

Characterization of Vibrational Modes and Absorbance Properties of MoO_x Nanoparticle Colloids Synthesized by Laser Ablation in Distilled Water Using FTIR and UV-Vis Spectroscopy

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Abstract – This study reports the synthesis of molybdenum oxide (MoO_x) nanoparticles by pulsed laser ablation of solids in liquids (PLAL) using a Nd:YAG laser (1064 nm, 80 mJ, 7 ns pulse width, and 10 Hz repetition rate) and distilled water as the liquid medium. A 99.95% molybdenum metal target was ablated for 1.5 hours with an alternating cycle of 10 min ablation and 10 min rest. The synthesized colloids were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and UV-Visible (UV-Vis) spectroscopy. The FTIR results confirmed the formation of vibrational modes corresponding to terminal Mo=O, bridging Mo-O-Mo bending, which are characteristic of the molybdenum oxide phases. The UV-Vis spectrum exhibited a strong absorption band at 299 nm, which can be attributed the ligand-to-metal charge transfer (LMCT) in the molybdenum oxide nanostructures. The influence of the distilled water medium on the synthesis process, colloidal stability and optical properties is discussed in detail along with the temporal changes observed in the colloid.

Keywords: Pulsed Laser Ablation; Molybdenum Nanoparticles; Distilled Water.

I. INTRODUCTION

Nanotechnology developed in the last decades and opened up enormous opportunities in different fields, including catalysis, sensing, photothermal applications, and healthcare. One of the main challenges in the creation of nanomaterials is the choice of synthesis methods that allow one to obtain nanoparticles with high purity, controlled dimensions, and long-term colloidal stability. Traditional wet-chemical synthesis methods such as hydrothermal synthesis and chemical reduction sometimes involve chemical precursors, reducing agents, or surfactants, leading to residues in the final product and complicated purification processes [1], [2].

Among the materials studied, molybdenum is a very interesting candidate with excellent optical, electrical, and biocompatible properties [3]. Some research projects have uncovered potential uses for molybdenum nanoparticles, especially in catalysis and healthcare. Shaker (2020) [4] research revealed molybdenum oxide (MoO₂) nanoparticles have been demonstrated as biocompatible contrast agents for in vivo biomedical imaging, enabling the assessment of nanoparticle distribution, organ uptake, and safety in preclinical studies

Pulsed laser ablation in liquid (PLAL) is an “green synthesis” that has attracted much interest due to the ability to synthesize clean nanoparticles without any surfactants or other chemicals [5]. The advantages of this method are simple synthesis, high purity of the product and control over the size and morphology of particles by tuning the laser parameters. Laser ablation is a

process where a laser (light amplification by stimulated emission of radiation) is used to ablate material from a solid target by disturbing it using high-energy laser pulses. The Nd:YAG laser with a wavelength of 1064 nm is one of the most widely used laser systems in PLAL because of its easy accessibility and stable pulse energy [6], [7], [8].

The liquid medium used in the laser ablation process is very important to the properties of the nanoparticles that are produced. Distilled water the most used solvent because of its environmentally friendly nature, low cost, and ability to be used to directly synthesize nanoparticles through the interaction of dissolved oxygen and water molecules under highly reactive plasma conditions during ablation [9]. The interaction of the ablation plasma with water molecules produces reactive species that enable the oxidation of the molybdenum target, which leads to the formation of different molybdenum oxide phases depending on the experimental circumstances.

In this work, MoOx nanoparticles were synthesized by pulsed laser ablation in liquid (PLAL) using a 1064 nm Nd:YAG laser on a molybdenum metal target of 99.95% purity in distilled water and characterized by Fourier Transform Infrared (FTIR) and Ultraviolet-Visible (UV-Vis) spectroscopy. The main discussion in this work is the effect of aqueous medium on colloidal stability and the change of optical properties.

II. EXPERIMENTAL PROCEDURE

1. Materials

This study used several materials: molybdenum metal with a purity level of 99.95%, an Nd: YAG laser device at 1064 nm, beaker glass, and distilled water. The molybdenum with a purity level of 99.95%, cut to approximately 2 x 2 cm, was first cleaned using alcohol and distilled water to remove any possible contaminants. Then the molybdenum plate was put into a beaker with 10 mL of distilled water. The sample preparation process is shown in Figure 1.

