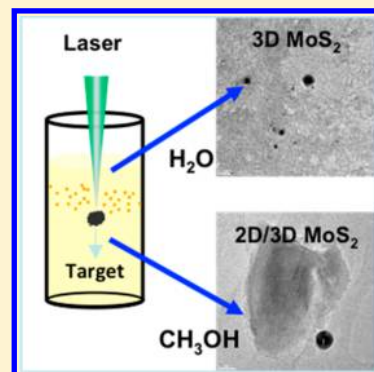


# Synthesis of Colloidal 2D/3D MoS<sub>2</sub> Nanostructures by Pulsed Laser Ablation in an Organic Liquid Environment

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**ABSTRACT:** Two-dimensional MoS<sub>2</sub> nanosheets (2D MoS<sub>2</sub> NS) and fullerene-like MoS<sub>2</sub> nanostructures (3D MoS<sub>2</sub> NS) with varying sizes are synthesized by nanosecond laser ablation of hexagonal crystalline 2H-MoS<sub>2</sub> powder in organic solution (methanol). Structural, chemical, and optical properties of MoS<sub>2</sub> NS are characterized by optical microscopy, scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and Raman and UV–vis–near infrared absorption spectroscopy techniques. Results of the structural analysis show that the obtained MoS<sub>2</sub> NS mainly present a layered morphology from micrometer to nanometer sized surface area. Detailed analysis of the product also proves the existence of inorganic polyhedral fullerene-like 3D MoS<sub>2</sub> NS generated by pulsed laser ablation in methanol. The possible factors which may lead to formation of both 2D and 3D MoS<sub>2</sub> NS in methanol are examined by ab initio calculations and shown to correlate with vacancy formation. The hexagonal crystalline structure of MoS<sub>2</sub> NS was determined by XRD analysis. In Raman spectroscopy, the peaks at 380.33 and 405.79 cm<sup>-1</sup> corresponding to the E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> phonon modes of MoS<sub>2</sub> were clearly observed. The colloidal MoS<sub>2</sub> NS solution presents broadband absorption edge tailoring from the UV region to the NIR region. Investigations of MoS<sub>2</sub> NS show that the one-step physical process of pulsed laser ablation–bulk MoS<sub>2</sub> powder interaction in organic solution opens doors to the formation of “two scaled” micrometer- and nanometer-sized layered and fullerene-like morphology MoS<sub>2</sub> structures.



## INTRODUCTION

The synthesis of semiconductor nanomaterials attracts a great deal of interest because of the physical, chemical, electrical, and optical properties of the nanomaterials.<sup>1</sup> The size- and shape-dependent properties of semiconductor nanomaterials possess potential applications in new nanomaterials-based photonics and optoelectronics devices.<sup>2</sup> One of the most rapidly growing scientific areas is the generation technique of nanocrystals from group IV elements. Nanocrystals from this group are two-dimensional (2D) honeycomb lattice (such as graphene) semiconductor materials. Alternately, MoS<sub>2</sub> is a newly emerging transition-metal dichalcogenide semiconductor material. Because of its natural bandgap (~1.2 eV indirect bandgap in multilayer/bulk form, ~1.85 eV direct bandgap in monolayer form), MoS<sub>2</sub> presents advantageous properties compared to group IV semiconductor or graphene in many applications.<sup>3,4</sup> It is also shown that both microscaled MoS<sub>2</sub> and nanoscaled MoS<sub>2</sub> have perfect resistance against oxidation in a moist air environment, which makes them more durable in device fabrication compared to group IV semiconductor nanosheets (NS).<sup>5,6</sup>

In literature, the existence of MoS<sub>2</sub> NS in the form of fullerene-like NS have been predicted and experimentally demonstrated.<sup>7</sup> The importance of such a kind of structures is due to the presence of peculiar features. It is now recognized that polyhedral closed-caged NS under certain energetic considerations are thermodynamically more stable than isolated basal sheets of the lamellar structure.<sup>8</sup> These MoS<sub>2</sub> NS have attracted considerable attention recently because of their

potential use in microlubrication,<sup>9</sup> oil refinement,<sup>10</sup> photocatalysis,<sup>11</sup> and photodetector applications.<sup>12</sup>

