IOP Conf. Series: Journal of Physics: Conf. Series **1230** (2019) 012100 doi:10.1088/1742-6596/1230/1/012100

# Effects of the solvent during the preparation of $MoS_2$ nanoparticles by laser ablation

**Makoto Kanazawa[1], Pankaj Koinkar[1*], Kei-ichiro Murai[2], Toshihiro Moriga[2], Akihiro Furube[1*]**

[1]Department of Optical System Engineering, Tokushima University, 2-1 Minamijosanjima-cho, Tokushima, Tokushima, 770-8506, Japan
[2]Department of Applied chemistry, Tokushima University, 2-1 Minamijosanjima-cho, Tokushima, Tokushima, 770-8506, Japan

Email: koinkar@tokushima-u.ac.jp*, furube.akihiro@tokushima-u.ac.jp*

**Abstract**. Pulsed laser ablation in liquid is a well-known and effective method which can be used to prepare the various nanostructures. However, ablated samples have various problems such as wide size distribution, and effect of solvent to sample during laser ablation in liquid has not been well understood. In response to these problems, in this study, we prepared nanoparticles by irradiating nanosecond laser to samples using different solvents. The experimental results of prepared samples were compared, and we evaluated how the different solvents affect to their morphological and optical properties. The morphology, crystal structures and optical properties of the $MoS_2$ nanoparticle were characterized by Scanning electron microscopy, X-ray diffraction, and UV-Vis absorption spectroscopy. Upon the laser ablation of the samples, the absorbance of UV-Vis spectra increased as approaching the shorter wavelength side. From the SEM images, it confirmed that the particle size became smaller for laser ablated $MoS_2$ sample, which is good agreement with the result of UV-Vis spectra. The XRD spectra shows the appearance of new peak for laser ablated $MoS_2$ in methanol as compared to those samples ablated in ethanol and *N*-methyl-2-pyrrolidone. It can be said that the crystal structure of the sample has changed after ablation. It suggested that because the particle size became smaller after ablation and the band gap increased. Such $MoS_2$ nanostructure has its own importance for optoelectronics devices.

## 1. Introduction

Nanomaterials have characteristics that are noticeable different from bulk materials. Two-dimensional (2D) atomically thin inorganic layered materials have attracted much attention as new nano-functional materials due to its outstanding electrical and optical properties [1-3]. Currently, the significant interest in planar devices have attracted great attention in transition metal dichalcogenide (TMDC) in this context, TMDC materials such as molybdenum disulfide ($MoS_2$), which has two-dimensional structure similar to graphene, is considered as promising material for future planer devices. The $MoS_2$ has been investigated and its shows that properties exhibited can be potential candidates for planar device technologies and to improve the performance of transistors, LED, solar cells and so on. In addition, few reports suggested methods to produce nanostructure of $MoS_2$ as well as nanoparticles of another material with good efficiency, which can be used practical application for the fabrication of technological various devices [4-6]. Among these various ways to produce nanostructure, pulsed laser

ablation in liquid (PLAL) is considered as one of useful, simple and easy ways to synthesize nanostructure. As compared to other experimental methods, PLAL can obtain stable suspensions of various nanostructures in a wide range of liquids with a one-step, simple and economic procedure [7,8]. However, ablated samples have various problems such as wide size distribution and effect of solvent during PLAL process is not completely elucidated yet. To addressed these problems, in the present study, we have prepared $MoS_2$ nanoparticles by irradiating nanosecond laser using the different solvents. The morphology, crystal structures and optical properties of the $MoS_2$ nanoparticle were characterized by scanning electron microscopy, X-ray diffraction, and UV-Vis absorption spectrum. After laser ablation, the experimental results of the all prepared samples have been compared, and we tried to evaluate how the solvents used affect the morphological changes and optical property.

## 2. Experimental procedure

### *2.1. Materials*

Commercial $MoS_2$ particles (average size less than 2μm) were purchased from Sigma-Aldrich and they were used without any prior treatment and purification treatment. Methanol, ethanol, and *N*-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich.

