Islamic Azad University

Journal of

Optoelectronical Nanostructures

Autumn 2016 / Vol. 1, No. 3

The effect of concentration and time of hydrothermal process on the fluorescent property of Molybdenum Diselenide nano-layers

Vahid Baroogh Miandoab [1], Esmaiel Saievar Iranizad [*,1], Khadijeh Hemmati Kahradeh [1]

[1]Department of Physics, Faculty of Basic Science,
Tarbiat Modares University, Tehran, Iran.

(Received 21 Sep. 2016; Revised 18 Oct. 2016; Accepted 10 Nov. 2016; Published 15 Dec. 2016)

Abstract: The group of 2D materials contains almost all the elements of the periodic table. In contrast to the graphene sheet, they are abundant, this creates a variety of electronic properties including metals, semimetals, insulators and semiconductors. Band gaps of these materials are direct or indirect by ranging from ultraviolet to infrared, for this reason, have received much attention for nanoelectronics, optoelectronics and flexible devices.

In this study, by a simple hydrothermal method, which is a bottom-up approach, molybdenum diselenide two-dimensional layers were synthesized. The samples were analyzed by X-ray diffraction spectroscopy, and the compound molybdenum diselenide was confirmed for the samples synthesized, Furthuremore, UV-visible spectroscopy (UV-Vis) and Fluorescence Spectroscopy (PL) were used to study the absorption spectrum and fluorescent properties of the samples, respectively. the nanoparticles were studied, and found that, by changing the concentration and time of hydrothermal process, the intensity of emission changes. Scanning electron micrographs indicate the size of 100 nanometers for particles synthesized.

Keywords: Nano layer, Molybdenum diselenide, Fluorescence

1. Introduction

Molybdenum diselenide is one of the Dichalcogenide of the transition metals. In this group, two atoms of chalcogen group binds with an atom of the metals. Transition Metal Dichalcogenide (TMD) have X-M-X layer structure, so that its single layer includes a layer of molybdenum (M), which is between two layers of selenium (X) [1-4].

[*]**Corresponding author. E-mail: saievare@modares.ac.ir**

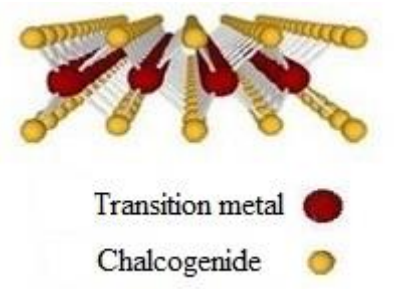

Fig. 1. Schematic of single-crystal layer of transition metal Dichalcogenides.

The bonding between atoms within the layer has been covalent, while, the weak Van Der Waals bonds are between the layers. This makes the layers to be separated easily[2]. The materials in bulk form of gap have indirect energy and the size of the gap is about 1 eV, but in single-layer mode, direct energy gap is about 2 eV[5, 6]. The thickness of each layer is between 6 to 7Å[7]. A single pair of Chalcogenides electron is limited to over the layer of surface, and these layers are stable in the reaction to the environmental species because of the absence of free bonds[8-10].

Molybdenum diselenide nano-layers can be widely used in areas such as lithium batteries, lubricants, electronic devices, optical devices, water splitting, solar cells and sensors [1, 11, 12, 13].

The synthesis of these materials by hydrothermal method, which is a bottom-up approach has been done. For the synthesis, Sodium molybdate is used as raw material for molybdenum and selenium powder as raw material for selenium[14].

2. Materials and Methods

Sodium molybdate dihydrate[†] ($Na_2MoO_4.2H_2O$) purchased from Merck was used as a raw material of molybdenum and selenium powder (Se) purchased from Merck was used as raw material for selenium. First, some Sodium molybdate dihydrate salt is dissolved in the twice distilled water, then a proportional amount of selenium powder is dissolved in hydrazine hydrate ($N_2H_4.2H_2O$) in a separate container. Molybdenum to selenium molar ratio in the solution should be 2/1. The final solution is red which is transferred to Teflon with a capacity of 100 ml, and up to 75% of Teflon with twice distilled water to be filled. Teflon is placed inside a stainless steel autoclave, and finally, the autoclave to be put inside the furnace. Process temperature is 200°C, and the

[†] Sodium molybdate, Na_2MoO_4, is useful as a source of molybdenum. It is often found as the dihydrate, $Na_2MoO_4 \cdot 2H_2O$.

process time varies from 8 hours to 24 hours. Then, the autoclave was naturally cooled to the room temperature and the resulting suspension was centrifuged to separate bulk particles, and the supernatant was collected for analysis [14].