On the other hand, MoS<sub>2</sub> has interesting properties in the case of a 2D ultrathin atomic layer structure. The unique properties of 2D MoS<sub>2</sub> NS make them a perfect alternative material for heterogeneous catalysis, hydrogen storage, lithium–magnesium ion batteries,<sup>13,14</sup> and various biomedical applications.<sup>15</sup> Since MoS<sub>2</sub> NS possess promising photoelectric properties that are tunable by physical layer thickness of 2D MoS<sub>2</sub> NS, various electronic and optoelectronic devices are fabricated based on MoS<sub>2</sub>.<sup>15</sup> Despite the fact that single-layer MoS<sub>2</sub> has a large direct band gap of 1.8 eV and low electron mobility, a single-layer transistor based on MoS<sub>2</sub> has been developed.<sup>16</sup> This work has been a great indicator to the usage of MoS<sub>2</sub> in optoelectronic applications. For MoS<sub>2</sub>-based transistor applications, it is even possible to achieve an applicable electron mobility level. In the literature, it was also shown that MoS<sub>2</sub> is a potential candidate in solar cell applications.<sup>17,18</sup> Various properties and possible applications of 2D-MoS<sub>2</sub> and its nanoribbons have also been an active subject of theoretical studies.<sup>19–23</sup> All these recent research results clearly demonstrate that 2D MoS<sub>2</sub> NS present a great potential for nanoelectronic and nanophotonic applications.

There are various methods to synthesize 2D and 3D MoS<sub>2</sub> NS including mechanical exfoliation,<sup>24,25</sup> solution-based ex-

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foliation,<sup>26</sup> CVD-based synthesis,<sup>27</sup> thermal decomposition,<sup>28</sup> powder sublimation,<sup>29</sup> and electrochemical/chemical synthesis.<sup>5</sup> In addition, most of the synthesis approaches for the formation of MoS<sub>2</sub> NS require hazardous compounds such as H<sub>2</sub>S and H<sub>2</sub> with difficulties in handling and storage.<sup>30</sup> Pulsed laser ablation (PLA) is another promising method to generate 2D and 3D NS.<sup>13</sup> The usage of unique scientific facilities of laser-matter interaction allows the generation of a wide variety of noble NS<sup>31</sup> and semiconductor nanocrystals<sup>32</sup> with different structural morphologies. Compared to other methods; PLA, especially in liquids, is a versatile method of generating colloidal, highly pure and agent-free NS. In the case of MoS<sub>2</sub> NS generation with PLA, chemical precursors are definitely not required. There have been a few reports about fullerene-like 3D MoS<sub>2</sub> NS generation by laser ablation technique only in water. Wu et al. showed that 3D MoS<sub>2</sub> NS obtained through laser ablation are fullerene-like and have good solubility and also are also biocompatible in nature, which makes 3D MoS<sub>2</sub> NS applicable in various biomedical areas.<sup>13</sup>

Here, we present a relatively simple, one step, faster method for the synthesis of different MoS<sub>2</sub> NS morphologies in organic liquid. The use of the PLA technique to crystalline 2H-MoS<sub>2</sub> powder in methanol generates both colloidal 2D and 3D MoS<sub>2</sub> NS. The majority of MoS<sub>2</sub> NS produced by PLA have a layered morphology from large size (micrometer) to small size (nanometer). Other parts of our sample consist of inorganic polyhedral fullerene-like 3D MoS<sub>2</sub> NS. In addition, ab initio calculations are performed in order to reveal the possible factors which may lead to different morphologies. The optical microscope analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman and UV–vis–near infrared (NIR) absorption measurements were used to further understand structure, composition, size, chemical, and optical properties of MoS<sub>2</sub> NS. XRD analysis provided evidence about formation of the hexagonal crystalline structure MoS<sub>2</sub> NS. In Raman spectroscopy, generation of the crystalline nature of the MoS<sub>2</sub> was confirmed. The colloidal MoS<sub>2</sub> NS solution presented broadband absorption edge tailoring from the NIR region to the UV region.