### *2.2. Synthesis of $MoS_2$ nanoparticle*

Commercial $MoS_2$ particles of 80 mg (from Sigma-Aldrich, average size less than 2μm) were magnetically stirred in methanol, ethanol, and NMP of 40 ml and its aqueous solution samples were sonicated using bath-type sonicator for 1 hour to obtain well dispersed solution. After sonification, these samples were exposed to the laser pulses from the second harmonic of a Spectra Physics Nd:YAG laser (wavelength 532 nm, repetition frequency 10 Hz , 10 ns fwhm/pulse, 55 mJ $pulse^{-1}$) for 120 minutes. After laser ablation, a colloidal suspension was heated to evaporate solvent to get the resulted $MoS_2$ in the form of dry powder. These samples were characterized using UV-visible spectrophotometry, X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) to confirm nanostructure formation and reveal the surface morphology changes and structural features. XRD spectra of synthesized $MoS_2$ nanostrcuture were measured by a X-ray diffractrometer (Rigaku SmartLab 9 kW) with CuKα (λ = 1.54184 Å) radiations operated at the voltage of 45 kV and the current of 15 mA in the 2θ range from 20° to 80°. The surface morphology was investigated using a FE-SEM (S4700, Hitachi High-Technologies) while the UV-Visible absorption spectra were recorded by means of the UV-Visible spectrophotometer (V-670, JASCO Corporation).

## 3. Results and discussion

### *3.1. XRD pattern analysis*

To identify the crystal structures of different $MoS_2$ powders prepared using different solvents, XRD measurements were carried out for each sample. Figure 1 shows the X-Ray diffraction pattern of the laser ablated $MoS_2$ nanostructures for 120 min in different solvents, namely ethanol, methanol, and NMP. In the sample before ablation, a characteristic peak was confirmed in bulk $MoS_2$. In case of laser ablated samples, it is clearly observed that there is a systematic decrease in intensity of characteristics peak and this could be due to the structural reflection from the crystal plane disappearing when irradiated with X-rays. Also, the diffraction patterns show that all major peaks present a broadening depend on the nature of the solvent. As ccompared to the sample before ablation, new peaks appeared for laser ablated samples and were confirmed their presence at 31.25, 34.8, 35.94, 42.45, 40.55 degrees. In addition, only peak at 40.5 degrees was observed for $MoS_2$ prepared using methanol as a solvent. According to the prior literature, the $MoS_2$ structure has been changed after the laser using methanol [15]. Furthermore, it can be seen that the peak intensity corresponding to a peak

at 44 degrees (106) is stronger in the samples treated with the laser ablation. Thus, the XRD pattern results indicate that $MoS_2$ size changes after the laser ablation with solvent medium.

