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The Effect of Precursors Concentration on the Structural Properties of MoS2 Nanosheet-Microsphere Synthesized Via Hydrothermal Route

I S Waskito[1,3], B Kurniawan[1]*, M I Amal[2] and M Hanifuddin[3]

[1]Department of Physics, Universitas Indonesia, Depok, Jawa Barat, Indonesia 16424
[2]Research Center for Metallurgy and Materials, Indonesian Institute of Sciences, Banten, Indonesia 15314
[3]Research and Development Centre for Oil and Gas Technology "LEMIGAS", Jakarta, Indonesia 12230

*Corresponding author: budhy.kurniawan@sci.ui.ac.id

Abstract. MoS$_2$ nanosheet-microsphere was successfully synthesized via hydrothermal route by applying precursor of ammonium heptamolybdate and thiourea. The precursor concentration was varied of 0.25 M, 0.5 M, 1.0 M and 1.5 M. The crystal structure, morphology and particle size of as-synthesized MoS$_2$ were observed as the effect of the precursors concentration. MoS$_2$ nanosheet-microspheres were prepared inside the hydrothermal autoclave at 200 ^{o}C for 24 hours. The X-ray diffraction (XRD) characterization result showed the structure of hexagonal 2H-MoS$_2$ crystals in the absence of other secondary phase. XRD characterization results also revealed that MoS$_2$ with a precursor concentration of 0.25 M has better crystallinity in 002 plane compared to MoS$_2$ synthesized with other precursor concentrations. The Scanning Electron Microscopy (SEM) observation indicated the shape of nanosheets with a thickness of several tens nanometers which were assembled to form microsphere. SEM result also showed precursor concentrations of 0.25M to 1.5M affects to the formation of nanosheet-microsphere MoS$_2$ particle in which along the increasing of the precursor concentration the nanosheet-microsphere particle not all well-formed. Particle Size Analyzer result showed the average particle size decreased and the average specific surface area increased with increasing precursor concentration.

1. Introduction

Molybdenum disulfide (MoS$_2$) is one of transitions metal dichalcogenide that has been attracted for study nowadays due to its unique anisotropic layered structure and widely uses as a functional materials. Each layer in the MoS$_2$ structure consists of covalent bond between S-Mo-S atoms and this each layer interacts to the adjacent layer between the S-S atoms with weak van der Waals interaction. The van der Waals bond between MoS$_2$ layers has different inter-layer arrangement and different atomic coordination between Mo-S atoms to form several polytypes or unit cell geometry, namely 1T-MoS$_2$, 2H-MoS$_2$ and 3R-MoS$_2$ [1]. The polytypes or unit cell geometry forms a hexagonal and rhombohedral crystal structure. Due to its anisotropic layered structure MoS$_2$ has mechanical, electrical and optical properties which can be used as functional material with wide range application such as solid additives [2], solid lubricants [3], lithium batteries [4], photo chemical catalysts [5], super capacitors [6] and antrachene hydrogenation [7].
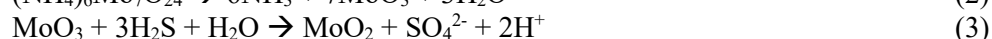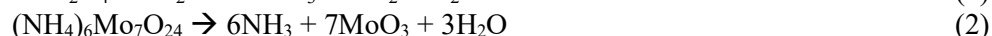
Various methods are used to synthesize MoS_2 such as chemical methods [8], high temperature sulfurization [9], chemical vapor deposition [10], microwave method [11] and hydrothermal method [12] to produce morphology such as nanosheets, nanoflowers, nanosphere [13] and different size and crystallinity. MoS_2 also synthesized with various parameters such as temperature, crystallization time and pH [7], surfactant [14], ionic liquid [15] and precursor concentrations [16]. Among the synthesis parameters, the concentration of precursors are rarely been reported. Lee C M *et al*. [17] synthesized MoS_2 with sodium molybdate and thiourea as precursors with different concentrations and showed the greater concentration of precursors the greater the size of the particles produced. While Xie *et al*. [18] synthesized MoS_2 with high precursor concentrations and then decreased the concentration of the precursors. Xie reported the thickness of the nanosheets increased by decreasing the precursor concentration.