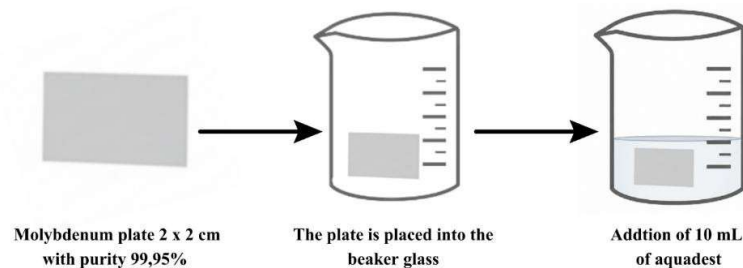


Figure 1. Preparation of molybdenum metal

2. Experimental Set-Up

The set-up and the synthesis mechanism of molybdenum nanoparticles are shown in Figure 2. The nanoparticles were synthesized using the pulsed laser ablation in liquid (PLAL) method with a Nd:YAG laser having a wavelength of 1064 nm. The laser parameters were set to an energy of 80 mJ, a focal length of 10 cm, a pulse width of 7 ns, and a repetition rate of 10 Hz. The laser was selected in order to increase the ablation efficiency and to get uniform size distribution nanoparticles [10].

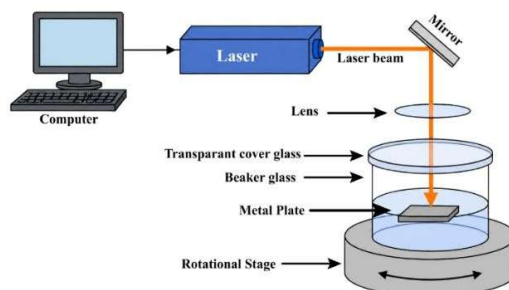


Figure 2. Set Up Experimental Pulsed Laser Ablation in Liquid

The molybdenum plate was rotated continuously at a speed of 10 rpm to ensure homogeneous ablation on the whole surface of the target. A transparent glass cover was used to seal the beaker, thereby minimizing solvent evaporation during the extended procedure. This process generated a laser-induced plasma plume at the molybdenum–distilled water interface. After 1.5 hours of ablation, the molybdenum nanoparticles were collected for subsequent characterization, an alternating cycle of 10 min of laser ablation and 10 min of rest was employed to minimize excessive heat accumulation in both the target and the liquid medium during the prolonged PLAL process. This duty cycle allows thermal relaxation of the system, reducing solvent evaporation and the formation of large cavitation bubbles that may interfere with plasma stability. In addition, the intermittent operation helps maintain consistent ablation conditions and may improve nanoparticle production efficiency by limiting adverse thermal effects during synthesis [11].

3. Characterization

Characterization was performed using a UV-Vis spectrophotometer (Shimadzu UV-2600) for optical analysis and a fourier transform infrared spectroscopy (Perkin-Elmer UATR Spectrum Two FTIR).

III. RESULT AND DISCUSSION

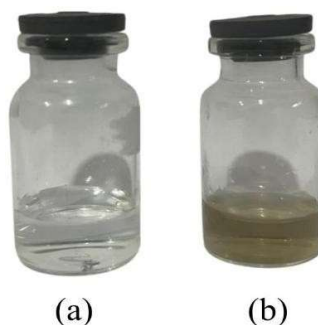


Figure 3. Results of the 1.5-hour synthesis. (a) Before synthesis (b) After 1.5 hours of synthesis

Figure 3a shows pure, clear, colorless distilled water before the ablation process. Figure 3b shows the distilled water turning yellowish after the PLAL process, indicating the formation of molybdenum oxide nanoparticle colloids.

During the ablation process, a 1064 nm Nd:YAG laser beam focused on the surface of the molybdenum target generates an extremely hot, high-pressure plasma at the target-liquid interface. This plasma contains excited atoms, ions and clusters of Molybdenum nanoparticles that strongly interact with the surrounding water molecules. The interaction causes rapid oxidation reactions on the surface of the newly formed nanoparticles, leading to the formation of various phases of molybdenum oxide [12].

The synthesis of molybdenum nanoparticles in distilled water is shown in Figure 3b. In general, during the aging process of MoO_x nanoparticles in aqueous medium, the colloidal color changes from clear white to golden yellow, is consistent with the formation of more oxidized molybdenum species, such as Mo(VI) polyoxomolybdates or hydrated MoO₃, which optically exhibit strong absorption in the UV-Vis region associated with the yellow coloration. This color is consistent with the dominance of Mo(VI) in the fully oxidized colloid, in contrast to the blue/brown coloration commonly observed for mixed Mo(IV) or Mo(V) species [13]. In this study the results of the synthesis of molybdenum nanoparticles in aqueous medium are golden yellow color.

