Influence of reaction temperature, time and molar ratio on hydrothermal synthesis of MoS_2 nanosheets

A. Arora[a,*], K. Sharma[b], S. K. Tripathi[a]
[a]*Centre of Advanced Study in Physics, Department of Physics, Panjab University, Chandigarh- 160014, India*
[b]*Department of Physics, Goswami Ganesh Dutta Sanatan Dharma College, Sector 32-C, Chandigarh-160030, India*

MoS_2 nanosheets (NS) were synthesized using a hydrothermal reaction between sodium molybdate and thiourea. The influence of various parameters like reaction temperature, time and molar ratio on hydrothermal synthesis is studied. It was found that the reaction temperature and molar ratio had a greater impact than reaction time. All these parameters influenced the structural and optical properties of MoS_2 that were verified by various characterization techniques like X-ray Diffraction (XRD), UV-Visible (UV) spectroscopy and Photoluminescence (PL) spectroscopy. The thin film of the sample was formed by utilizing drop casting method and current voltage characteristics were measured to calculate the conductivity. The results reveal that optimization of the reaction is must before employing it for certain application and the work will further motivate researchers to utilize it in supercapacitors, Field Effect Transistors (FETs) and various optoelectronic applications.

(Received: April 21, 2022; Accepted August 8, 2022)

Keywords: Hydrothermal, MoS_2, Optimization, 2D materials

1. Introduction

The electronic materials researchers have been drawn to atomically thin two-dimensional semiconductors by the persistent miniaturization of electronics based on silicon combined with graphene. While graphene has received a lot of interest, it lacks a bandgap, rendering it incompatible with digital electronics [1,2]. As a result, a lot of time and effort has gone into finding new two-dimensional semiconductors. Metal chalcogenides, hydroxides, oxides, and boron nitride are among the nongraphene layered compounds that have recently garnered attention. Several recent assessments have reported on a thorough list of all known layered Van der Waals solids [3]. However, semiconductors among them are only a few, and even fewer have been categorized as high-quality and stable two-dimensional crystals. Transition Metal Dichalcogenides (TMDs), in particular, exhibit a diverse set of electrical, thermal, chemical, mechanical and optical characteristics that have been investigated for decades. Because of recent breakthroughs in sample preparation, optical detection, transfer and manipulation of 2D materials, there is a rejuvenation of scientific interest in TMDs in their atomically thin 2D forms [4]. The characteristics of the 2D exfoliated forms of TMDs are complementary to but distinct from those of graphene. Several 2D TMDs, unlike graphene, have large bandgaps of 1–2 eV [5,6], offering exciting new FET and optoelectronic devices. TMDs have the general formula MX_2, where M is a transition metal element (Mo,W etc.) and X is a chalcogen (S, Se or Te). The chalcogen atoms are arranged in two hexagonal planes separated by a plane of metal atoms in these materials, forming layered structures of type X–M–X. In a variety of polytypes, adjacent layers are weakly bound together to create the bulk crystal, which varies in stacking orders and metal atom coordination. The metal atoms exhibit octahedral or trigonal prismatic coordination, while the overall symmetry of TMDCs is hexagonal or rhombohedral [7].

*Corresponding author: aroraanmol.physics@gmail.com
https://doi.org/10.15251/DJNB.2022.173.871

MoS_2 has a sizeable bandgap (1.8 eV) that changes from an indirect to a direct gap in thin structures, which appears to alleviate many of the issues encountered by earlier devices [8]. Rather than graphene, which has a practically zero-band gap, this might allow downscaling of electrical devices [9]. Even with high-dielectric materials, it exhibits strong mobility and no surface dangling bonds. It's perfect for thin-film transistors, and it's easy to make, resulting in a high manufacturing yield and low cost [10,11]. It is ideal for gas sensing because of the covalent links between Molybdenum and Sulfur, as well as the Van der Waals bonds between its layers [12]. One of the most significant issues with Silicon devices was the metal-semiconductor interaction. MoS_2 is a high-performance material with low contact resistance. In other words, MoS_2 has the ability to be employed in nanoscale gate transistors with high efficiency and outstanding on/off switching characteristics. In a variety of sectors, MoS_2 has plenty of applications like biosensing and optical sensors, similar to silicon and graphene, but the most significant are those connected to bio-applications such as DNA, cancer, and Corona Virus detection [13,14]. Its applications aren't limited to electronics; it may also be utilized as a lubricant and in hydrogen evolution processes. It's a good material for the electrodes of batteries [15]. The characteristics and structure of MoS_2 made it attractive for a variety of microwave, sensor and electronic applications.