3. Results and discussion

Figure 2 shows X-ray diffraction for synthesized samples (03-065-3481: JCPDS number). X-ray diffraction peaks are observed respectively at angles of 15.91, 36.91, 48.63, 55.41, 63.24, 66.13, 70.84 degree and index of plates related to any angle has been determined in the figure. It shows that the synthesized $MoSe_2$ nanolayers maintain the 2H–$MoSe_2$ structure, and the broad diffraction peaks shows that the products are in the nanometric region. The distance between the planes (002) 6.46Å is obtained. For layered $MoSe_2$ particles the thickness is 6-7Å and the results show their thickness about 6.5Å. The results of X-ray diffraction indicate $MoSe_2$ composition for synthesized particles.

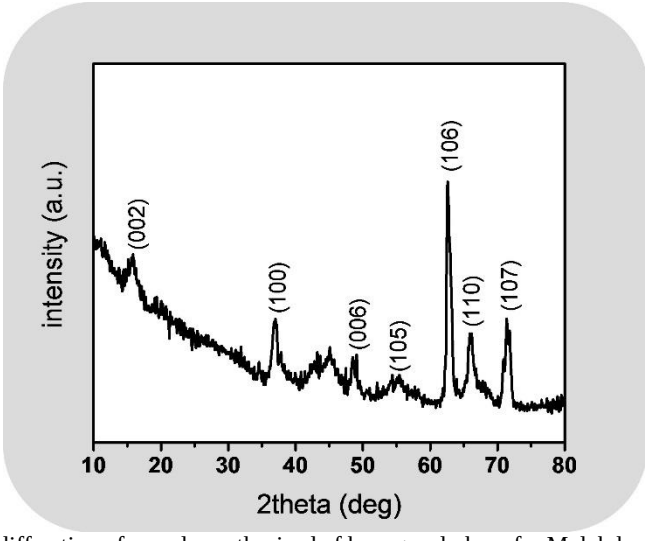

Fig. 2. X-ray diffraction of sample synthesized of hexagonal phase for Molybdenum diselenide particles.

Figure 3 shows UV-visible absorption spectrum for the synthesized samples. According to the figure, the particles absorb in the wavelength range of 300-700 nm; so these particles can be suitable for optical applications.

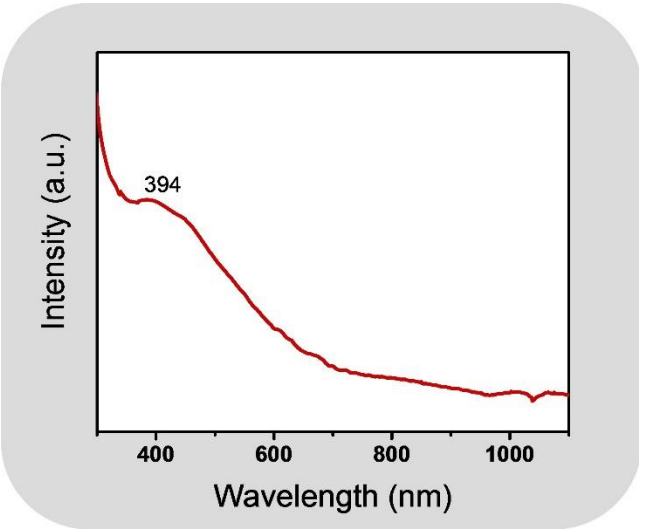

Fig. 3. Ultraviolet visible absorption spectrum for the synthesized samples.

Table 1 shows the effect of concentration and hydrothermal process time on the intensity of emission spectrum. In this table, the sodium molybdate oncentration is given as one of the raw materials, and the selenium concentration is calculated using a molar ratio of molybdenum to the selenium (2/1). It can be seen that, with increasing hydrothermal processing time from 8 hours to 16 hours, the emission intensity will be 1.25 times and with increasing up to 24 hours, emission intensity has decreased. Also, by increasing the concentration of sodium molybdate $2.75*10^{-4}$ to $5.51*10^{-4}$ M, intensity of emission will be 3.2 times.