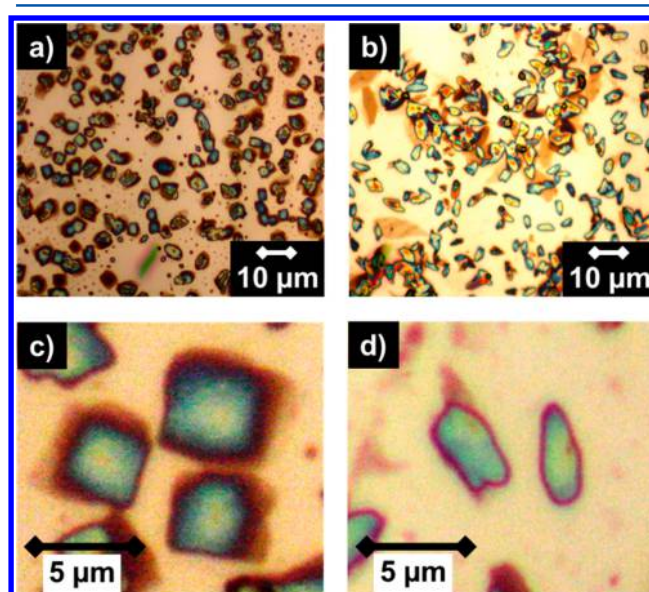
## EXPERIMENTAL SECTION

Bulk MoS<sub>2</sub> powder (99.99%, Sigma-Aldrich) and pure methanol (>99%, Sigma-Aldrich) were used as-received without any additional purification. Colloidal MoS<sub>2</sub> NS solution was generated by using the PLA technique in methanol. The commercial nanosecond pulsed ND:YLF laser operated at 527 nm with a pulse duration of 100 ns, average output power of 16 W at a pulse repetition rate of 1 kHz corresponding to a pulse energy of 16 mJ being used. A 1 mg portion of bulk MoS<sub>2</sub> powder was added to 10 mL of pure methanol for the PLA experiment. The laser beam was focused on the bulk MoS<sub>2</sub> powder target, which is placed in a glass vial containing 10 mL of methanol, using a plano-convex lens with a focal length of 50 mm. The PLA process was carried out for 15 min. To obtain a well dispersed NS solution, the colloidal NS were continuously stirred by a magnetic stirrer at 800 rpm during the laser ablation process. The color of the final product became dark-orange. Then, the produced NS were characterized via optical microscope analysis, SEM, TEM, XRD, Raman spectroscopy, and UV–vis spectroscopy to get information in detail about their physical and chemical properties.

To investigate the atomistic nature, structural effects, and MoS<sub>2</sub>-solvent interaction, we used first-principles computational techniques based on density functional theory,<sup>33,34</sup> implemented in the Vienna ab initio simulation package.<sup>35,36</sup> The exchange-correlation potential was approximated within the generalized gradient approximation (GGA) using PBE functional<sup>37</sup> including van der Waals correction (VdW)<sup>38</sup> and projector augmented-wave (PAW)<sup>39</sup> potentials. The calculations for nanomeshes were done at  $\Gamma$ -point using a plane-wave basis set with a kinetic energy cutoff of 500 eV. All structures were optimized with simultaneous minimization of the total energy and interatomic forces. The convergence on the total energy and force was set to 10<sup>-5</sup> eV and 10<sup>-2</sup> eV/Å, respectively.

## RESULTS AND DISCUSSION

The first structural investigation of MoS<sub>2</sub> NS was performed by using an optical microscope (Carl Zeiss, Axio Imager). Figure 1

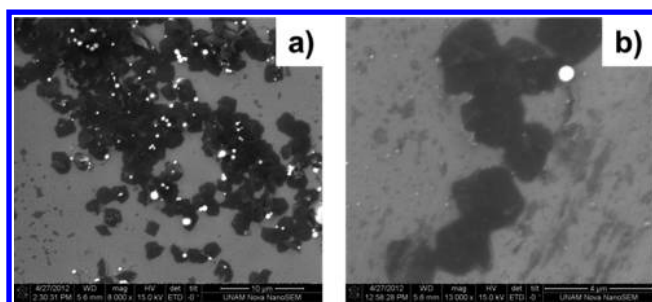


**Figure 1.** Optical microscope images of MoS<sub>2</sub> NS showing micrometer size layered morphology on a silicon substrate.

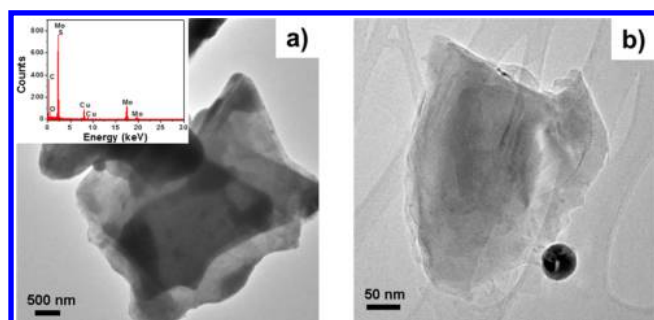
shows the optical microscope images of MoS<sub>2</sub> NS. The images clearly prove that the obtained MoS<sub>2</sub> NS have layered morphology, and their sizes reach up to the micrometer scale. We also observed that 2D MoS<sub>2</sub> NS have a quadratic shape or elliptical-like structure.