Numerous methods for the synthesis of MoS_2 nanosheets (NS) have been invented till date. Out of all the methods, hydrothermal method is low cost and reliable technique for synthesis of MoS_2 NS [16]. As compared to prior approaches, hydrothermal synthesis offers advantages: (I) there are no hazardous precursors required and all the initial materials are readily available and stable under ambient circumstances. (II) The solvent used is water that is preferred over dangerous organic solvents hence, making hydrothermal method suitable for industrial applications. Ghaleghafi et. al [17] synthesized few layered MoS_2 nanosheets under different hydrothermal reaction times. They studied the effect of time on elemental composition, morphological, elemental, structural, optical and electrical properties. The sample synthesized at 24 hours reaction time was found to have best UV response. Corderio and co-workers [18] analyzed the effect of time and temperature on microwave assisted hydrothermal method for MoS_2 nanostructures. It was observed that the amount of MoS_2 grown varies with synthesis parameters. They concluded that with increase in reaction time, there was improvement in results of electrical measurements. Xuan et. al [19] synthesized MoS_2 nanostructures by using ammonium heptamolybdate and thiourea in hydrothermal synthesis and studied the effect of reaction temperature and time on morphology, structure and optical properties of MoS_2. They observed that MoS_2 morphology changed from cluster of particles to flower like spherical entities to nanosheets like structure as the temperature is varied from 160°C to 220°C. The reaction time affected the refinement and restacking of MoS_2 structure with no effect on its morphology.

In this work, we synthesized MoS_2 nanosheets using hydrothermal reaction between sodium molybdate and thiourea. The reaction was optimized for different temperature, time and molar ratio of precursors. The effect of these parameters on structural and optical properties was studied using X-ray Diffraction (XRD), UV-Visible spectroscopy (UV) and Photoluminescence spectroscopy (PL). The final confirmation of nanostructure was done using Field Emission Scanning Electron Microscopy (FE-SEM) analysis. The current-voltage characteristics of the best sample were studied using two probe method. This type of material finds application in various electronic, photonic and optoelectronic devices. To best of our knowledge, no work in this much detail has been done earlier on hydrothermal synthesis using sodium molybdate and thiourea. This work indicates that temperature, time and molar ratio are crucial factors for hydrothermal reaction of MoS_2 and they affect its optoelectronic properties.

2. Experimental Details

2.1. Synthesis

Sodium molybdate was purchased from Sigma Aldrich and thiourea from Central Drug House and both were used as such. Precursors were weighed and the molar ratio was fixed to 1:12 and added to 60ml DI water. The reaction mixture using the precursor was stirred at 60°C for

about half an hour. The mixture was transferred to stainless steel autoclave for hydrothermal reaction at fixed time and temperature. Firstly, the reaction was optimized with respect to temperature i.e. keeping reaction time and molar ratio fixed. After that the reaction was optimized at different reaction time and lastly at different molar ratio. In all the optimization process, the other two parameters were kept constant for all the reactions. The sample obtained from all the reactions were analyzed using various characterizations and the best among all were further processed to form thin films using the drop casting method.

2.2. Characterizations

XRD was done using X-ray Diffractometer (Rigaku Miniflex600, Source: Cu-Kα wavelength 1.54 A˚), UV and PL were performed using spectrophotometer of LABINDIA and Spectro Fluorophotometer RF6000 by Shimadzu respectively. FESEM was done by model HITACHI FE-SEM SU8010. Electrical measurements were done using a 2-probe setup under vacuum condition.

3. Results and Discussion

3.1. Optimization with respect to reaction temperature

The hydrothermal reaction of sodium molybdate and thiourea is optimized at three different temperatures to find the favorable temperature for MoS_2 NS growth. Keeping all other conditions similar i.e. fixed molar ratio and reaction time for all, the hydrothermal reaction was performed at 180°C, 195°C, and 210°C. The powder obtained from all the reactions was characterized using XRD, UV-Vis spectroscopy and PL spectroscopy.