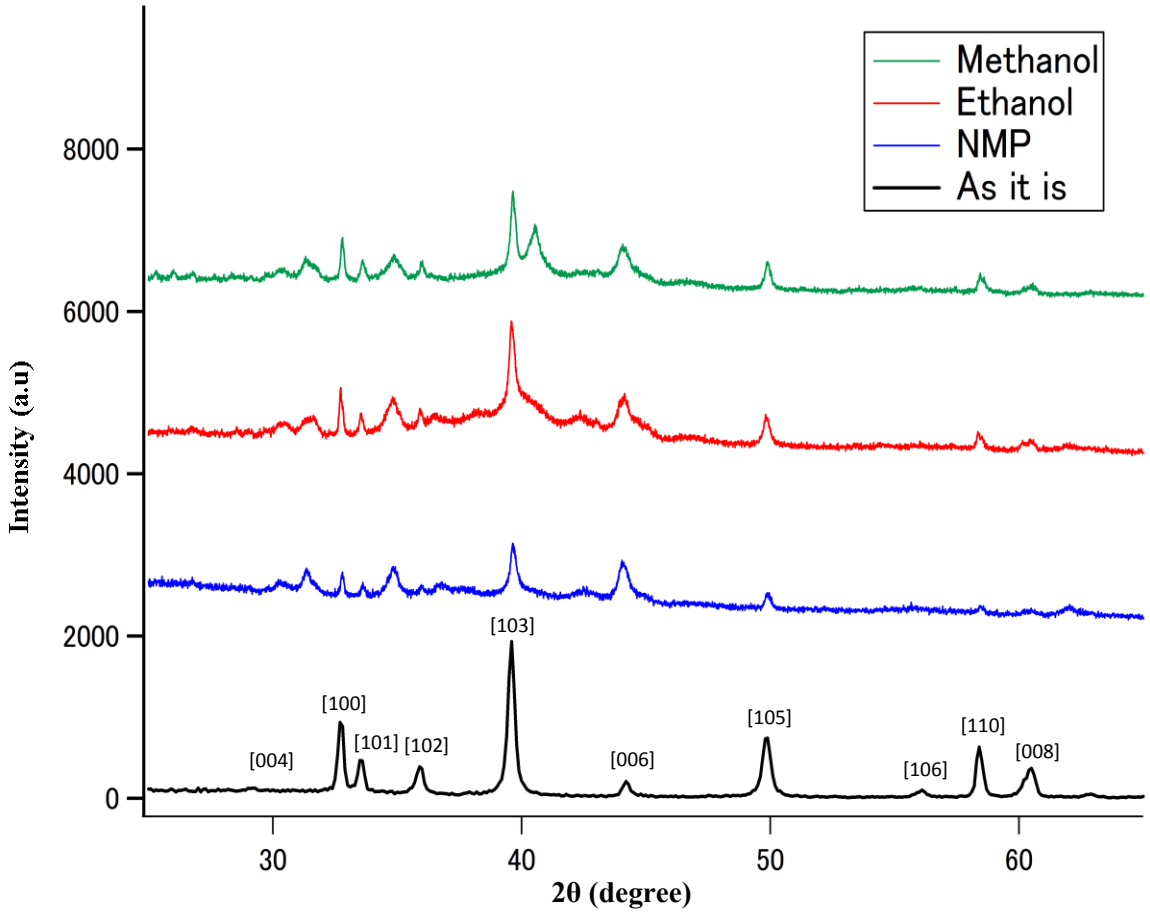


**Figure 1.** XRD patterns of (a) bulk $MoS_2$ and laser ablated $MoS_2$ in different solvents (b) ethanol (c) methanol and (d) NMP.

*3.2. Scanning electron microscopy analysis*

Typical SEM images of the bulk and as prepared $MoS_2$ nanoparticles in different solvents are illustrated in in Figure 2(a-d). The scale bars indicated in all images are 1 µm. Fig. 2 (a) displays SEM image of bulk $MoS_2$ with micron-scale sheets (microflake) having the size about 2 µm . It is found that that the morphology and the size of $MoS_2$ nanoparticles depend on the nature of solvent used during the laser ablation. In case of NMP used as a solvent, the formation of nanosheets of approximately several hundred nm to less than 50 nm could be observed as shown in Fig. 2(b). When ethanol was used as a solvent, the uniform formation and large amounts of spherical particles having the diameter about 20 nm to 50 nm were observed as shown in Fig 2(c). However, when methanol was used as a solvent, nanosheets from 500 nm to less than 50 nm as well as spherical particles having a diameter of 20 nm to several hundred nm as illustrated in Fig. 2(d). These results indicate the formation of spherical or nanosheet-like nanoparticles as confirmed by the SEM image and becomes sufficiently smaller than the bulk $MoS_2$. In particular, it is reported that 2D and 3D nanosheet $MoS_2$ can be formed by laser ablation using methanol [15]. Focusing only on the result of methanol, the sheet-like structure in SEM images seems to be 2D nanosheet $MoS_2$, while the spherical shape one obtained in this experiment seems to be 3D nanosheet $MoS_2$ as indicated with XRD patterns, which showed the characteristic of morphology with new peak. Furthermore, SEM image of bulk $MoS_2$ show microsheets with sharp corner whereas for the $MoS_2$ samples, laser-treated in different solvents,

revealed that most of the nanosheets and nanoparticles are found with the rounded. This could be caused by the heat generated during the ablation process.