In this work, MoS_2 nanosheet-microsphere synthesized using ammonium heptamolybdate tetrahydrate and thiourea as the starting materials with different concentrations with mole ratio Mo:S of 1:30. The effect of precursor concentration on structural properties, morphology and particle size was investigated using X-ray diffractometer, Scanning Electron Microscope and Particle Size Analyzer.

2. Experimental

2.1. Synthesis
All of the chemical reagent were analytical purity and used directly without further purification. The MoS_2 nanosheet-microsphere were synthesized in different precursor concentration 0.25 M, 0.5 M, 1.0 M and 1.5 M. In a typical synthesis, some amount of ammonium heptamolybdate tetrahydrate and thiourea were dissolved in 35 ml deionized water in 1:30 molar ratio under vigorous stirring to form a homogeneous solution. After stirring for 30 min the solution was then transferred into a 50 ml Teflon-lined stainless steel autoclave, sealed tightly and heated with temperature maintained at 200 °C. After 24 hours the autoclave was then naturally cooled down to room temperature. Black precipitates were collected and washed by centrifugation with distilled water and absolute ethanol for several times and finally dried in vacuum at 80 °C for 12 hours. In the synthesis process, MoS_2 was prepared from $(NH_4)_6Mo_7O_{24}$ and CSN_2H_4 by the following reactions:

$$CSN_2H_4 + 2H_2O \rightarrow 2NH_3 + CO_2 + H_2S \qquad (1)$$
$$(NH_4)_6Mo_7O_{24} \rightarrow 6NH_3 + 7MoO_3 + 3H_2O \qquad (2)$$
$$MoO_3 + 3H_2S + H_2O \rightarrow MoO_2 + SO_4^{2-} + 2H^+ \qquad (3)$$
$$MoO_2 + 2H_2S \rightarrow MoS_2 + 2H_2O \qquad (4)$$

2.2. Characterization
The structure of the samples were characterized by X-ray diffractometer (XRD) using X'pert PANalytical diffractometer with CuKα (λ=1.5406 Å). The morphologies of the as-synthesized samples were observed by Scanning Electron Microscopy (FEI Quanta 650) and average of particle size recorded by Particle Size Analyzer (Beckman Coulter LS 100Q).

3. Result and Discussion
Figure 1 shows the diffraction pattern from MoS_2 samples synthesized by the hydrothermal method at 200 °C for 24 hours with variations of precursor concentration. The diffraction pattern shows the main diffraction peaks at 2θ which are assigned to the (002), (100), (103) and (110) planes of the hexagonal MoS_2 and there is no obvious peak from impurity compared with the standard diffraction pattern. Diffraction patterns also shows different peaks intensities for different precursor concentration. Diffraction peaks appears at concentration 1.5 M (figure 1.a) but in low intensities and the intensities increased as the precursor concentration decreased. The increasing of peak intensities (002), (100), (103), and (110) as the precursor concentration decrease indicates better crystalline of MoS_2 nanosheet-