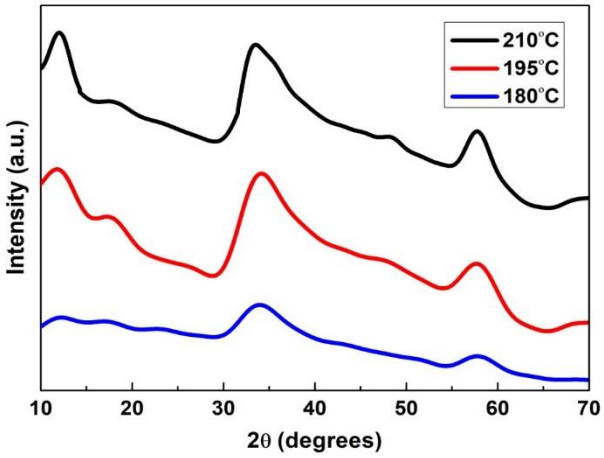

Fig. 1. XRD spectra of samples prepared at different reaction time.

Figure 1 reveals the XRD pattern of the sample prepared at different tempratures. It could be seen that only two peaks at position 2θ = 34.85° and 57.35° corresponding to (100) and (110) planes respectively are prominent in the sample prepared at 180°C [20]. It is clear that as the temperature is increased to 195°C, the peak at 13.03° corresponding to plane (002) starts to originate and peaks corresponding to plane (100) and (110) become more intense and sharp depicting the effect of increase of temperature. Along with this, an additional small peak around 18° is observed which can be indexed to hexagonal MoO_3 phase (JCPDS 00-021-0569). However, some researchers have stated that appearance of peak around low angle region in case of MoS_2 is ascribed to oxygen substituted sulfur in MoS_2 [21]. As oxygen is more electronegative than sulfur, therefore it can easily replace S and form a Mo-O bond resulting in greater repulsive force among adjacent layers. When the temperature is not sufficient for the complete reaction process, then this peak in the X-ray diffraction pattern originates. When we further increase the temperature to

210°C, it is found that the peak at 13.03° sharpens along with the other two peaks of MoS_2. This peak corresponds to (002) plane of MoS_2 and suggests the preferential development of high quality 2H- MoS_2 nanosheets. It can be seen that the best XRD results are obtained at 210°C.

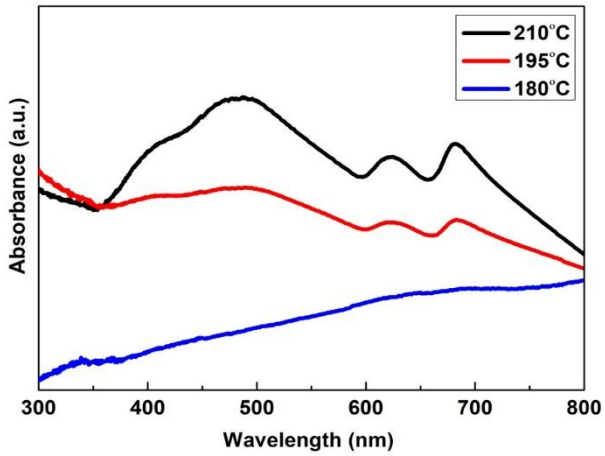

Fig. 2. UV-Vis spectra of MoS_2 samples at different temperatures.

The UV-Vis spectra of all the prepared samples at different temperature are displayed in Figure 2. It could be found that the sample synthesized at 180°C does not show any distinct peak indicating that it is not the sufficient temperature for MoS_2 synthesis. The sample prepared at 195°C exhibited two weak peaks at 627nm and 685nm that are characteristic peaks of MoS_2 suggesting the growth of MoS_2 NS [22]. The sample obtained at reaction temperature of 210°C displayed peaks at the same position as 195°C but the peaks are more intense and sharp. Additionally, there is a hump as well in the case of 210°C temperature around 470nm that arises due to Van hove singularity in MoS_2 nanosheets. From UV-Vis analysis it is clear that the reaction temperature of 210°C is the best among all the temperatures.

Figure 3 represents the PL spectra of the prepared samples at different temperature. All the samples exhibit a peak around 570 nm which is a characteristic of MoS_2 nanosheets [23]. The sample synthesized at 180°C displays no other peak whereas the one synthesized at 195°C displays a broad peak around 627 nm and the third sample prepared at 210°C exhibit peak at 627 and 673 nm as well that corresponds to a few layer MoS_2 NS. It could be inferred that at temperature of about 180°C, MoS_2 starts to form but few layer nanosheets are formed at a higher temperature of 210°C only.

After all these investigations, it is found that 180°C is not the adequate temperature for the hydrothermal reaction of ammonium molybdate and thiourea for 12 hours of reaction time. Similarly at 195°C, there is the formation of Mo-O bonds in addition to MoS_2 due to incomplete reaction between the precursors. The temperature of 210°C is found to be the best suitable temperature for formation of MoS_2 NS.

