Synthesis of nanosize manganese oxides from its ore using solvothermal method

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Abstract. Nano-sized manganese oxide was successfully synthesized from local manganese ore using solvothermal method. The manganese ore were obtained from Jereweh District, Sumbawa, West of Nusa Tenggara, Indonesia. The aims of this research are to study the effects of temperature and time to the morphology, size and phase of manganese oxide obtained by solvothermal method. In the first step, we performed the extraction of manganese precursor from manganese ore. The method to extract the manganese precursor was hydrometallurgy. The second step, manganese precursor that obtained in the first step was used to synthesis manganese oxide using solvothermal method. NaOH was used as precipitating agent. The phase, morphologies and particle size of manganese oxides were examined by x-ray diffractometer and scanning electron microscopy.

1. Introduction

Nano-sized particles have features in their properties and applications. And for several decades this research has been related to the synthesis and application of interesting nanoparticles to be studied in depth. Nanoparticles are 1-100 nm particles that have unique properties and are different from other sized particles. Some properties attached to a particle will increase many times when the particles are nanosize. This is because nano-sized particles are in a range of sizes that separate and are between atomic/compounds sizes and bulk materials [1].

Manganese has many types of oxidation state which affected the type of manganese oxide formation. The stable manganese oxide forms are MnO, Mn3O4, Mn2O3 and MnO2. The each of manganese oxide type has its function in any field. As widely known, MnO2 is applied in battery [2, 3]. Some studies reported that MnO2 also has good antimicrobial activity [4] and enhanced the image contrast of Magnetic Resonance Image (MRI) instrument [5]. Hausmannite which have molecular formula as Mn3O4 reported can use in water treatment process [6]. The large specific surface area of MnO 1-D nanorod indicating that its can be used as catalyst, energy storage and biomedical images
Nanoparticle size of manganese oxide improves their surface area, change their properties to be great and different from that bulky material [7]. Nano-sized manganese oxide can be synthesized by several methods such as co-precipitation, sonochemical, solgel and hydrothermal. The hydrothermal/solvothermal is simple method, inexpensive, and promising to synthesis nanosize particles. Li et al reported the hydrothermal method can controlled the MnO$_2$ morphology transformation during different reaction time [8]. The type and morphology of manganese oxide nano-sized also be affected by the starting material that use in the reaction system. Manganese ore, especially from Sumbawa West of Nusa Tenggara is a huge potential resource that has a low economic value and not treated optimally. This study focuses on the synthesis of nano-sized manganese oxide by solvothermal which the manganese precursor is obtained from manganese ore directly.

2. Experimental

2.1 Materials
Nanoparticle size of manganese oxide was synthesized immediately from manganese sulphate precursor as leaching process of manganese ore. Manganese ore that we used for this study were collected from Jereweh District, Sumbawa, West of Nusa Tenggara. As well, our previous study, the manganese ore were in pyrolusite (MnO$_2$) phase with the manganese content was 78.80% and iron was 17.77% as a major impurity [9]. Reagent that used in this study was sulphuric acid 95-97%, hydrogen peroxide 30%, ammonium hydroxide 25, and sodium hydroxide, which were obtained from Merck. The other materials that we used in this study were Whatmann 42 D 110 mm filter paper, ethanol 96% and aqua demineralization.

2.2 Preparation of Manganese Precursor
Manganese rock was crushed into small chunk using hammer and was dried in the oven at 80 °C for 2 hours. The small chunk of manganese ore was milled using disk mill for 30 seconds and repeated three times until the powder was obtained. To get the homogeneous particle size, the powder of manganese ore was sieved to size of -200 mesh. Sieved powder of manganese ore was ready for use in the leaching process. The leaching process was adopted from Nayl et al studies which used sulphuric acid and hydrogen peroxide [10]. In the beginning, fifty grams of sulphuric acid 4 M was heated until temperature reach out 70°C in beaker glass then manganese ore and hydrogen peroxide 0.8 M was added slowly. The heating and stirring were continued for 90 minutes. After leaching process, the residues and liquor was separated using Buchner vacuum. The leach liquor was added ammonium hydroxide 25% drop by drop till pH solution at 7 and brown cake formed. This brown cake precipitated was iron impurities. Filtration was carried out to obtained manganese sulphate precursor which then used to synthesis nano-sized manganese oxide.