microsphere [19]. The preferred orientation of crystal growth can be indicated by the highest peak intensity which is (002) plane and the increasing its intensity indicates a formation of well crystalline MoS_2 with ordered layered stacking along the *c*-axis during the synthesis process [20].
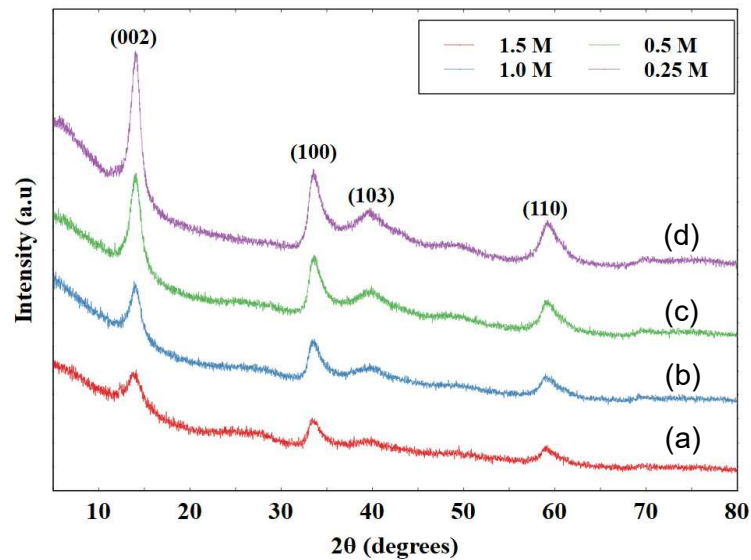
Figure 1. XRD patterns of as-synthesized MoS_2 samples, (a) 1.5 M, (b) 1.0 M, (c) 0.5 M, (d) 0.25M

In order to further confirm the crystallinity, diffraction pattern of as-synthesized samples were refined using Rietveld method to obtain FWHM (002), d-spacing (002), crystallite size (002), average crystallite size and estimate number of layer in (002) plane. Table 1 shows the refinement result of the as-synthesized samples.

**Tabel 1**. Refinement result as synthesized samples.

Parameters	0.25 M-MoS_2	0.5 M- MoS_2	1.0 M- MoS_2	1.5 M- MoS_2
Structure	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	P 63/mmc (194)	P 63/mmc (194)	P 63/mmc (194)	P 63/mmc (194)
$d_{<002>}$ (Å)	6.3098	6.3138	6.3433	6.3537
$FWHM_{<002>}$	1.20	1.410	1.60	2.12
Crystallite size$_{<002>}$ (Å)	54.0392	43.3846	36.7685	27.3980
Avg crystallite size (Å)	37.0836	36.0321	34.0095	32.8466
Estimation number of layers	8	6	5	4

Refinement result of the as-synthesized samples shows that all samples have hexagonal structure with space group P 63/mmc (194) and 2 layers in each unit cell (2H-MoS_2). Interlayer distance ($d_{<002>}$) tend to increase as the precursor concentration increase. This value larger than MoS_2 bulk of 6.20 Å. the increasing of interlayer distance $d_{<002>}$ is probably due to intercalation of NH_4^+ and H_2O molecules from precursors decomposition and high pressure and temperature in autoclave [7]. Higher concentration higher intercalation of NH_4^+ and H_2O molecules.

Crystallite size in (002) plane obtained were 54.0392 Å, 43.3846 Å, 36.7685 Å and 27.3980 Å for 0.25 M, 0.5 M, 1.0 M and 1.5 M MoS_2 respectively. This result is in accordance with the XRD pattern where 0.25 M-MoS_2 produces a higher intensity (002) plane with a small FWHM value. The crystallite

size (002) plane correlates with the number of layers of MoS_2. With interlayer distance of 6.3098 Å, 6.3138 Å, 6.3433 Å and 6.3537 Å can be estimated the number of layers are 8, 6, 5 and 4 layers for 0.25 M, 0.5 M, 1.0 M and 1.5 M respectively [21]. Further investigation of the number of layers formed will be more clearly informed by TEM characterization which is not discussed in this paper.

