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Analysis on Effect of Electrolyte Concentration on Molybdenum Sulfide (MoS_2) Thin Film via Bottom-Up Approach of Electrodeposition for Solar Cell Applications

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Solar cells, also known as photovoltaic (PV) cells, convert light through electricity using the photovoltaic effect. Third-generation solar cells utilize advanced thin-film technologies and improved production methods to achieve high efficiency. Molybdenum sulfide (MoS_2) is a transition metal dichalcogenide (TMDC), shows great potential for applications in solar cells, such as Dye Sensitized Solar Cells (DSSC) and Perovskite Solar Cells (PSC), due to its high electrical conductivity and strong catalytic activity. MoS_2 can be synthesize using two methods: Top-down and bottom-up approaches. The Bottom-up Approach, particularly electrodeposition, is cost-effective and provides better control over the quality and scale of the layers. However, the concentration of the deposition electrolyte in electrodeposition can affect the properties of the resulting thin films. In this study, MoS_2 thin films were made using electrodeposition with different electrolyte concentrations: 5 mM, 10 mM, and 0.1M. These films were then examined using Scanning Electron Microscopy (SEM), Energy-dispersive X-ray (EDX), Cyclic Voltammetry (CV), and Ultraviolet-visible (UV-vis) spectroscopy to see how the electrolyte concentration affects their structure, electrochemical properties, and optical properties. The study found that the electrolyte concentration significantly influences the thin film's grain distribution and structure. It also affects the electrochemical properties, such as the rate of electron and mass transfer between the electrode and the electrolyte. Higher concentrations result in faster electron and mass transfer, but lower light absorption and transmission, meaning lower concentrations are better for the film's optical properties.

Keywords: TMDC materials; electrodeposition; thin film; deposition; photovoltaics

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Transition Metal Dichalcogenides (TMDs) are a class of materials that have gained significant attention in recent decades due to their unique properties and potential applications in renewable energy technologies. TMDs are composed of transition metals and chalcogenides, such as molybdenum and selenium (MoSe2), tungsten and selenium (WS2), and molybdenum and sulfur (MoS_2). These materials exhibit exceptional electronic and optical properties, making them suitable for various applications, including solar cells. TMD materials such as MoS_2 and WSe2 have high optical absorption coefficients, desirable band gaps for use in single-junction and tandem solar cells (~1.0–2.5 eV), and self-passivated surfaces free of dangling bonds, enabling high performance even for ultrathin absorber layers on the order of 100 nm [1].

One of the most promising TMDs is MoS_2, which has been extensively studied for its potential in solar cell applications. MoS_2 is a 2D material with a direct bandgap of approximately 1.8 eV, making it suitable for photovoltaic applications. Its high carrier mobility and high optical absorption coefficient also contribute to its potential in solar cells [2-3]. Soonmin et. al. reported MoS_2 has high charge carrier mobility and can facilitate efficient charge transport in solar cells [4]. In application of perovskite solar cells, MoS_2 is suitable to use as a hole transport layer in perovskite solar cells since MoS_2 can enhance charge collection at the electrode interface, leading to improved photocurrent and power conversion efficiency 5].

MoS_2 has a direct bandgap in the visible spectrum, allowing it to absorb light efficiently [4]. Incorporating MoS_2 thin films in DSSCs can increase light harvesting, especially in the red and near-infrared regions, leading to higher photocurrent generation (Juang et al., 2019).

Among all atomically thin semiconductors, MoS_2's synthesis techniques are more developed. Synthesis of MoS_2 consists of two approaches which is top-down approach and bottom-down approach [7-8]. The top-down approach involves breaking down larger pieces of material to generate the required nanostructures. The top–down methods start from bulk MoS_2 crystal forms the raw material such as mechanical exfoliation, chemical exfoliation, and ultra- sonication based on the weak interlayer Van der Waals force. Though simple, these methods have such drawbacks like small scale, random shape, and hard-controlled thickness, thus limiting their practical applications. Comparably, bottom–up methods that have high quality, controllable layer number and scale [8].