The morphology of MoS<sub>2</sub> NS was then studied by using SEM (FEI, Quanta 200 FEG) at an accelerating voltage to 20 kV to be able to get information in detail about their structure. SEM images (see Figure 2) demonstrate that 2D MoS<sub>2</sub> NS were produced on both the microscale and nanoscale. On the other hand, we recognize that 3D MoS<sub>2</sub> NS were also produced by using a one-step PLA technique in methanol. It is understood that the majority of MoS<sub>2</sub> NS have a layered shape and the size of the 3D MoS<sub>2</sub> NS is relatively small.

The morphology and the elemental analysis of the MoS<sub>2</sub> NS drop-cast onto carbon-coated TEM grid were also performed by using FEI–Tecnai G<sup>2</sup>F30 at an operating voltage of about 300 kV equipped with an energy dispersive X-ray spectroscopy (EDS) system. Figure 3 indicates that the morphology of the final 2D MoS<sub>2</sub> NS product presents both few and multilayer



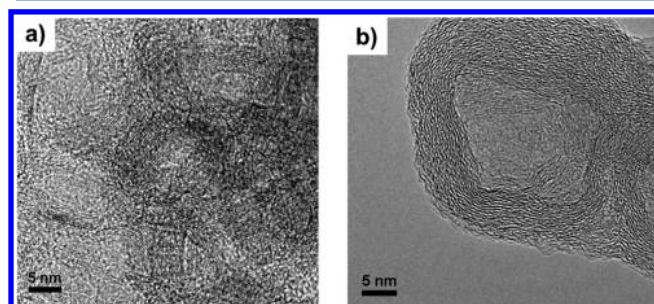
**Figure 2.** Representative SEM images of MoS<sub>2</sub> NS obtained by PLA in an organic liquid. SEM images confirm 2D MoS<sub>2</sub> NS and 3D MoS<sub>2</sub> NS production in one step.



**Figure 3.** Representative TEM images of the MoS<sub>2</sub> NS indicating multilayer and few NS by the PLA of bulk MoS<sub>2</sub> powder in methanol. Inset, EDS spectrum.

NS, and their surface area sizes vary from the micrometer to nanometer scale. Furthermore, EDS analysis shows that our sample includes only Mo, S, C, Cu, and O atoms. The peaks related to carbon (C), oxygen (O), and copper (Cu) are associated with the TEM grid used. The presence of the Mo and S peaks in the EDS spectrum confirms that MoS<sub>2</sub> NS were successfully generated by the PLA technique with a small of amount of impurities observed.

TEM results in detail are given in Figure 4. This figure shows that 3D MoS<sub>2</sub> NS have a fullerene-like crystalline structure, and



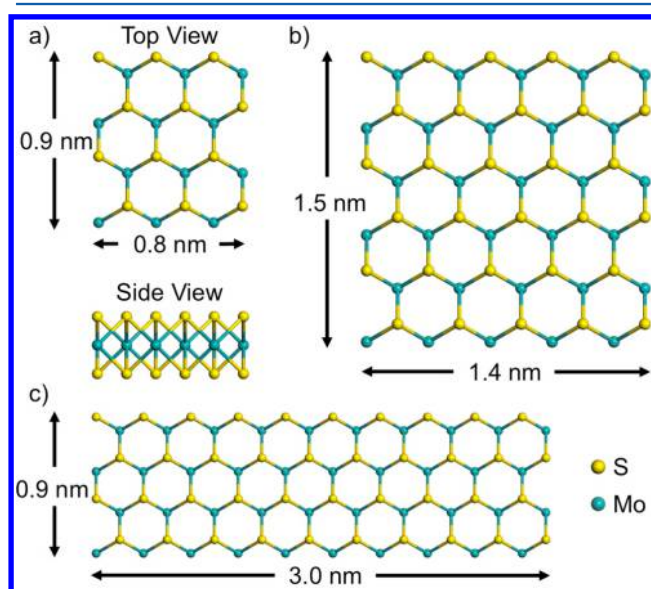
**Figure 4.** HRTEM images of 3D MoS<sub>2</sub> NS and zoom of single isolated 3D MoS<sub>2</sub> nanosheet showing fullerene-like structure.

it also clearly demonstrates that the diameters of the generated 3D MoS<sub>2</sub> NS are in the range of few nanometers.