Table1. The effect of initial concentrations and time of hydrothermal processes on the intensity.

Sample No	Emission intensity (unit)	Time (hours)	The concentration of sodium molybdate (M)
1	$2.4*10^4$	8	$2.75* 10^{-4}$
2	$3*10^4$	16	$2.75* 10^{-4}$
3	$1.2*10^4$	24	$2.75* 10^{-4}$
4	$7*10^4$	8	$5.51* 10^{-4}$
5	$7.6*10^4$	16	$5.51* 10^{-4}$
6	$6.9*10^4$	24	$5.51* 10^{-4}$

Figure 4 shows the emission spectra for different samples. Excitation wavelength is 330 nm. In this study, the excitation wavelength is fixed and intensity of emission spectra for samples with different concentrations and different synthesis times has been compared. It is clear that with regard to the

emission intensity increases with increasing concentration. Also, the optimal time was obtained 16 h for hydrothermal processes.

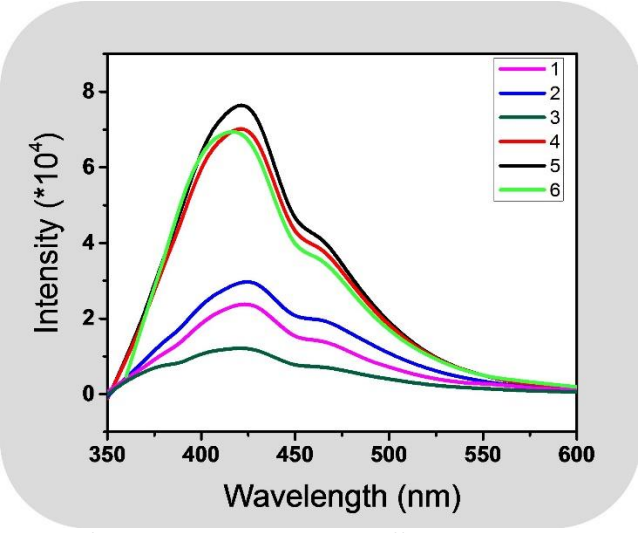

Fig. 4. Emission spectra for synthesized samples with different initial concentrations and different time of synthesis.

In a previous research [15], the sharp emission spectrum is at 800 nm, while our results are different due to the very small size of our particles, and the emission peak shifts to 432 nm.

Figure 5 shows field emission scanning electron microscope image for the synthesized samples. For imaging, the samples were deposited on a glass substrate.

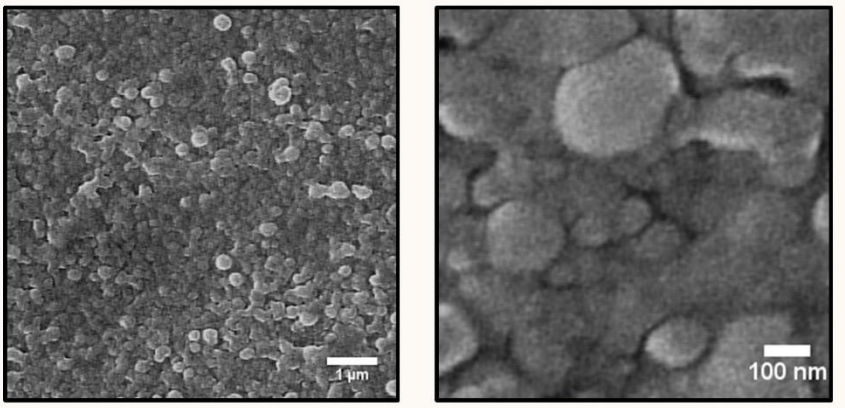

Fig. 5. The field emission scanning electron microscope image of molybdenum diselenide nano-layers.