The bottom-up approach, on the other hand, involves assembling single atoms and molecules into larger nanostructures. This method typically consists of physical vapor deposition, Chemical Vapor Deposition (CVD) and Solution Chemical Process to create MoS_2 layers from individual atoms and molecules. CVD is the most studied way to synthesize MoS_2 on a large scale. However, this method requires a sulfurization process where sulfur powder is placed in a furnace to facilitate the embedding of sulfur atoms in the 2D lattice structures. The toxic materials used in this method are a weakness when manufacturing. Solution processes for 2D materials are developed due to the advantages of a simpler method, high throughput, large size, low cost with an environmentally friendly process and sulfurization process free. Electrodeposition is a bottom–up method of Solution Chemical Process to synthesize MoS_2 NPs at a low cost. Compared to top-down approaches that break down larger pieces of material, electrodeposition as a bottom- up technique allows for more control over the atomic arrangement and formation of uniform, high-quality nanostructures [8-10].

Based on previous report, researchers reported that concentration of material significant influence the properties of the synthesis material. Shikha et. al. reported that increasing concentration of the precursor in ZnSe thin films in 0.8 M, 1.0 M, 1.2 M, and 1.4 M [11] leads to larger particle sizes, reduced optical band gaps, and variations in electrical properties, demonstrating a direct influence on the material's structural, optical, and electrical characteristics. Barua et. al. [12] described that increasing the concentration of the precursor solution negatively impacts the properties of the TiO2 thin film by degrading surface quality and adhesion, reducing the absorbance peak, and shifting it toward lower wavelengths, ultimately lowering the film's overall performance. Reports have shown that concentration affects the properties of thin films. Therefore, the influence of concentration on the properties of MoS_2 thin films needs to be investigated. In this work, MoS_2 thin films were synthesized using a bottom-up approach through electrodeposition at varying concentrations of 5 mM, 10 mM, and 0.1 M. The MoS_2 films were characterized to study the influence of concentration on the morphology, electrochemical, and optical properties of the synthesized thin films.

EXPERIMENTAL

Preparation of Precursor

A 30 ml volume of DI water contains 5 mM, 10 mM and 0.1 M of ammonium tetrathiomolybdate ((NH4) 2MoS4, tracemetal base, 99.97% Sigma Aldrich) and 0.1 M of potassium chloride (KCl, 99% ACS reagent, Sigma Aldrich) as the electrolyte for the precursor materials deposition. Following its production, the precursor electrolyte is in a base condition with a pH of 7.

Electrodeposition Method of MoS_2 Synthesis

The process began with the electrodeposition of MoS_2 onto Indium Tin Oxide (ITO) substrate glass based on previous research [13, 14] with some modifications. This was accomplished by subjecting the ITO substrates to a series of ten-minute ultrasonic cleansing with several solvents, including an aqueous soap solution, DI water, ethanol, acetone, and finally IPA. The substrates were then dried in an oven set at 100℃ for ten minutes. For the deposition of MoS_2 films, three electrode systems of electrodeposition setup were used. The setup comprised a graphite rod as counter electrode, an ITO substrate as the working electrode and Ag/AgCl (sat. KCl) served as the reference electrode. Constant potential of -1V vs Ag/AgCl reference electrode, which was chosen as the constant applied potential for the MoS_2 potentiostatic electrodeposition (Ossila Potentiostat). The MoS_2 thin was deposited for 30 min at room temperature then rinsed with DI water after depositing finished. To allow grain growth, deposited thin film was anneal in a furnace at 450℃ for 30 minutes. Figure 1 shows the overall experiment setup.