In our previous study, we produced MoS<sub>2</sub> NS with the PLA technique in DI water and we only observed 3D MoS<sub>2</sub> NS generation.<sup>12</sup> In this study, we repeat the same procedure except for the solvent type, which is methanol instead of water; we recognize that the obtained NS have different morphologies. The use of the PLA technique to crystalline 2H-MoS<sub>2</sub> powder in methanol generates both colloidal 2D and 3D MoS<sub>2</sub> NS. In

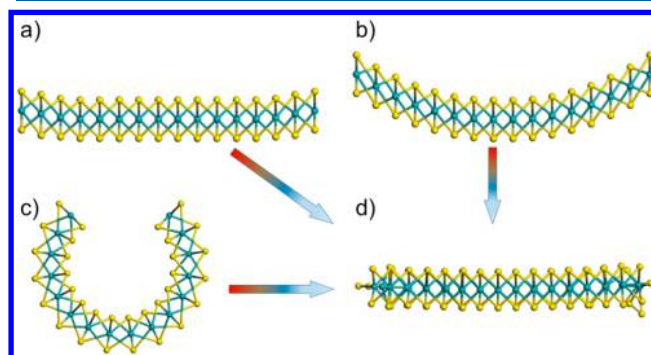
this respect, we analyze the factors, which may drastically affect the nanoparticles structure, by ab initio methods.

In literature it has been proposed that nanoparticles of layered compounds can be unstable against folding and close into fullerene-like structures.<sup>40</sup> The folding and rolling of 2D nanosheets have been experimentally observed.<sup>41,42</sup> Moreover a scroll-like morphology of the folded structures is considered to be a possible route to inorganic fullerenes.<sup>43</sup> Following these discussions, in our model, we start with ideal (without any defects) monolayer MoS<sub>2</sub> nanomeshes with varying sizes (Figure 5) and consider the deviation from planar structure



**Figure 5.** Side and top view of MoS<sub>2</sub> nanomeshes with varying sizes. Blue and yellow spheres indicate Mo and S atoms, respectively.

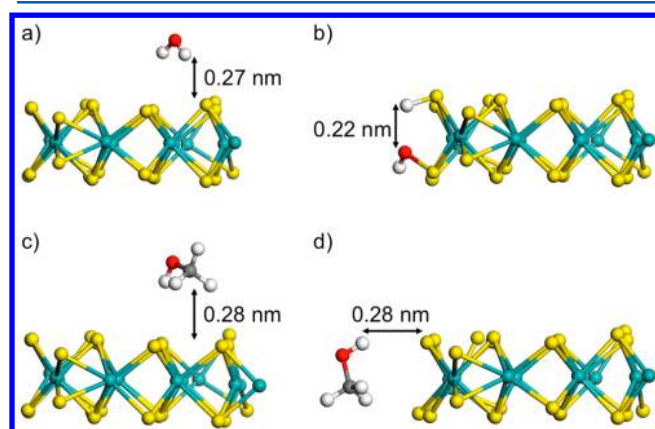
as an indication of a clustering tendency. In our experimental results, the typical size for nanosheets is larger than 50 nm, whereas it is around 5 nm for nanoparticles, which indicates that the clustering occurs for relatively small sizes and there is no need to analyze particle sizes larger than 5 nm. In this respect we only cover the size range between 1 and 3 nm. When we optimize the structures in vacuum by minimizing the total energy and forces on the atoms, all ideal nanomeshes are found to be planar except for small distortions at the edges (which are expected due to the broken bonds). Even when we break the symmetry of the system and deform the planar structures as shown in Figure 6, the nanomeshes revert back to



**Figure 6.** (a–c) initial (deformed) and (d) final (optimized) structures of MoS<sub>2</sub> nanomesh.

their ideal planar form after geometry optimization. When compared, the planar form is even energetically more favorable ( $\sim 0.2$  eV/atom) than the completely curved system in which all dangling bonds are eliminated.<sup>44</sup>

To investigate the effect of solvents, we first examine the interaction of water and methanol molecules with MoS<sub>2</sub> nanomeshes starting from a single molecule adsorption. Both molecules do not bind to the MoS<sub>2</sub> nanomesh surface<sup>45,46</sup> as shown in Figure 7. The adsorption energy ( $E_a$ ) is calculated to