The distilled water medium serves as both an oxidizing agent and a dispersing medium in the synthesis of PLAL. The temperature and pressure of the ablation plasma are sufficiently high to dissociate water molecules and produce very reactive OH• and H• radicals as the plasma is generated. These oxidative radicals react quickly with the Mo atoms just ejected from the target, facilitating the formation of various MoO_x phases[12].

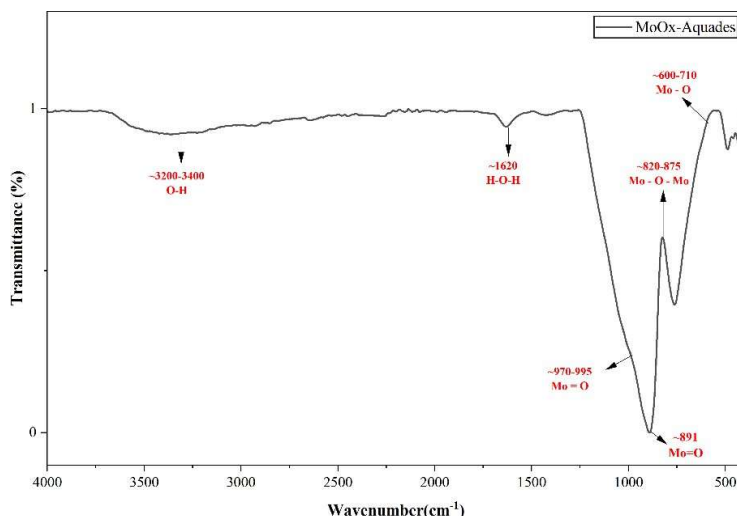


Figure 4. Fourier Transform Infrared (FTIR) of molybdenum in distilled water

FTIR analysis revealed characteristic terminal Mo=O bands, as well as bands associated with bridging Mo-O-Mo and Mo-O bending vibrations. The terminal Mo=O vibrations are generally observed in the range of approximately 970–995 cm⁻¹, corresponding to the symmetric stretching mode, while the band around 891 cm⁻¹ is commonly assigned to the antisymmetric stretching mode of terminal Mo=O groups. In addition, the bands observed in the 820–875 cm⁻¹ region are typically attributed to bridging Mo-O-Mo vibrations. The broad absorption region between 600 and 710 cm⁻¹ is generally associated with Mo-O bending vibrations and skeletal lattice vibrational modes related to the molybdenum oxide structure [14], [15], [16], [13]. Weak peaks are present at ~3200–3400 cm⁻¹ and ~1620 cm⁻¹, distributed across O-H stretching and H-O-H bending modes, indicating that the MoO_x nanoparticles synthesized in an aqueous medium possess a hydrated water layer on their surfaces[17], [18],

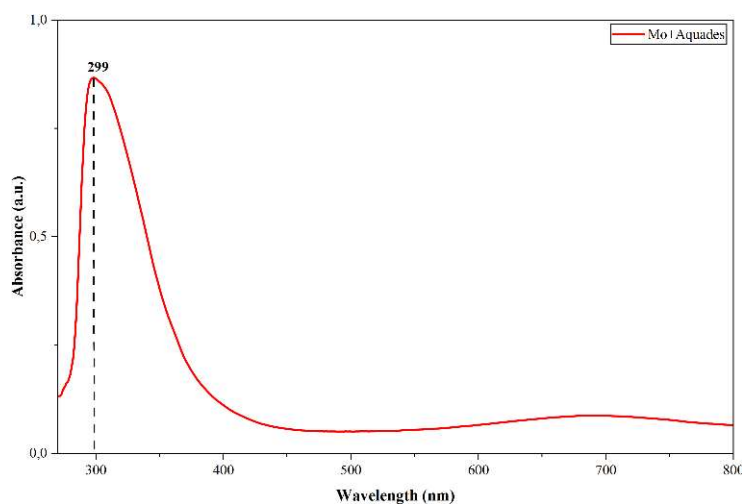


Figure 5. Ultraviolet Visible Spectroscopy (UV-Vis) of molybdenum in distilled water