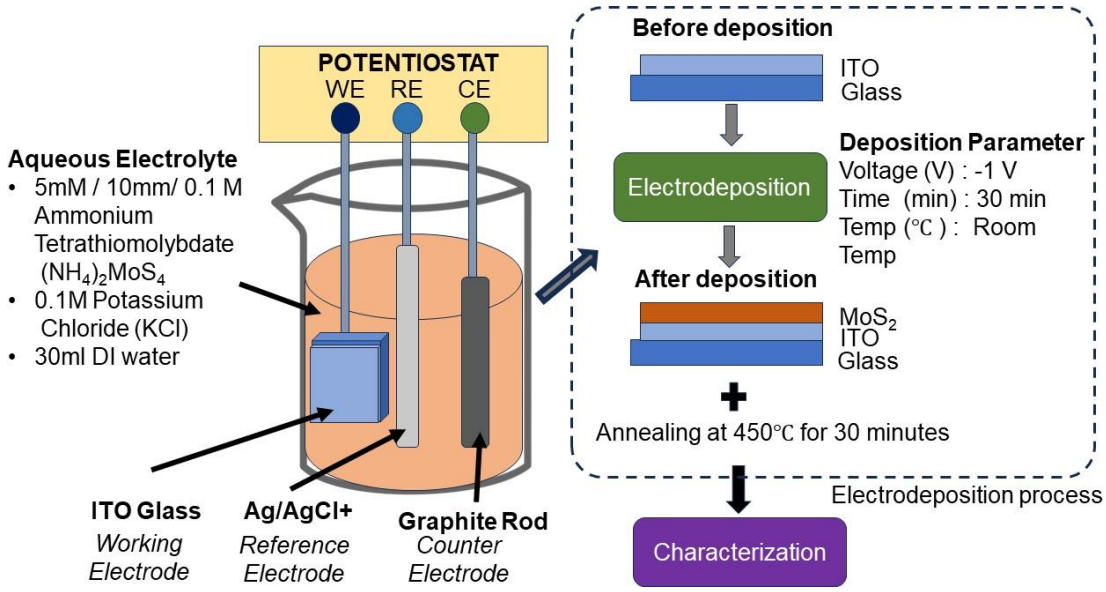

Figure 1. Overall experiment setup.

Characterization Methods

The morphology studies of the deposited MoS_2 thin film were analyzed through field-emission scanning electron microscopy (SEM, Hitachi FE-SEM S4800). Moreover, elemental analysis of fabricated thin film was analyzed via EDX. Optical transmission study was completed in 400–800 nm wavelength region using UV–Vis-NIR Spectrophotometer (Carry 5000, Agilent Technologies). From the absorbance spectra, the bandgap of the fabricated MoS_2 can be achieved via Tauc plot as equation 1.1.

$$(\alpha h\nu)^{\frac{1}{n}} = A\,(h\nu - E_g) \qquad (1.1)$$

where α is absorption coefficient being a function of wavelength α(λ), h is Planck constant, Eg is an optical band gap of a semiconductor, ν is frequency, A is proportionality constant, and n is Tauc exponent.

RESULTS AND DISCUSSION

Deposition Condition of MoS_2 Thin Film

The image shows the deposition conditions of synthesized molybdenum disulfide (MoS_2) thin films at three different concentrations: 5 mM, 10 mM, and 0.1 M. In Figure 2, representing a 5 mM concentration, the thin film appears light brown with a certain level of transparency. As the concentration increases to 10 mM, shown in Figure 2b, the color of the film becomes a slightly darker shade of brown, but it still retains some transparency. In contrast, at the highest concentration of 0.1 M, depicted in Figure 2c, the thin film turns a much darker brown, with significantly reduced transparency. The gradual darkening of the films with increasing MoS_2 concentration suggests that higher concentrations result in thicker, less transparent films, indicating an increase in the deposited material's density.