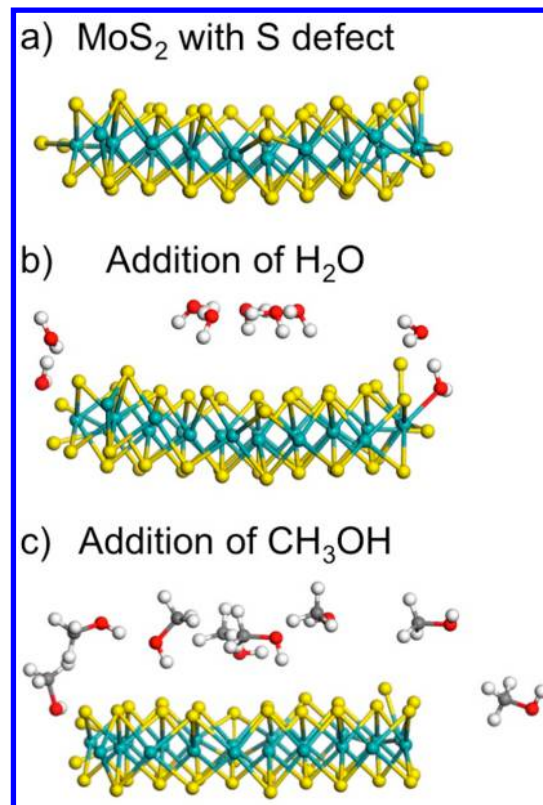


**Figure 7.** Single H<sub>2</sub>O molecule (a) adsorption on surface (b) and dissociation at the edge; and single CH<sub>3</sub>OH molecule adsorption (c) on surface (d) at the edge of MoS<sub>2</sub> nanomesh.

be 0.3 and 0.4 eV/molecule for water and methanol, respectively. When VdW interactions are included,  $E_a \approx 0.1$  eV increases for both molecules. Alternately, a single H<sub>2</sub>O strongly interacts with the edges and even can dissociate,<sup>47</sup> while CH<sub>3</sub>OH remains intact. Next, we gradually increase the number of surrounding molecules to resemble the solvent medium. In a similar manner, except for H<sub>2</sub>O molecules at the edges, neither methanol nor water molecules interact with MoS<sub>2</sub> nanomesh and do not modify the planar geometry even when the VdW interactions are taken into account. We obtain similar results when we increase the temperature, once again indicating a tendency for nanosheet formation instead of clustering.

Our analysis shows that MoS<sub>2</sub> NS are successfully generated by the PLA technique, with no chemical impurities but intrinsic structural defects in monolayer MoS<sub>2</sub> NS can occur during the formation process. Accordingly we consider possible defects, namely, S, Mo, Mo–S, Mo–2S vacancies in nanomeshes. The geometry optimization results at different temperatures demonstrate that the planar structures are deformed upon introducing defects. The amount of deformation is stronger for the S-vacancy case (Figure 8a) but also significant for other types as well. Interestingly, while the presence of H<sub>2</sub>O molecules around a nanomesh enhances deformation (Figure 8b), CH<sub>3</sub>OH molecules reduce the effect (Figure 8c).

Finally, depending on our first-principles calculations, we propose that the production of nanoclusters by the PLA method is linked with the amount of vacancy formation, as ideal structures have a tendency to stay in the planar form. While the interaction between the water molecules and nanomesh enhances the deformation resulting from defects, surrounding methanol molecules reduce the amount of deformation. Thus, using methanol as solvent increases the possibility of nanosheet formation which can explain the