2.3 Manganese oxide nano-sized synthesis
Nanoparticle size of manganese oxide was synthesized by solvothermal method. 45 mL of manganese sulphate precursor was mixed with sodium hydroxide 4M and the ratio was 1:1 (v/v). This mixture solution was stirred at room temperature for 15 minutes and transferred into autoclave teflon covered up with stainless steel. The hydrothermal was carried out at 150°C for 24 hours. The precipitated formed was washed using ethanol and aqua demineralization until pH 7.

2.4 Characterization
The phase that formed after solvothermal process was observed by X-ray diffraction (Smartlab, Rigaku, Japan). Microstructure of manganese oxide product were analysed by scanning electron microscopy (SEM, JIB-461OF, Jeol, Japan) with voltage and probe current was 10 kV and 3 mA, respectively. Average particle size of manganese oxide was calculated statistically by analysing SEM images.
3. Results and Discussion

Jacob et al reported the thermodynamic data for Mn$_3$O$_4$, Mn$_2$O$_3$ and MnO$_2$ transformation by oxidation reaction approach as summarized in Table 1 [11]. This result showed that Mn$_3$O$_4$ are favourable instead of Mn$_2$O$_3$ and MnO$_2$ since the Gibbs free energy is the lowest among of those manganese oxides. This phenomenon indicating the oxidation reaction of Mn$^{2+}$ has been occurring even it take very slow at room temperature. However, the manganese oxide obtained in the previous report [11] used chemical precursor. In this study, we used manganese sulphate from manganese ore without any further treatment.

Table 1. Thermodynamic Data of Manganese Oxide Oxidation [11]

| T (°C) | Mn$_3$O$_4$ | Mn$_2$O$_3$ | MnO$_2$ |
|-------|------------|------------|---------|
|       | $\Delta H_f^o$ | $S_f^o$ | $\Delta G_f^o$ | $\Delta H_f^o$ | $S_f^o$ | $\Delta G_f^o$ | $\Delta H_f^o$ | $S_f^o$ | $\Delta G_f^o$ |
| 27    | -1386.176  | 166.48    | -1283.78 | -961.536 | 113.70 | -884.475 | -521.449 | 52.75   | -446.405 |
| 127   | -1385.372  | 209.41    | -1249.75 | -961.512 | 114.38 | -883.998 | -521.450 | 53.09   | -466.064 |
| 227   | -1384.332  | 245.01    | -1215.97 | -960.818 | 144.93 | -858.275 | -521.220 | 70.11   | -447.620 |
| 327   | -1383.264  | 275.48    | -1182.39 | -960.126 | 169.79 | -832.719 | -520.615 | 84.82   | -429.286 |
| 427   | -1382.210  | 302.25    | -1149.01 | -959.359 | 191.17 | -807.309 | -519.895 | 97.56   | -411.088 |

The solvothermal is one promising method to synthesis nano-sized material because simple and can take place at low temperature. Besides that, this method offers fine and single-phase compound. The oxidation reaction of Mn$^{2+}$ already occurred spontaneously at sodium hydroxide addition at room temperature which is indicated by observation of this precursor colour changes from clear to brownish. This colour becomes solid during heating process. The oxidation reaction can be written in below (Hu et al, 2008):

$$4\text{Mn}^{2+} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{Mn}^{3+} + 4\text{OH}^- \quad (1)$$