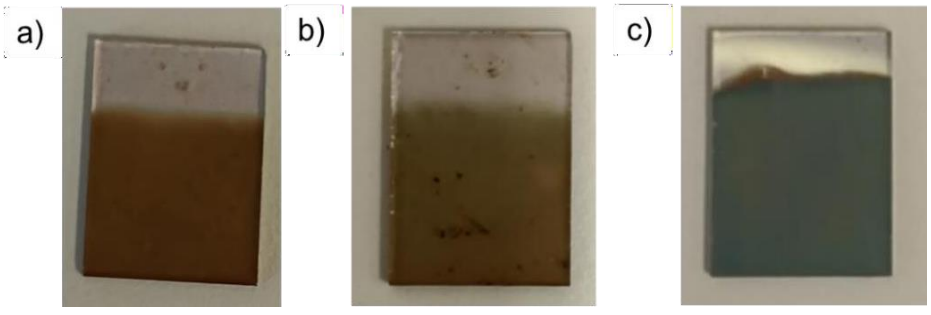

Figure 2. MoS_2 thin film a) MoS_2 at 5 mM. b) MoS_2 at 10 mM. c) MoS_2 at 0.1 M.

Scanning Electron Microscopy (SEM) Analysis

The SEM images in Figure 3 display MoS_2 thin films at magnifications of 50K and 2K. These images reveal that the MoS_2 exhibits a distinct 2D sheet-like morphology with a hexagonal structure, consistent with previous studies [15-16], confirming the successful formation of nanosheet MoS_2 in this work.

The concentration of the MoS_2 precursor has a noticeable impact on the grain distribution within the film. At a concentration of 5 mM, the MoS_2 grains are distributed more uniformly across the surface. However, at higher concentrations of 10 mM and 0.1 M, the uniformity of the grain distribution decreases, indicating that an optimal concentration is critical for maintaining uniformity in the film.