3.2. Optimization with respect to reaction time

The hydrothermal reaction between sodium molybdate and thiourea is optimized at three different times to find the favorable temperature for MoS_2 NS growth. Keeping all other conditions similar i.e. fixed molar ratio and reaction temperature for all, the hydrothermal reaction was optimized at different reaction times. Figure 4 shows XRD spectra of the samples prepared at different reaction times i.e. 12 hours, 24 hours and 48 hours. It is clear that there are three peaks at 2θ = 13.03°, 34.85° and 57.35° corresponding to (001), (100) and (110) plane of 2H- MoS_2 respectively [24]. These three peaks appear for all the reaction times. As the reaction time increases, the intensity of the peaks increases indicating preferential growth of MoS_2 NS along the planes. The MoS_2 NS can be obtained even at a reaction time of 12 hours. With the increase in time, the nanosheets begin to restack [25]. So, if few layered nanosheets are desired then reaction

time of 12 hours is sufficient. A very small peak around 17° started to originate for sample at 48 hours that is mainly due to oxide formation at higher reaction time.

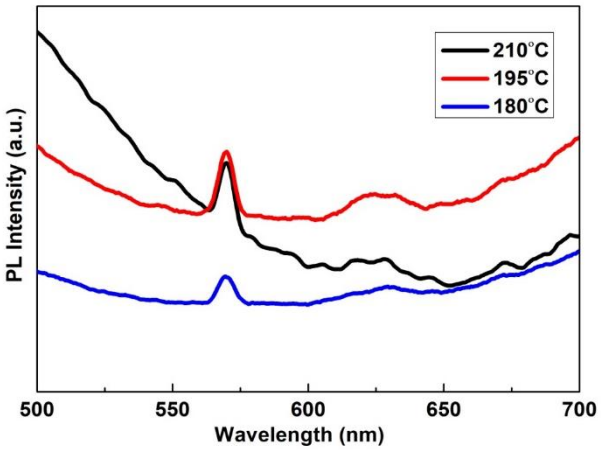

Fig. 3. PL spectra of MoS_2 samples prepared at different temperatures.

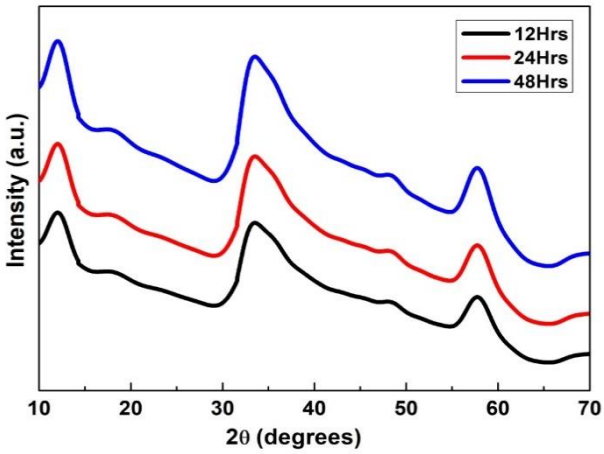

Fig. 4. XRD spectra of samples prepared at different reaction time.

The absorption spectra of the samples synthesized at different reaction time are shown in figure 5. It is observed that all the samples exhibited peak around 627 and 685 nm that is signature of few layered MoS_2 NS. With increase in reaction time, the intensity of the peaks increases. The sample prepared at 12 hours has less intense peaks than the sample synthesized at 24 hours that in turn has a little less intensity than the peaks of the sample prepared at 48 hours of reaction time. It could be seen that there is not much effect of reaction time on UV-Vis spectra of the samples. Even 12 hours of reaction time is sufficient for the reaction of thiourea and sodium molybdate.

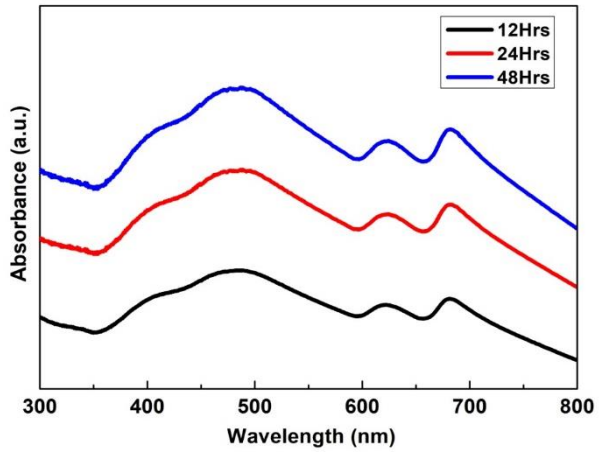

Fig. 5. Absorption spectra of samples prepared at different reaction time.