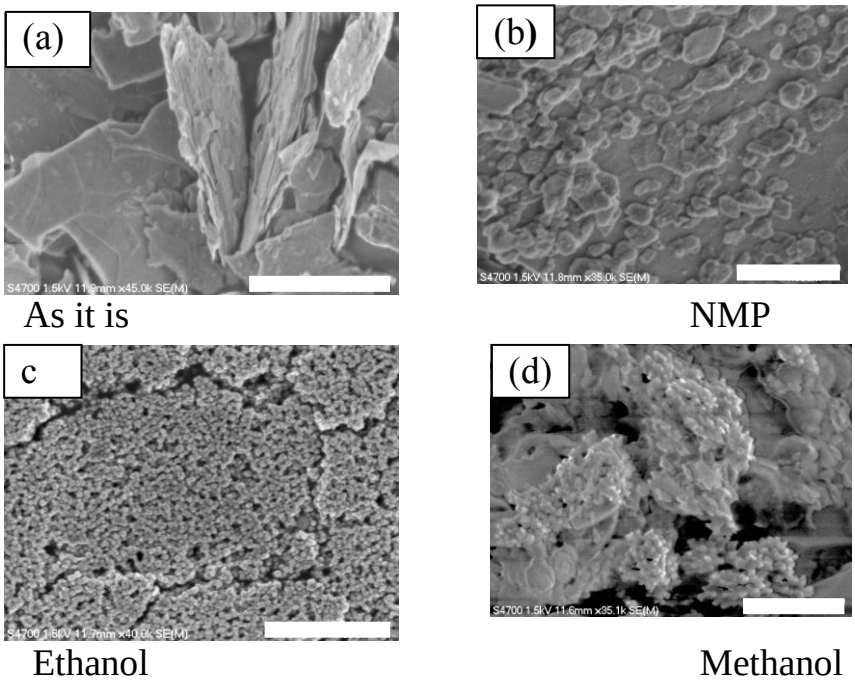


**Figure 2.** FE-SEM images of bulk $MoS_2$ and laser ablated $MOS_2$ in different solvents .

*3.3. UV-visible spectroscopy analysis*

In order to measure UV-vis spectrum spectra of nanoparticles, each sample of 2 ml taken out from ablated samples was centrifuged at 6000 r.p.m for 10 min. and then UV-vis spectra of precipitate liquid and the supernatant liquid of each samples were measured as shown in Fig. 3 and Fig.4 respectively. The UV-Vis optical absorption spectra were recorded at room temperature in the wavelength region of 200–800 nm. Fig.3 shows UV-vis spectra of bulk and laser ablated $MoS_2$. Each sample is diluted to 100 times so that the sample peak can be confirmed. In case of bulk $MoS_2$ sample i.e. before ablation, characteristic peaks at about 630 nm and 690 nm in the form of a small noticeable hump were observed. According to earlier literature, the separation energy (about 59 nm) between A and B excitonic transitions can be explained with spin-orbit splitting, and their characteristic energy can be assigned to A and B excitonic transitions on the high energy side of first absorption threshold splitting value is approximately 60 nm (0.17 eV) [11-14]. In case of laser ablated $MoS_2$ using NMP as a solvent, a noticeable peak was not observed around 260 nm in the sample after ablation. However, the value of the absorbance became larger as approaching the shorter wavelength side and this could be because of the particle size reduced by laser ablation and the band gap is increased by the quantum size effect. [10]. In order to confirm this, only the supernatant was collected from the sample set at a speed of 6000 rpm and subjected to centrifugation for 10 minutes. In this way, we have obtained a high concentration of exfoliated particles in the supernatant and thus the absorbance of the sample containing only exfoliated particles was measured as displayed in Fig. 4. As a result, unlike the spectrum before applying the sample to the centrifugal separator, it showed significant absorption on the short wavelength side. While, in the sample using ethanol, the effect of miniaturization by laser ablation was confirmed as there are increase in the absorbance on the shorter wavelength side as well as a small hump of two characteristic peaks at 260 nm and 280 nm observed as shown in Fig. 3. In addition, when the absorption spectrum of the supernatant liquid of the sample employed to the centrifuge was measured, it was clearly seen that that the peak intensities at 260 nm and 280 nm

became stronger as depicted in Fig 4. Even with a sample prepared using methanol as a solvent, the effect of miniaturization by laser ablation was confirmed due to the increase in absorbance on the shorter wavelength side. This result is well in agreement with the earlier reported data [15]. Similarly to ethanol, when the absorption spectrum of the supernatant liquid taken from centrifuged sample was measured, it was found that the peak intensities at 260 nm and 280 nm became stronger as indicated in Fig. 4. Therefore, it suggested that the particle size became smaller after laser ablation and also the band gap increased due to the quantum size effect. This result well explains that the absorbance of the absorption spectrum of the sample has greatly increased on the short wavelength side.