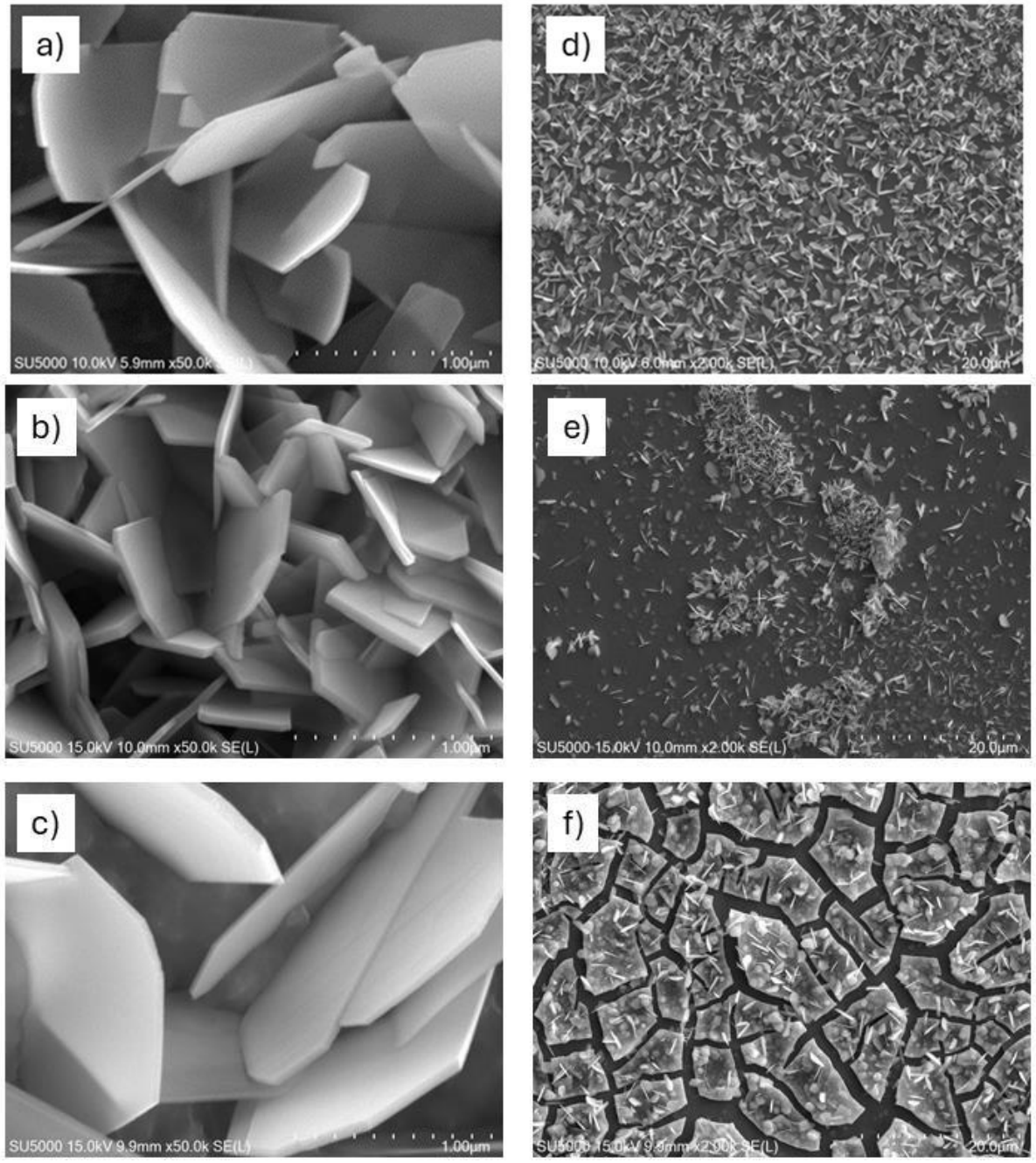

Figure 3. SEM image of annealed MoS_2 thin film at different magnification. a) MoS_2 5 mM at 50k. b) MoS_2 5 mM at 2k. c) MoS_2 10 mM at 50k. d) MoS_2 10 mM at 2k. e) MoS_2 0.1 M at 50k. f) MoS_2 0.1 M at 2k.

Cyclic Voltammetry (CV) Analysis

The cyclic voltammetry (CV) analysis of MoS_2 at varying concentrations (5 mM, 10 mM, and 0.1 M) reveals significant changes in the electrochemical behavior as the concentration increases. The Figure 4 shows an increase in current response with rising concentration, indicating enhanced redox activity. This is further supported by the extracted parameters in Table 1, where both the cathodic peak current (Ipc) and anodic peak current (Ipa) increase with concentration, signifying stronger reduction and oxidation reactions at higher MoS_2 concentrations. Additionally, the peak potentials (Epc and Epa) shift negatively with increasing concentration, which suggests a slight effect on the reversibility of the redox process. However, the peak potential separation (ΔEp) remains relatively stable, indicating that the electron transfer kinetics are quasi-reversible and only marginally influenced by concentration. Overall, the CV results suggest that higher concentrations of MoS_2 lead to more pronounced electrochemical activity without significantly altering the reaction reversibility.

Ultraviolet-Visible (UV-Vis) Spectroscopy Analysis

The UV-Vis analysis of MoS_2 thin films at different concentrations (5 mM, 10 mM, and 0.1 M) demonstrates the optical properties of the material across absorption, bandgap determination, and transmission measurements. In the Figure 5a, the MoS_2 thin films exhibit higher absorbance with increasing concentration, with the 0.1 M sample showing the strongest absorption in the visible region, particularly between 400-800 nm. This indicates that the optical absorption of MoS_2 is concentration-dependent, with higher concentrations allowing for greater light interaction.