The PL spectra of the samples prepared at 12 hours, 24 hours and 48 hours are displayed in figure 6. In the case of photoluminescence, the results are a bit different from that of XRD and UV. The sample prepared using 12 hours of reaction time has the highest photoluminescence whereas the sample synthesized at 24 hours has least. This may be due to the impurities being introduced or may be due to the oxide that may be formed if the precursors are allowed to react for longer duration. It could be inferred that the reaction time does not have much influence on the structure of MoS_2 NS. As the reaction time increases, the restacking ability of MoS_2 individual layer increases. Thinner MoS_2 NS can be obtained by keeping a shorter reaction time.

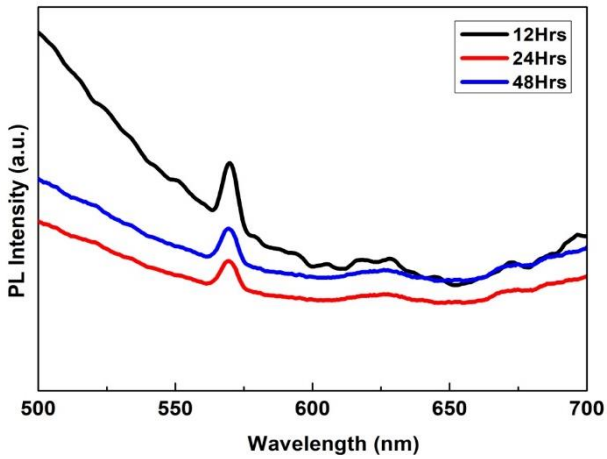

Fig. 6. PL spectra of samples prepared at different reaction time.

3.3 Optimization with respect to molar ratio

To have complete understanding of effect of various parameters on hydrothermal synthesis of MoS_2, the reaction was optimized with respect to molar ratio of precursors. The ratio of Mo:S was varied as 1:10, 1:15, 1:20, 1:25 and 1:30. The other reaction conditions were kept similar in all the reactions. The samples were characterized using XRD, UV and PL.

Figure 7 displays the XRD spectra of all the samples synthesized using different precursor ratio. It is observed that in case of molar ratio 1:10, there is no significant peak around $2\theta=13°$ corresponding to (001) plane of MoS_2 NS but there are two peaks around position $2\theta = 34°$ and 57° corresponding to the plane (100) and (110) respectively. As the molar ratio is increased to 1:15, the peak for (001) plane is visible and is intense suggesting growth of 2H- MoS_2 NS. As the

molar ratio is further increased to 1:20, 1:25 and 1:30, this peak again diminishes and a new peak around 17.5° appears that arises due to intercalation of NH_4^+ [26], NH_3 [27] etc. This result from excess of thiourea that is left unreacted and it could be seen that the intensity of this peak increases with increase in the molar ratio i.e. with an increase in the concentration of thiourea.

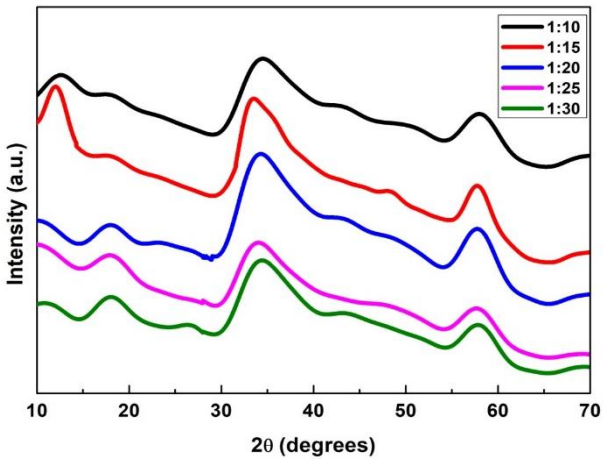

Fig. 7. XRD spectra of samples synthesized at different molar ratio.

The absorption spectra of samples prepared using various molar ratio of Mo:S are shown in figure 8. The sample synthesized using molar ratio 1:10 exhibited very weak peaks around 627 and 685 nm that are characteristics of few layered MoS_2 NS. As the molar ratio is increased to 1:15, the peaks at same position become more sharp and intense depicting the growth of MoS_2 NS. As the molar ratio is further increased to 1:20, the intensity of peak decreases which may be due to intercalation of various ions as per XRD results. The intensity and sharpness of peak decreases further with increase in molar ratio due to unreacted thiourea left after the reaction.