Formation of MoS_2 particles with different precursor concentrations are shown in figure 2. MoS_2 particles are consist of many nanosheets with tens nanometer in thickness and aggregates to form microsphere particles 1-3 μm in size. From SEM image there was no clear the different in particle size due to precursor concentrations. Particles morphology of nanosheet-microsphere sample of 0.25 M more homogeneous and the particle boundaries were also more clearly compared to 0.5 M, 1.0 M and 1.5 M. Sample of 0.5 M appears a slight morphology of inhomogeneous particles forms and this inhomogeneous particles forms are more detected in sample of 1.0 M and particle boundaries were also increasingly unclear. And sample of 1.5 M morphology nanosheet-microspheres are only partially formed.
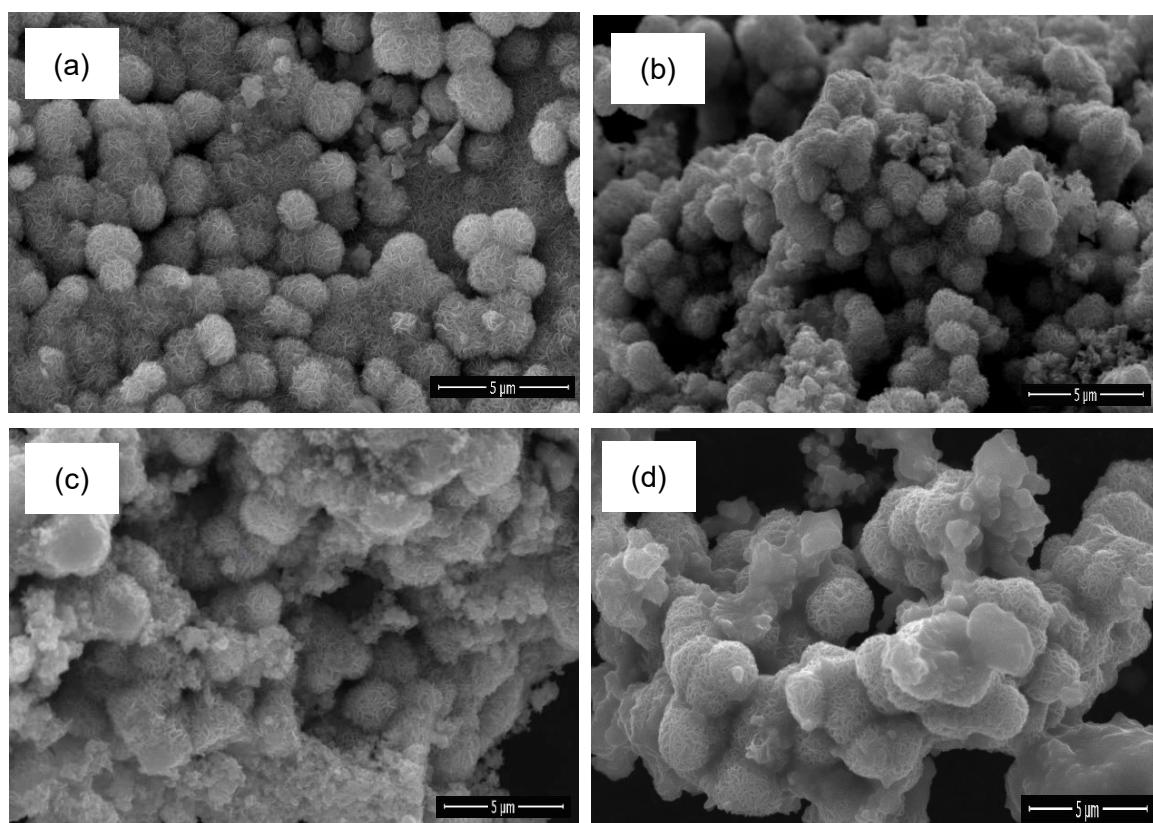
Figure 2. SEM images of MoS_2 nanosheet-microsphere, (a) 0.25 M, (b) 0.5 M, (c) 1.0 M, (d) 1.5 M.