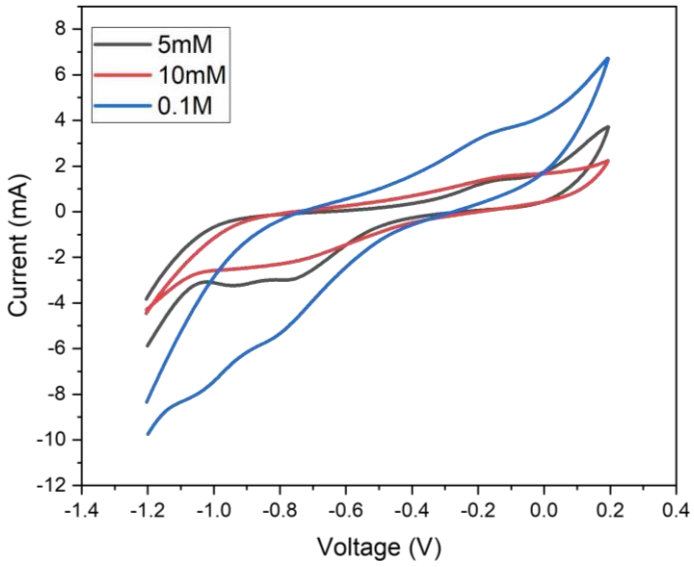

Figure 4. Cyclic Voltammetry of MoS_2 precursor in different concentrations.

Table 1. Cyclic Voltammetry parameters extracted from the CV graph.

Concentration	Peak Potentials, Ep (V)		Peak Currents, Ip (mA)		Peak Potential Separation, ΔEp
	Cathodic peak potential, Epc	Anodic peak potential, Epa	Cathodic peak Current, Ipc	Anodic peak Current, Ipa	
5 mM	-0.147	-0.743	0.4575	2.0441	0.596
10 mM	-0.102	-0.776	0.297	1.004	0.6737
0.1 M	-0.174	-0.815	0.66	3.203	0.641