Figure 9 reveals PL spectra of all the samples synthesized using different molar ratio of precursors. All the samples exhibit peak around 570 nm that corresponds to MoS_2 NS. The sample using molar ratio of 1:15 displays additional peaks around 625 nm and 675 nm that are characteristics peak of few layered MoS_2 NS [28]. As the molar ratio is increased, the PL intensity of the peak decreases due to impurity/intercalation of different particles. From all these characterizations, it is found that molar ratio of 1:15 is most suitable for synthesis of MoS_2 NS.

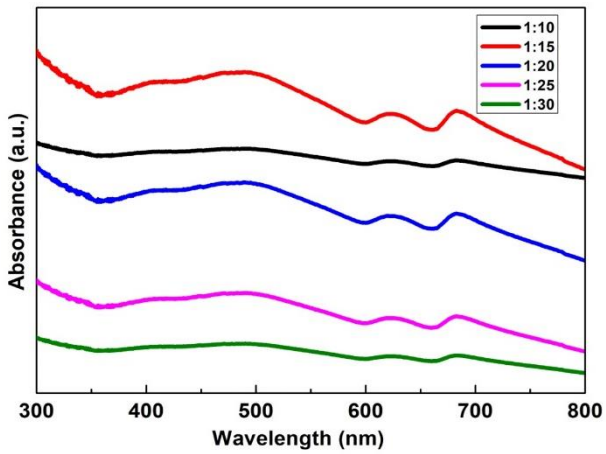

Fig. 8. Absorption spectra of samples synthesized at different molar ratio.

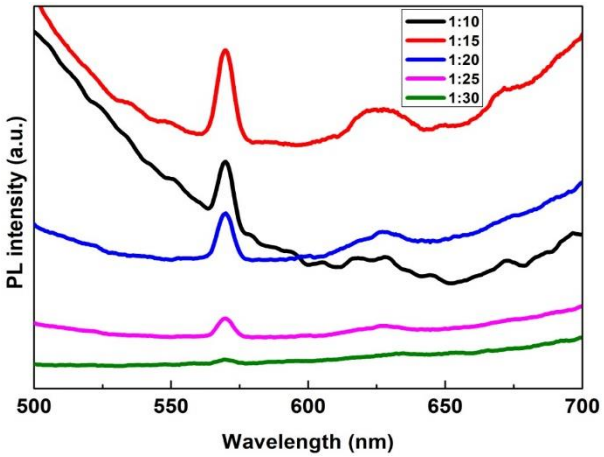

Fig. 9. PL spectra of samples synthesized at different molar ratio.

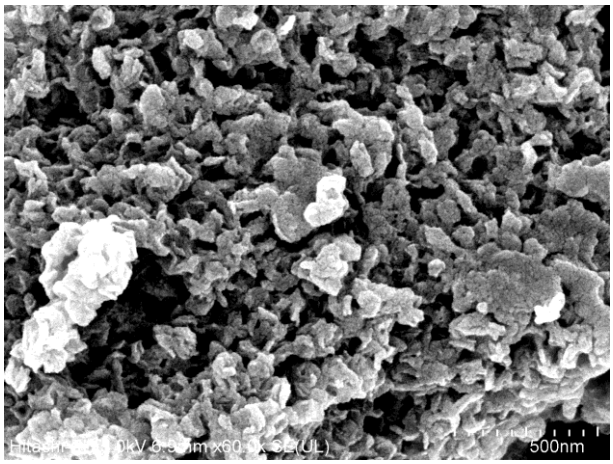

Fig. 10. FE-SEM image of MoS_2 powder.

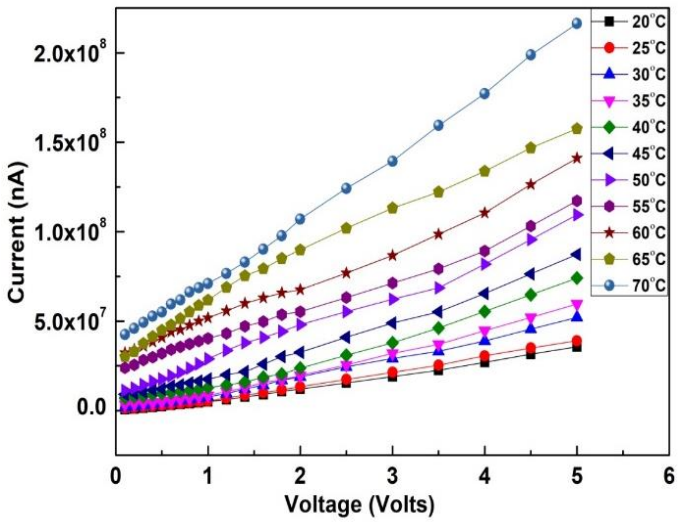

Fig. 11. Current-Voltage Characteristics of MoS_2 film.

