesized with the three different molar ratio. The diffraction peaks observed at 2θ values of 28.9°, 37.8°, 40.9°,

49.7°, and 60.5° respectively indexed to (110), (101), (200), (411), and (521) plane reflections of a tetragonal phase of β-MnO_2 and α-MnO [1,3]. However, the crystallinity of the molar ratio of 1:2 has small rods and irregularity (**Figure 2.** (a)), indicating that the product presents an amorphous structure. The diffraction patterns show that, of the three samples, the molar ratio of 1:8 has the best crystallinity. However, the peaks of intensity are broad and low, indicating the presence of low degree crystallinity of MnO_2 nanorods.

Table 1. shows the crystallite size of MnO_2 nanorods as calculated according to the equation (1). The crystallite sizes increase with increasing the molar ratio of samples. However, because of the amorphous structure of MnO_2 with molar ratio 1:2, the crystallite size of the sample is below the detection limit for XRD.

Table 1. Crystallite sizes of MnO_2 nanorods

Molar Ratio	Crystallite Size (nm)
1:2	-
1:6	10.09
1:8	20.61

The mechanism of the crystallographic structure transformation has been illustrated in **Figure 4.** At the molar ratio of 1:2, the high concentration of precursors lead to rapid formation of numerous nuclei, which these nuclei self-assemble to form nearly amorphous spheres [15,16]. Increasing molar ratio from 1:2 to 1:6 and 1:8, the spherical morphology with amorphous structures are changed to nanorod morphology with the crystal structure. This is attributed that more HCl could lead to a decrease in the nucleation rate, thus the structures becoming to nanorods [5].

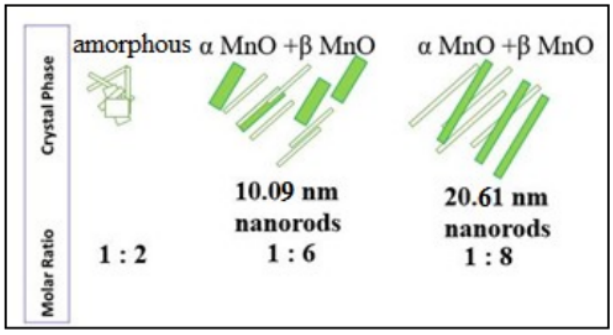

Figure 4. Schematic illustrations of mechanism of phase transformation

4. Conclusions

This work shows that MnO_2 nanorods have been successfully prepared by hydrothermal method. We have synthesized β-MnO_2 and α-MnO_2 nanorods with the combination of sphere and wire nanostructures by tuning the molar ratio of Mn precursor solution to HCl. The peaks of intensity are still broad and low, indicating the presence of low degree crystallinity of MnO_2 nanorods. The uniform morphology can be controlled by increasing the molar ratio. Synthesis process studies reveal that the molar ratio is one of the parameters to get the nanorod structures. These products would be potentially used in energy storage devices.

5. Acknowledgments

We would like thank to Diponegoro University, Ministry of Research Technology and the Higher Education Republic of Indonesia for funding our research from Program KreativitasMahasiswa (PKM). We are also indebted to Mr. Chasbullah Hindratmo for his valuable assistance in Laboratory Nanotechnology, Diponegoro University.

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