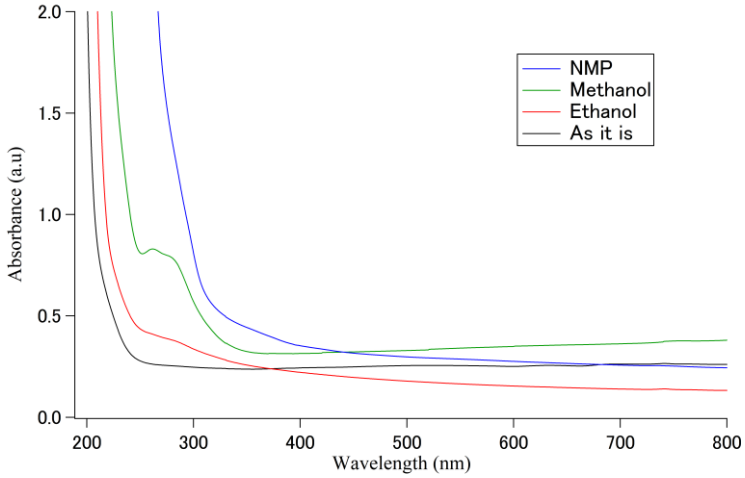


**Figure 3.** UV-vis spectra of precipitated bulk $MoS_2$ and laser ablated $MoS_2$ ablated in various solvents

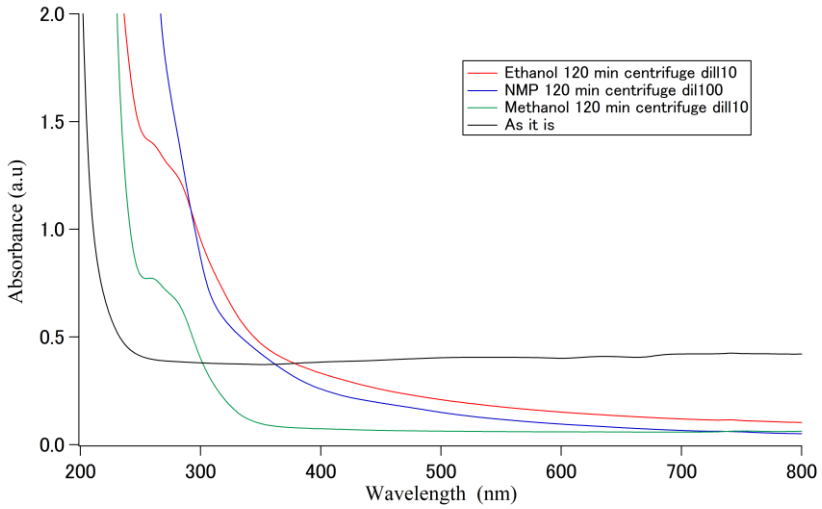


**Figure 4.** UV-vis spectra of supernatant bulk $MoS_2$ and laser ablated $MoS_2$ ablated in various

## 4. Conclusions

In this study, we have prepared $MoS_2$ nanoparticles by irradiating nanosecond laser to samples in different solvents and compared the experimental results of the prepared samples to evaluate the effect of the solvent based on their morphological, structural and optical properties. The XRD pattern results indicate that $MoS_2$ size changes after the laser ablation with different solvent medium and the presence of new peaks were confirmed in laser ablated samples. Particularly in samples using methanol, presence of particles of $MoS_2$ having different shapes was confirmed. From the results of the SEM

image, it was seen that there was a difference in shape of particles produced by ablation using different solvents. Furthermore, UV-Vis spectra confirm the effect of miniaturization by laser ablation due to the increase in absorbance on the shorter wavelength side. There are still various problems even for the synthesis of nanoparticles by laser ablation in liquid medium. Comparing and examining the results obtained by actually changing the conditions of the sample will help to understand the effect of laser ablation on the preparation of nanoparticles. In the future, we will plan to study and clarify how to effectively and efficiently produce $MoS_2$ nanoparticles with desired shape and optical properties using PLAL. It may accelerate application to planar devices such as LEDs and solar panels.