Figure 5 shows the peak wavelength of molybdenum oxide. The UV-Vis results in Figure 5 show an absorption peak at a wavelength of 299 nm with an absorbance value of about 0.85. This strong absorption in the Near-UV (<400 nm) is a characteristic feature of molybdenum oxide nanoparticles produced via the pulsed liquid laser ablation method. The 299 nm peak is attributed to the ligand-to-metal charge transfer (LMCT) transition from the oxygen orbital to the molybdenum orbital ($O^{2-} \rightarrow Mo^{n+}$), which is a characteristic sign of the presence of the MoO_3 phase and molybdenum oxide hydrate [19], [20]. The UV-Vis spectrum shows a weak shoulder around 700 nm, which may be associated with d-d transitions or intervalence absorption from reduced Mo species. Although its intensity is lower than that of the LMCT peak, this feature suggests the presence of a small fraction of reduced species in the colloid, which may provide a minor contribution to the overall optical properties [13].

IV. CONCLUSIONS

Molybdenum oxide (MoO_x) nanoparticles were successfully synthesized using the pulsed laser ablation (PLAL) method with a 1064 nm Nd:YAG laser at an energy of 80 mJ, a pulse width of 7 ns, and a frequency of 10 Hz on a 99.95% pure molybdenum target in a distilled water medium. The 1.5-hour synthesis process yielded a MoO_x colloid that maintained its yellow color over the synthesis duration. The FTIR analysis confirmed the formation of molybdenum oxide structures through the presence of terminal $Mo=O$ vibrations at $970-995\text{ cm}^{-1}$ (symmetric) and 891 cm^{-1} (antisymmetric), bridging $Mo-O-Mo$ vibrations at $820-875\text{ cm}^{-1}$, and $Mo-O$ bending and skeletal lattice modes between $600-710\text{ cm}^{-1}$, indicating the successful synthesis of MoO_x -based colloids. The UV-Vis results show a strong absorption peak at 299 nm which is related to $O^{2-} \rightarrow Mo^{n+}$ charge transfer transition, consistent with MoO_3 -like polyoxomolybdate species. It has been shown that the aqueous medium is an efficient synthesis medium for the synthesis of hydrated MoO_x nanoparticles with unique optical properties. To understand better the dynamics of MoO_x nanoparticles in an aqueous medium, a temporal study of the colloidal stability and the evolution of the optical properties is needed.

REFERENCES

- [1] V. Amendola and M. Meneghetti, "Laser ablation synthesis in solution and size manipulation of noble metal nanoparticles," *Phys. Chem. Chem. Phys.*, vol. 11, no. 20, p. 3805, 2009, doi: 10.1039/b900654k.
- [2] W.-B. Zhang, Q. Qu, and K. Lai, "High-Mobility Transport Anisotropy in Few-Layer MoO_3 and Its Origin," *ACS Appl. Mater. Interfaces*, vol. 9, no. 2, pp. 1702–1709, Jan. 2017, doi: 10.1021/acsami.6b14255.
- [3] N. Zamora-Romero et al., "Synthesis of molybdenum oxide nanoparticles by nanosecond laser ablation," *Mater. Chem. Phys.*, vol. 240, p. 122163, Jan. 2020, doi: 10.1016/j.matchemphys.2019.122163.