In order to get further information about the average particle size of the samples due to the effect of precursor concentration, particle size analysis was performed and the result shown in figure 3. And the average particle size shown in table 2. Double measurements performed to each sample and the average particle size of the samples were 2.276 μm, 1.855 μm, 0.994 μm and 0.936 μm for sample 0.25 M, 0.5 M, 1.0 M and 1.5 M respectively. The average particle size tend become smaller as the concentration increased. This is suspected due to the number of MoS_2 layers were formed was also smaller as the concentration increased. From the result above sample of 1.5 M has less number of layers and smaller crystallite size compared to other samples. And this result consistent with Xie *et al*. [18] which reported the thickness of the nanosheets increased by decreasing the precursor concentration and decreased as the precursor concentration increased.
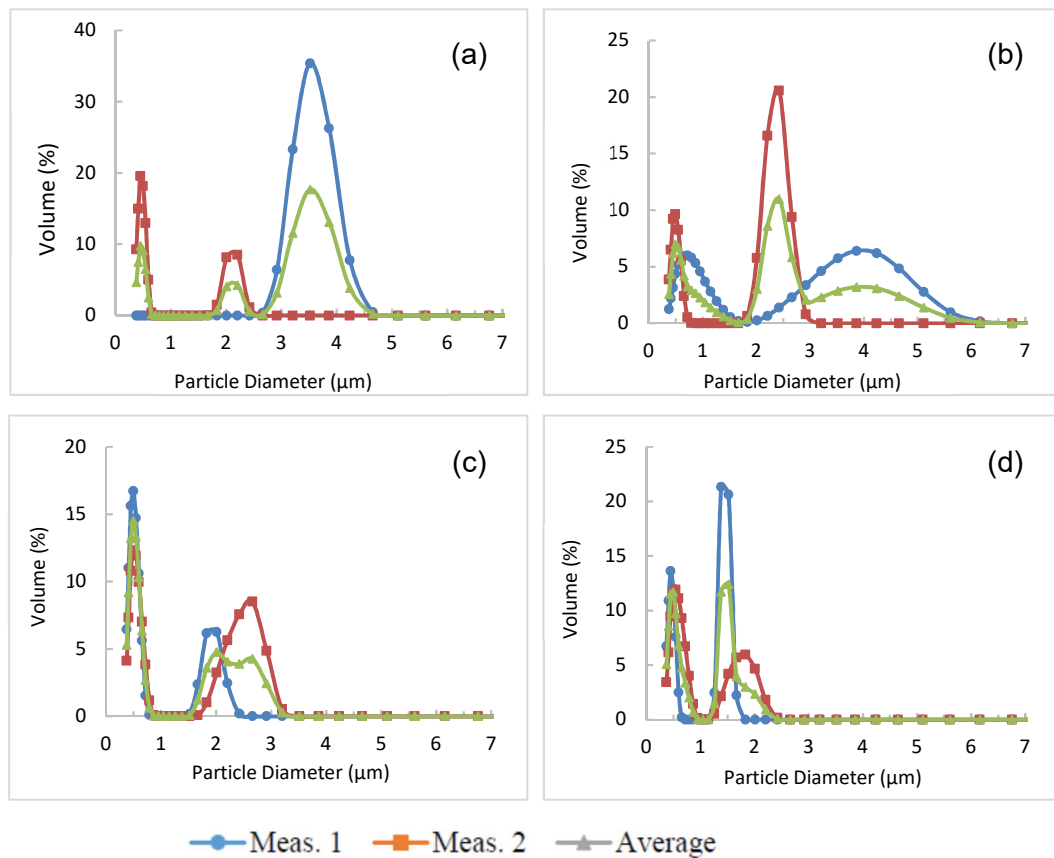
Figure 3. Particle size analysis (a) 0.25 M, (b) 0.5 M, (c) 1.0 M (d) 1.5 M.

Tabel 2. Particle Size Analysis.

Sample Name	Average Particle Size (μm)	Average Specific Surface Area (m^2/g)
0.25 M – MoS_2	2.276	6.066
0.5 M – MoS_2	1.8155	6.226
1.0 M – MoS_2	0.994	9.261
1.5 M – MoS_2	0.936	9.655

4. Conclusion

MoS_2 nanosheet-microsphere has been successfully synthesized using hydrothermal method. The XRD pattern shows the sample has a single phase without impurities. The refinement result shows that all samples formed a hexagonal structure with P 63/mmc space group and 2 layers in each unit cell (2H-MoS_2). Increasing precursor concentration causes change in interlayer distance, crystallite size, estimation number of MoS_2 layers and average particle size.

Acknowledgement

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