**References**

[1] Castellanos-Gomez, A.; Poot, M.; Steele, G. A.; van der Zant, H. S. J.; Agraït, N.; Rubio-Bollinger, G. Elastic Properties of Freely Suspended $MoS_2$ Nanosheets. Adv. Mater. 2012, 24, 772−775.

[2] Gaur, A. P. S.; Sahoo, S.; Ahmadi, M.; Guinel, M. J.-F.; Gupta, S. K.; Pandey, R.; Dey, S. K.; Katiyar, R. S. Optical and Vibrational Studies of Partially Edge-Terminated Vertically Aligned Nanocrystalline $MoS_2$ Thin Films. J. Phys. Chem. C 2013, 117, 26262−26268.

[3] Ruinart de Brimont, M.; Dupont, C.; Daudin, A.; Geantet, C.; Raybaud, P. Deoxygenation Mechanisms on Ni-Promoted $MoS_2$ Bulk Catalysts: A Combined Experimental and Theoretical Study. J. Catal. 2012, 286, 153−164.

[4] Late, D. J.; Liu, B.; Matte, H. S. S. R.; Rao, C. N. R.; Dravid, V. P. Rapid Characterization of Ultrathin Layers of Chalcogenides on SiO2/Si Substrates. Adv. Funct. Mater. 2012, 22, 1894−1905.

[5] Late, D. J.; Liu, B.; Matte, H. S. S. R.; Dravid, V. P.; Rao, C. N. R. Hysteresis in Single-Layer $MoS_2$ Field Effect Transistors. ACS Nano 2012, 6, 5635−5641.

[6] Kashid, R. V.; Late, D. J.; Chou, S. S.; Huang, Y. K.; De, M.; Joag, D. S.; More, M. A.; Dravid, V. P. Enhanced Field-Emission Behavior of Layered $MoS_2$ Sheets. Small 2013, 9, 2730−2734.

[7] S. Barcikowski, F. Devesa, K. MoldenhauerImpact and structure of literature on nanoparticle generation by laser ablation in liquids J. Nanopart. Res., 11 (2010), pp. 1883-1893

[8] G.W. YangLaser ablation in liquids: application in the synthesis of nanocrystals, Progr. Mater. Sci., 52 (2007), pp. 648-698

[9] Shuichi Hashimoto. Pulsed Laser-Ablation-Induced Fabrication of Metal Nanoparticles in Liquids.Volume 45, Number 5 2017, The Review of Laser Engineering.

[10] Herme G. Baldovı , Marcos Latorre-Sanchez . Ivan Esteve-Adell . Anish Khan . Abdullah M. Asiri . Samia A. Kosa . Hermenegildo Garcia (2016) Generation of mos2 quantum dots by laser ablation of mos2 particles in suspension and their photocatalytic activity for H2 generation. (J Nanopart Res) 18:240

[11] Wilcoxon, J. P.; Newcomer, P. P.; Samara, G. A. Synthesis and Optical Properties of MoS2 and Isomorphous Nanoclusters in the Quantum Confinement Regime. J. Appl. Phys. 1997, 81, 7934−7944.

[12] Abrams, B. L.; Wilcoxon, J. P. Nanosize Semiconductors for Photooxidation. Crit. Rev. Solid State Mater. Sci. 2005, 30, 153−182.

[13] Thurston, T. R.; Wilcoxon, J. P. Photooxidation of Organic Chemicals Catalyzed by Nanoscale MoS2. J. Phys. Chem. B 1999, 103, 11−17.

[14] Wilcoxon, J. P.; Newcomer, P. P.; Samara, G. A.; Venturini, E. L.; Williamson, R. L. Fundamental Science of Nanometer-Size Clusters; Sandia National Labs.: Albuquerque, NM (USA), October 1995; pp 19−30.

[15] Tugba Oztas,Huseyin Sener Sen, Engin Durgun, and Bülend Ortaç.Synthesis of Colloidal 2D/3D $MoS_2$ Nanostructures by Pulsed Laser Ablation in an Organic Liquid Environment. *J. Phys. Chem. C*, 2014, 118 (51), pp 30120–30126.