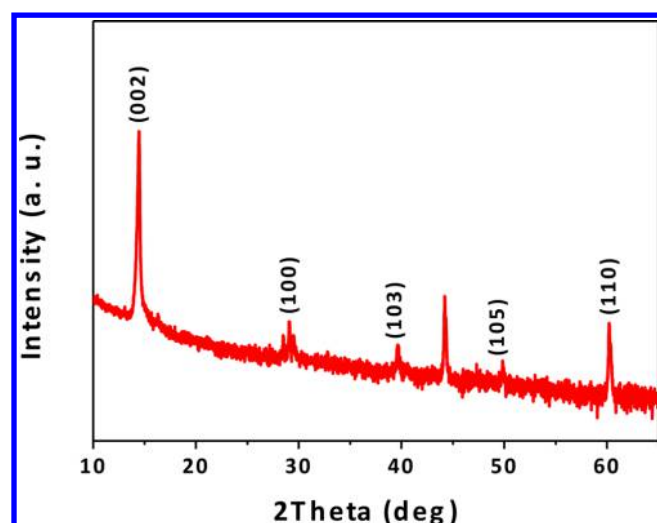


**Figure 8.** Optimized structures of MoS<sub>2</sub> nanomesh with a single sulfur defect (a) in vacuum, (b) with surrounding H<sub>2</sub>O molecules, and (c) with surrounding CH<sub>3</sub>OH molecules.

formation of both colloidal 2D and 3D MoS<sub>2</sub> NS in methanol distinct from water.

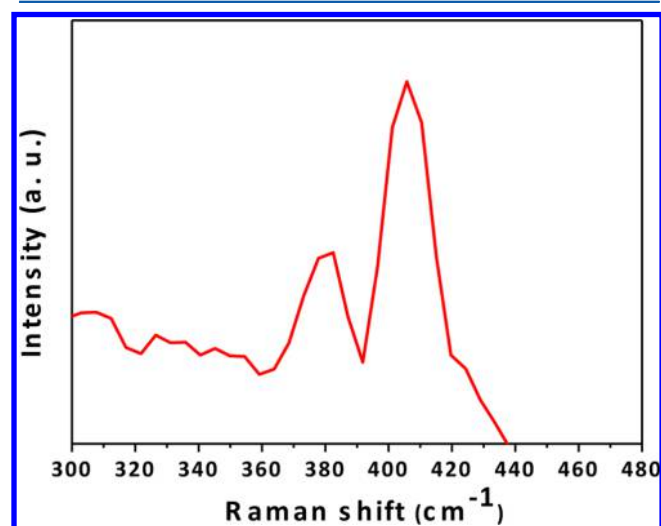
To better understand the crystallographic structure of MoS<sub>2</sub> NS, an XRD study was performed. The PANalytical X'Pert PRO multipurpose diffractometer operated at a voltage about 45 kV and a current of 40 mA using a CuK $\alpha$  radiation source was used. The MoS<sub>2</sub> NS sample was prepared by depositing and drop-casting the MoS<sub>2</sub> NS on a low-intensity background silicon (100) substrate. XRD measurement analysis was carried out to determine the crystalline structure and the composition of the MoS<sub>2</sub> NS. First we studied XRD analysis of 2H-MoS<sub>2</sub> powder. Nine sharp diffraction peaks at 14.43°, 29°, 32.7°, 33.46°, 35.85°, 38.56°, 44.15°, 49.82°, and 58.35° corresponding to the (002), (004), (100), (101), (102), (103), (006), (105), and (110) reflections of hexagonal 2H-MoS<sub>2</sub> with lattice constants  $a = 3.160$ ,  $c = 12.295$  Å (ICDD-JPDS card No. 39-1492) are observed.<sup>13</sup> No other diffraction peaks were observed indicating that the 2H-MoS<sub>2</sub> powder used for this experiment was of a crystalline structure. The XRD pattern of MoS<sub>2</sub> NS is shown in Figure 9. Five main sharp diffraction peaks at 14.46° (002), 29.08° (100), 39.61° (103), 49.84° (105), and 60.2° (110) are clearly observed.<sup>13</sup> This result indicates that MoS<sub>2</sub> NS with a crystalline structure were successfully generated by the PLA technique.

Raman spectroscopy is a very useful technique for the structural characterization of nanomaterials. Raman spectroscopy of MoS<sub>2</sub> NS was performed using a Witec Alpha 300S Micro Raman spectrometer with a Nd:YAG laser at an excitation wavelength 532 nm (laser power, 10 mW) and Nikon 100 $\times$  (N.A. = 0.9) air objective, and the Raman spectrum was recorded at room temperature. The sample was



**Figure 9.** XRD pattern of MoS<sub>2</sub> NS drop-cast onto a low intensity background silicon (100) substrate showing reflections characteristic of the crystalline structure of MoS<sub>2</sub>.