The best sample of MoS_2 NS is obtained with hydrothermal reaction of sodium molybdate and thiourea at 210°C for 12 hours with a molar ratio of 1:15. The confirmation of NS is done using FE-SEM. Figure 10 shows FE-SEM image of as obtained MoS_2 NS. It is clearly seen that there is nanopetal like morphology with irregular distribution [29]. The sheets have arranged themselves in the form of petal of nano dimension. There is stacking of layered structure over each other. The sheets are randomly stacked over one another to form nanopetals.

Thin films of as synthesized powder are obtained by dissolving the powder in ethanol and sonicating the dispersion for 1 hour. The films are formed on glass substrate using drop casting technique and dried in an oven afterwards. The electrodes on the film are formed using conducting silver paste. The electrical measurements are done using 2-probe sample holder under vacuum of 10^{-3} mbar. The voltage is varied from 0.1V to 5V and the corresponding value of current is noted down. The temperature of the sample is also varied from 20°C to 70°C. The current-voltage characteristics of the device are displayed in figure 11. The conductivity of the best sample is found to be 1.13 Sm^{-1}.

4. Conclusions

This work presented the effect of various parameters on hydrothermal synthesis of MoS_2 NS. The effect of reaction temperature, reaction time and molar ratio of precursor is studied using XRD, UV-Vis spectroscopy and PL spectroscopy. It was found that all these parameters had an impact on structural and optical properties of obtained MoS_2 NS. The reaction temperature and molar ratio had a strong influence on the MoS_2 NS whereas reaction time had the least effect. The best conditions to obtain few layered MoS_2 NS using hydrothermal reaction of sodium molybdate and thiourea were found to be: reaction temperature of 210°C, reaction time- 12 hours and molar ratio (Mo:S) of 1:15 for precursors. Nanopetal like morphology of obtained powder was confirmed with FE-SEM. The Thin film of the sample was formed using drop casting method and electrical measurements were done under vacuum conditions. This type of optimization would help researchers to look forward to various electronic and optoelectronic applications of MoS_2 NS. It can be further utilized to make Field Effect Transistors (FETs), gas sensors, bio sensors and supercapacitors.

Acknowledgements

Dr. Kriti Sharma appreciates the Extra Mural Research grant EMR/2016/006336 from DST-SERB.

References

[1] V.B. Mohan, K. tak Lau, D. Hui, D. Bhattacharyya, Compos. Part B Eng. 142, 200 (2018); https://doi.org/10.1016/j.compositesb.2018.01.013

[2] N. Joshi, T. Hayasaka, Y. Liu, H. Liu, O.N. Oliveira, L. Lin, Microchim. Acta 185 (2018); https://doi.org/10.1007/s00604-018-2750-5

[3] J.H. Kim, T.V. Pham, J.H. Hwang, C.S. Kim, M.J. Kim, Nano Converg. 5 (2018); https://doi.org/10.1186/s40580-018-0149-y

[4] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, A. Kis, Nat. Rev. Mater. 2 (2017); https://doi.org/10.1038/natrevmats.2017.33

[5] H. Chen, S. Li, S. Huang, L.A. Ma, S. Liu, F. Tang, Y. Fang, P. Dai, Acta Mater. 222, 117438 (2022); https://doi.org/10.1016/j.actamat.2021.117438

[6] X.C. Lu, Y.Z. Lu, C. Wang, Y. Cao, Rare Met. 41, 1142 (2022); https://doi.org/10.1007/s12598-021-01875-1

[7] B. Zhao, D. Shen, Z. Zhang, P. Lu, M. Hossain, J. Li, B. Li, X. Duan, Adv. Funct. Mater. 31, 1