4. Conclusion

By hydrothermal method, which is a bottom-up approach, molybdenum diselenide nano-layers were synthesized. Concentration of raw material and time of hydrothermal processes were changed. Using X-ray diffraction, hexagonal phase was identified for molybdenum diselenide nano-layer MoSe2. UV-visible absorption spectrum shows absorption in the visible region (394 nm) for particles synthesized. Also using fluorescence spectroscopy it was found that by increasing the concentration of sodium molybdate $2.75*10^{-4}$ to $5.51*10^{-4}$ M, intensity of emission will be 3.2 times, with increasing hydrothermal processing time from 8 hours to 16 hours, the emission intensity will be 1.25 times and with increasing up to 24 hours, emission intensity has decreased. So it can be concluded that, with increasing concentration, the intensity of emission has increased, but the optimal timing of hydrothermal processes for emission intensity was obtained equal to 16 h. Scanning electron microscope images show the approximate size of 100 nm for particles.

5. References

[1] D. M. Andoshe, J.-M. Jeon, S. Y. Kim, and H. W. Jang, *Two-dimensional transition metal dichalcogenide nanomaterials for solar water splitting*, Electronic Materials Letters, 11 (2015) 323-335.

[2] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, and H. Zhang, *The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets*, Nature chemistry, 5 (2013) 263-275.

[3] P. Miro, M. Audiffred, and T. Heine, *An atlas of two-dimensional materials*, Chemical Society Reviews, 43 (2014) 6537-6554.

[4] S. Balendhran, S. Walia, H. Nili, J. Z. Ou, S. Zhuiykov, R. B. Kaner, et al., *Two-dimensional molybdenum trioxide and dichalcogenides*, Advanced Functional Materials, 23 (2013) 3952-3970.

[5] Y. Zhang, T.-R. Chang, B. Zhou, Y.-T. Cui, H. Yan, Z. Liu, et al., *Direct observation of the transition from indirect to direct bandgap in atomically thin epitaxial $MoSe_2$*, Nature nanotechnology, 9 (2014) 111-115.

[6] J. Kang, S. Tongay, J. Zhou, J. Li, and J. Wu, *Band offsets and heterostructures of two-dimensional semiconductors*, Applied Physics Letters, 102 (2013) 012111.

[7] C. Fan, Z. Wei, S. Yang, and J. Li, *Synthesis of $MoSe_2$ flower-like nanostructures and their photo-responsive properties*, RSC Advances, 4 (2014) 775-778.

[8] D. Kong, H. Wang, J. J. Cha, M. Pasta, K. J. Koski, J. Yao, et al., *Synthesis of MoS_2 and $MoSe_2$ films with vertically aligned layers*, Nano letters, 13 (2013) 1341-1347.

[9] C. Xu, S. Peng, C. Tan, H. Ang, H. Tan, H. Zhang, et al., *Ultrathin S-doped $MoSe_2$ nanosheets for efficient hydrogen evolution*, Journal of Materials Chemistry A, 2 (2014) 5597-5601.

[10] H. Wang, D. Kong, P. Johanes, J. J. Cha, G. Zheng, K. Yan, et al., *$MoSe_2$ and WSe_2 nanofilms with vertically aligned molecular layers on curved and rough surfaces*, Nano letters, 13 (2013) 3426-3433.

[11] L. Ma, X. Zhou, L. Xu, X. Xu, L. Zhang, and W. Chen, *Ultrathin few-layered molybdenum selenide/graphene hybrid with superior electrochemical Li-storage performance*, Journal of Power Sources, 285 (2015) 274-280.

[12] C. Dai, E. Qing, Y. Li, Z. Zhou, C. Yang, X. Tian, et al., *Novel $MoSe_2$ hierarchical microspheres for applications in visible-light-driven advanced oxidation processes*, Nanoscale, 7 (2015) 19970-19976.

[13] S. Balendhran, S. Walia, H. Nili, J. Z. Ou, S. Zhuiykov, R. B. Kaner, et al., *Two-dimensional molybdenum trioxide and dichalcogenides*, Advanced Functional Materials, 23 (2013) 3952-3970.

[14] Z. Zhang, X. Yang, Y. Fu, and K. Du, *Ultrathin molybdenum diselenide nanosheets anchored on multi-walled carbon nanotubes as anode composites for high performance sodium-ion batteries*, Journal of Power Sources, 296 (2015) 2-9.

[15] Tonndorf, Philipp, Robert Schmidt, Philipp Böttger, Xiao Zhang, Janna Börner, Andreas Liebig, Manfred Albrecht et al, *Photoluminescence emission and Raman response of monolayer MoS_2, $MoSe_2$, and WSe_2*, Optics express 4 (2013) 4908-4916.