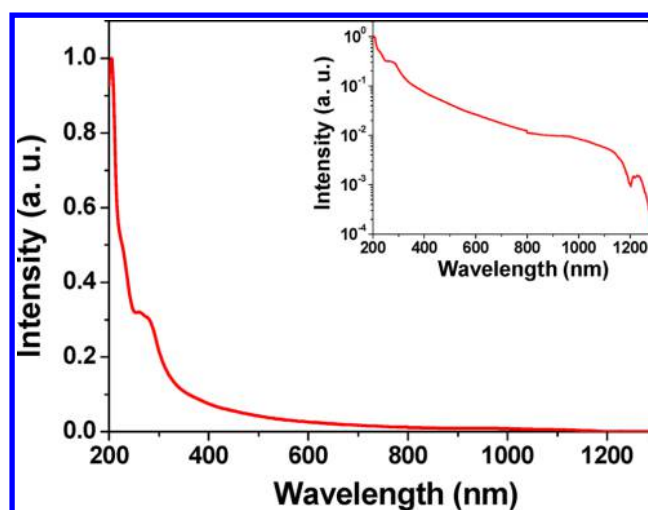
obtained by drop-casting the MoS<sub>2</sub> NS onto a silicon wafer for optical microscopy, SEM, and Raman analysis. Raman spectroscopy is a widely applicable technique to investigate optical and structural properties of nanomaterials. Further evaluations can be made for vibrational modes of MoS<sub>2</sub> NS in Raman spectroscopy. The Raman spectrum of MoS<sub>2</sub> NS, which is given in Figure 10, shows two peaks centered at 381.7 and 407.5



**Figure 10.** Raman spectra of MoS<sub>2</sub> NS generated by nanosecond laser ablation in methanol.

cm<sup>-1</sup>. In literature, these peaks are attributed to in-plane E<sub>2g</sub><sup>1</sup> and out-of-plane A<sub>1g</sub> vibrations of MoS<sub>2</sub>, respectively.<sup>13</sup> The Raman result also provides that the obtained nanomaterials are MoS<sub>2</sub> NS.

The optical absorption spectrum of MoS<sub>2</sub> NS was obtained with a Varian Cary 5000 UV–vis–NIR spectrophotometer operating in the 200–1300 nm wavelength range. The MoS<sub>2</sub> NS solution was added into a quartz cuvette for optical absorption measurement. MoS<sub>2</sub> is a new semiconductor material exhibiting structure-dependent optical properties. Figure 11 shows normalized optical absorption spectra of MoS<sub>2</sub> NS in methanol. The optical absorption spectrum of



**Figure 11.** UV–vis absorption spectrum of MoS<sub>2</sub> NS in methanol showing broadband optical absorption behavior.

colloidal MoS<sub>2</sub> NS shows a minimum optical absorption feature at 1300 nm and also prominent shoulders at 265 nm, and the strong rising absorption edge shifts toward the UV region. Compared to the optical properties of 3D MoS<sub>2</sub> NS from the PLA technique in DI water,<sup>12</sup> laser-generated MoS<sub>2</sub> NS have broadband optical absorption properties tailoring from the NIR region to the UV region, and therefore, MoS<sub>2</sub> NS can be considered as a prime candidate for various photonics and optoelectronics applications.

## CONCLUSION

Different-shaped nanostructures of MoS<sub>2</sub> have been synthesized through a one-step PLA technique of hexagonal crystalline 2H-MoS<sub>2</sub> powder in organic liquid. Structural analysis of colloidal nanocomposites demonstrated that the obtained MoS<sub>2</sub> product presents layered morphology with micrometer- to nanometer-sized surface area structures. The inorganic fullerene-like MoS<sub>2</sub> NP are also successfully synthesized in a one-step technique. Ab initio calculations indicate that the formation of fullerene-like structures is linked with vacancies. Methanol reduces the deformation resulting from vacancies, which can clarify the concurrent production of nanoclusters and nanosheets. The synthesized MoS<sub>2</sub> NS gave characteristic Raman peaks at 381.7 and 407.5 cm<sup>-1</sup> that are attributed to the in-plane E<sub>2g</sub><sup>1</sup> and out-of-plane A<sub>1g</sub> vibration modes of MoS<sub>2</sub> and MoS<sub>2</sub> NS having a hexagonal crystal structure. Broadband optical absorption behavior was observed for the colloidal MoS<sub>2</sub> NS synthesized in organic solution by pulsed laser ablation. Our study reveals a one-step synthesis method for the generation of “two scales—(2D and 3D)” micrometer- and nanometer-sized layered and spherical fullerene-like morphology MoS<sub>2</sub> structures.

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### Notes

The authors declare no competing financial interest.

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