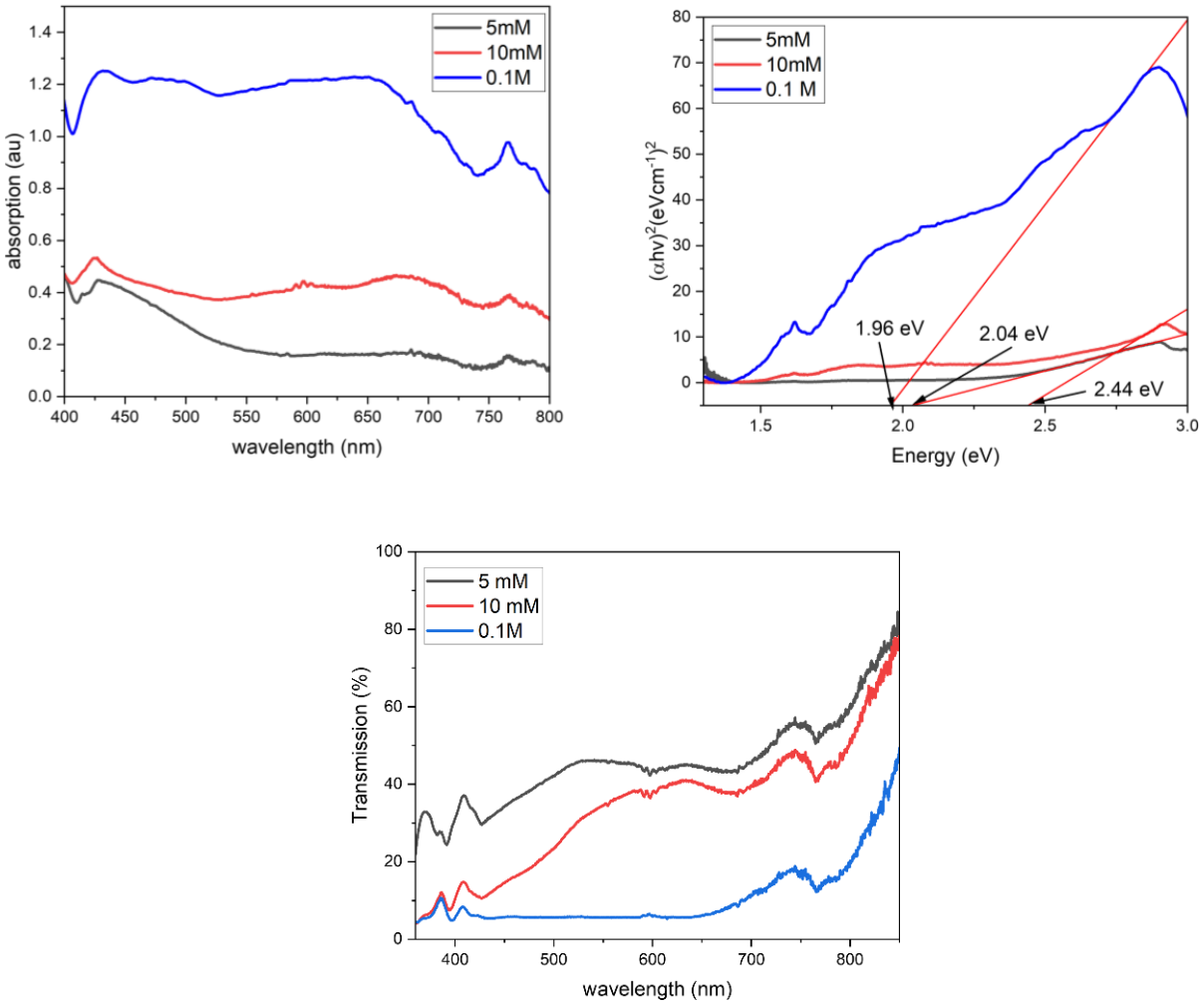

Figure 5. UV Vis Analysis of MoS_2 a) Absorption of MoS_2 thin film b) Bandgap of MoS_2 thin film via Tauc Plot. c) Transmission measurement of MoS_2 thin film.

The tauc plot was used to estimate the optical bandgap of the MoS_2 thin films as shown in figure 5b. The intercept of the linear portion with the energy axis gives the estimated bandgap values, which range from 1.96 eV for the 0.1 M sample to 2.44 eV for the 5 mM sample. This suggests that the bandgap decreases as the concentration of MoS_2 increases, potentially due to changes in film thickness or structural properties at higher concentrations. In the Figure 5c, the MoS_2 thin films exhibit decreased transmission with increasing concentration, with the 0.1 M sample allowing the least amount of light to pass through, indicating greater optical density. The transmission values are lowest in the visible range (400-800 nm), confirming that MoS_2 is opaquer at higher concentrations.

From the optical analysis, highlights a clear correlation between the concentration of MoS_2 and its optical properties. As the concentration increases from 5 mM to 0.1 M, the absorption of light in the visible spectrum becomes more pronounced, suggesting enhanced light interaction at higher concentrations. This is further supported by the Tauc plot, which reveals a decrease in the optical bandgap with increasing concentration, possibly due to changes in the electronic structure or film thickness. Additionally, the transmission measurements show that higher concentrations of MoS_2 result in reduced light transmission, indicating increased optical density. In conclusion, higher concentrations of MoS_2 thin films lead to stronger absorption, lower bandgap values, and

reduced transmission, showcasing the concentration-dependent optical behavior of MoS_2.

CONCLUSION

In conclusion, the study demonstrates that increasing the concentration of MoS_2 from 5 mM to 0.1 M significantly influences the physical, morphological, electrochemical, and optical properties of the deposited thin films. The films become progressively darker and less transparent with higher concentrations, reflecting an increase in material thickness and density. SEM analysis reveals a uniform distribution of MoS_2 grains at lower concentrations, with reduced uniformity at higher levels. Cyclic voltammetry results indicate that higher MoS_2 concentrations enhance redox activity without significantly affecting electron transfer kinetics. Additionally, optical analysis shows that increased concentrations result in stronger light absorption, a decrease in the optical bandgap, and reduced light transmission. These findings suggest that the concentration of MoS_2 plays a crucial role in determining the overall properties and performance of the thin films, providing valuable insights for applications in optoelectronics and energy storage.

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