- [4] K. Shaker et al., “Longitudinal In-Vivo X-Ray Fluorescence Computed Tomography With Molybdenum Nanoparticles,” *IEEE Trans. Med. Imaging*, vol. 39, no. 12, pp. 3910–3919, Dec. 2020, doi: 10.1109/TMI.2020.3007165.
- [5] D. Zhang, B. Gökce, and S. Barcikowski, “Laser Synthesis and Processing of Colloids: Fundamentals and Applications,” *Chem. Rev.*, vol. 117, no. 5, pp. 3990–4103, Mar. 2017, doi: 10.1021/acs.chemrev.6b00468.
- [6] M. Kim, S. Osone, T. Kim, H. Higashi, and T. Seto, “Synthesis of Nanoparticles by Laser Ablation: A Review,” *KONA Powder Part. J.*, vol. 34, no. 0, pp. 80–90, 2017, doi: 10.14356/kona.2017009.
- [7] A. Subhan, A.-H. I. Mourad, and Y. Al-Douri, “Influence of Laser Process Parameters, Liquid Medium, and External Field on the Synthesis of Colloidal Metal Nanoparticles Using Pulsed Laser Ablation in Liquid: A Review,” *Nanomaterials*, vol. 12, no. 13, p. 2144, Jun. 2022, doi: 10.3390/nano12132144.
- [8] G. W. Yang, “Laser ablation in liquids: Applications in the synthesis of nanocrystals,” *Prog. Mater. Sci.*, vol. 52, no. 4, pp. 648–698, May 2007, doi: 10.1016/j.pmatsci.2006.10.016.
- [9] A. V. Kabashin and M. Meunier, “Synthesis of colloidal nanoparticles during femtosecond laser ablation of gold in water,” *J. Appl. Phys.*, vol. 94, no. 12, pp. 7941–7943, Dec. 2003, doi: 10.1063/1.1626793.
- [10] J. Theerthagiri et al., “Fundamentals and comprehensive insights on pulsed laser synthesis of advanced materials for diverse photo- and electrocatalytic applications,” *Light Sci. Appl.*, vol. 11, no. 1, p. 250, Aug. 2022, doi: 10.1038/s41377-022-00904-7.
- [11] S. Molina-Prados, N. M. Bulgakova, A. V. Bulgakov, J. Lancis, G. M. Vega, and C. Doñate-Buendia, “Beam shaping techniques for pulsed laser ablation in liquids: Unlocking tunable control of nanoparticle synthesis in liquids,” *Beilstein J. Nanotechnol.*, vol. 17, pp. 309–342, Feb. 2026, doi: 10.3762/bjnano.17.22.
- [12] H. Zeng et al., “Nanomaterials via Laser Ablation/Irradiation in Liquid: A Review,” *Adv. Funct. Mater.*, vol. 22, no. 7, pp. 1333–1353, Apr. 2012, doi: 10.1002/adfm.201102295.
- [13] I. A. De Castro et al., “Molybdenum Oxides – From Fundamentals to Functionality,” *Adv. Mater.*, vol. 29, no. 40, p. 1701619, Oct. 2017, doi: 10.1002/adma.201701619.
- [14] T. Chiang and H. Yeh, “The Synthesis of α -MoO₃ by Ethylene Glycol,” *Materials*, vol. 6, no. 10, pp. 4609–4625, Oct. 2013, doi: 10.3390/ma6104609.
- [15] A. Chithambararaj and A. C. Bose, “Investigation on structural, thermal, optical and sensing properties of meta-stable hexagonal MoO₃ nanocrystals of one dimensional structure,” *Beilstein J. Nanotechnol.*, vol. 2, pp. 585–592, Sep. 2011, doi: 10.3762/bjnano.2.62.
- [16] M. H. Mahdieh and B. Fattahi, “Size properties of colloidal nanoparticles produced by nanosecond pulsed laser ablation and studying the effects of liquid medium and laser fluence,” *Appl. Surf. Sci.*, vol. 329, pp. 47–57, Feb. 2015, doi: 10.1016/j.apsusc.2014.12.069.
- [17] G. P. Nunna et al., “Biogenic Synthesis of High-Performance α -MoO₃ Nanoparticles from Tryptophan Derivatives for Antimicrobial Agents and Electrode Materials of Supercapacitors,” *Int. J. Energy Res.*, vol. 2023, pp. 1–15, Feb. 2023, doi: 10.1155/2023/6715319.
- [18] M. A. Moghazy, “Leidenfrost green synthesis method for MoO₃ and WO₃ nanorods preparation: characterization and methylene blue adsorption ability,” *BMC Chem.*, vol. 17, no. 1, p. 5, Feb. 2023, doi: 10.1186/s13065-023-00916-3.
- [19] H. Tian, C. A. Roberts, and I. E. Wachs, “Molecular Structural Determination of Molybdena in Different Environments: Aqueous Solutions, Bulk Mixed Oxides, and Supported MoO₃ Catalysts,” *J. Phys. Chem. C*, vol. 114, no. 33, pp. 14110–14120, Aug. 2010, doi: 10.1021/jp103269w.

- [20] S. Camacho-Lopez et al., “Hydrated MoO₃ nanoparticles and α -MoO₃ nanosheets synthesis by fs laser irradiation,” Mater. Chem. Phys., vol. 297, p. 127376, Mar. 2023, doi: 10.1016/j.matchemphys.2023.127376.