![Diffractogram of synthesized particles using XRD.](image)
Confirmation the phase of the product synthesis is showed in Figure 2. It was confirmed a single phase of Mn$_3$O$_4$ was observed without any trace of secondary phase. The main peak showed at 2 theta 36.05°; 32.54°; 29.03°; 60.02°; 29.03°; 18.06°; 64.47°; 38.34°; 44.31°; 51.29° and 30.98°. The reason is probably caused by limited oxygen supply in solvothermal system, encourage the existence of Mn$^{2+}$ and Mn$^{3+}$ combined to form Mn$_3$O$_4$. The single phase of Mn$_3$O$_4$ also formed by hydrothermal method in Hu et al studies [12]. This Mn$_3$O$_4$ seem has good crystallinity even it performed at low temperature. This indicates the pressure of reactor has a main role to determine its crystallinity. The morphology confirmed from image SEM showed that the Mn$_3$O$_4$ has a nano-sphere shape.

**Figure 2.** Scanning electron microscope image of Mn$_3$O$_4$.

The particle size of manganese oxide was 48 ± 12 nm. It showed that particle of manganese oxide experience agglomeration as a nature of nanoparticle. The nano-sized of Mn$_3$O$_4$ has good application as electrode material for supercapacitors [13]. The other studies reported that nanoparticle Mn$_3$O$_4$ with carbon black give higher specific capacitance [14]. The proposed of overall reaction in this systems follow reaction Equation 2.

$$6\text{MnSO}_4 (aq) + 12\text{NaOH (aq)} + \text{O}_2 (g) \rightarrow 2\text{Mn}_3\text{O}_4 (s) + 6\text{Na}_2\text{SO}_4 (aq) + 6\text{H}_2\text{O (l)}$$

(2)

4. Conclusion

Mn$_3$O$_4$ nanoparticle was successfully synthesized from its ore by simple solvothermal method. The synthesized nanoparticle appears as a single phase of nano-sphere Mn$_3$O$_4$ with high crystallinity which had particles size was 48 ± 12 nm. This study offers the opportunity to process manganese ore from with potential of added value.
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References
[1] Schmid G 2004 Nanoparticles from theory to application (Weinheim:WILEY-VCH)
[2] Cheng F, Zhao J, Song W, Li C, Ma H, Chen J and Shen P, 2006, J. Inorg. Chem., 45, 2038-2044
[3] Zhang L L, Wang Z L, and Xu D, 2012, Chin Sci Bull, 57: 4210–4214
[4] Rutz A., 2009, Synthesis and Properties of Manganese Oxide Nanoparticles for Environmental Applications, NNIN REU Research Accomplishments.
[5] Pan D, Schmieder A H, Wickline S A and Lanza G M, 2011, Tetrahedron, 67, 8431-8444
[6] Chen H and He J, 2008, J. Phys. Chem. C, 112, 17540–175450
[7] Zheng M, Zhang H, Gong X, Xu R, Xiao Y, Dong H, Liu X and Liu Y, 2013, Nanoscale Res. Lett., 8, 166
[8] Li Y, Zhou X, Zhou H, Shen Z and Chen T, 2008, Front. Chem. China, 3, 128–132
[9] Kusumaninggrum R, Rahmani S A, Widayatno W B, Wismogroho A S, Nugroho D W, Maulana S, Rochman N T, and Amal M I, 2016, AIP Conf. Proc., 1964, 020042-1–020042-6
[10] Nayl A A, Ismail L M, and Aly H F, 2011, Int. J. Miner. Process., 100, 116-123
[11] Jacob K T, Kumar A, Rajitha G, and Waseda Y, 2011, J. High Temp. Mater. Proc., 30, 459–472
[12] Hu C C, Wu Y T, and Chang K H, 2008, J. Chem. Mater., 20, 2890–2894
[13] Raj B G S, Asiri A M, Wu J J, Anandan S, 2015, J. Alloy Compd., 636, 234-240
[14] Ahmed K A M, Zeng Q , Wu K, Huang K, 2010, J. Sol Stat Chem, 183, 744–751