(2021); https://doi.org/10.1002/adfm.202105132
[8] H. Tang, B. Neupane, S. Neupane, S. Ruan, N.K. Nepal, A. Ruzsinszky, Sci. Rep. 12, 1 (2022); https://doi.org/10.1038/s41598-022-06741-3
[9] X. Xu, C. Liu, Z. Sun, T. Cao, Z. Zhang, E. Wang, Z. Liu, K. Liu, Chem. Soc. Rev. 47, 3059 (2018); https://doi.org/10.1039/C7CS00836H
[10] A. Mukhopadhyay, S. Kanungo, H. Rahaman, J. Comput. Electron. 20, 161 (2021); https://doi.org/10.1007/s10825-020-01636-w
[11] X. Yang, B. Li, Nanophotonics 9, 1557 (2020); https://doi.org/10.1515/nanoph-2019-0533
[12] M. Mathew, P. V. Shinde, R. Samal, C.S. Rout, J. Mater. Sci. 56, 9575 (2021); https://doi.org/10.1007/s10853-021-05884-4
[13] M. Liu, H. Zhu, Y. Wang, C. Sevencan, B.L. Li, ACS Mater. Lett. 3, 462 (2021); https://doi.org/10.1021/acsmaterialslett.1c00073
[14] J. Wei, Z. Zhao, F. Luo, K. Lan, R. Chen, G. Qin, 2D Mater. 9(2022); https://doi.org/10.1088/2053-1583/ac40c4
[15] Z. Zhu, A. Mosallanezhad, D. Sun, X. Lei, X. Liu, Z. Pei, G. Wang, Y. Qian, Energy and Fuels 35, 5613 (2021); https://doi.org/10.1021/acs.energyfuels.1c00165
[16] R. Kaur, K.P. Singh, S.K. Tripathi, J. Alloys Compd. 905, 164103 (2022); https://doi.org/10.1016/j.jallcom.2022.164103
[17] E. Ghaleghafi, M.B. Rahmani, Z.H. Wei, J. Mater. Sci. 56, 11749 (2021); https://doi.org/10.1007/s10853-021-06083-x
[18] N.J.A. Cordeiro, C. Gaspar, M.J. de Oliveira, D. Nunes, P. Barquinha, L. Pereira, E. Fortunato, R. Martins, E. Laureto, S.A. Lourenço, Appl. Sci. 11, 1 (2021); https://doi.org/10.3390/app11031234
[19] T.T. Xuan, L.N. Long, T. Van Khai, Vietnam J. Chem. 58, 92 (2020); https://doi.org/10.1002/vjch.2019000144
[20] K. Krishnamoorthy, G.K. Veerasubramani, S. Radhakrishnan, S.J. Kim, Mater. Res. Bull. 50, 499 (2014); https://doi.org/10.1016/j.materresbull.2013.11.019
[21] L. Luo, M. Shi, S. Zhao, W. Tan, X. Lin, H. Wang, F. Jiang, J. Saudi Chem. Soc. 23, 762 (2019); https://doi.org/10.1016/j.jscs.2019.01.005
[22] A. Arora, K. Sharma, S.K. Tripathi, 3Rd Int. Conf. Condens. Matter Appl. Phys. 2220, 020069 (2020).
[23] S. Mukherjee, R. Maiti, A. Midya, S. Das, S.K. Ray, ACS Photonics 2, 760 (2015); https://doi.org/10.1021/acsphotonics.5b00111
[24] W. Xu, Y. Fu, W. Yan, Y. Xu, M. Xue, J. Xu, Dig. J. Nanomater. Biostructures 16, 81(2021);
[25] M. Li, D. Wang, J. Li, Z. Pan, H. Ma, Y. Jiang, Z. Tian, RSC Adv. 6, 71534 (2016); https://doi.org/10.1039/C6RA16084K
[26] D. Wang, X. Zhang, S. Bao, Z. Zhang, H. Fei, Z. Wu, J. Mater. Chem. A 5, 2681 (2017); https://doi.org/10.1039/C6TA09409K
[27] X. Geng, Y. Zhang, Y. Han, J. Li, L. Yang, M. Benamara, L. Chen, H. Zhu, Nano Lett. 17, 1825 (2017); https://doi.org/10.1021/acs.nanolett.6b05134
[28] S. Golovynskyi, I. Irfan, M. Bosi, L. Seravalli, O.I. Datsenko, I. Golovynska, B. Li, D. Lin, J. Qu, Appl. Surf. Sci. 515, 146033 (2020); https://doi.org/10.1016/j.apsusc.2020.146033
[29] M. Ikram, M.I. Khan, A. Raza, M. Imran, A. Ul-Hamid, S. Ali, Phys. E Low-Dimensional Syst. Nanostructures 124, 114246 (2020); https://doi.org/10.1016/j.physe.2020.114246