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TEMPERATURE-DEPENDENT EXFOLIATION BEHAVIOR OF MoS_2 *VIA* QUENCHING

This study presents a novel method to exfoliate molybdenum disulfide (MoS_2) using quenching. MoS_2 is considered a promising material for energy storage and catalysis due to its excellent electronic and catalytic properties. Exfoliation maximizes surface area and enhances performance. Quenching involves rapid cooling from high temperatures, inducing thermal stress that effectively separates the layers of MoS_2. In this study, bulk MoS_2 was heat treated at various temperatures and then quenched to promote exfoliation. X-ray diffraction analysis confirmed the optimal exfoliation temperature at 150°C, while Atomic Force Microscope measurements revealed exfoliated MoS_2 layers with a thickness of 4-6 nm. This method offers a cost-effective approach with potential for large-scale production of high-quality MoS_2 layers.

Keywords: Molybdenum disulfide; exfoliation; quenching; electrochemical performance

1. Introduction

Molybdenum disulfide (MoS_2) is a key material in transition metal dichalcogenides (TMDs) and widely studied in two-dimensional (2D) materials research [1,2]. Its electronic, optical, and catalytic properties make MoS_2 valuable for energy storage, catalysis, electronics, and optoelectronics [3,4]. One critical characteristic that enhances the functionality of MoS_2 is its ability to exfoliate into monolayers or few-layer sheets [5], which increases surface area and enables tunable electronic properties. Exfoliating bulk MoS_2 into few-layer structures unlocks its unique 2D properties by increasing surface exposure, access to active sites, and electronic tunability. These changes are crucial for applications where high reactivity, fast charge transport, or tunable electronic behavior are required. Therefore, developing efficient exfoliation methods is key to advancing the practical use of MoS_2 in emerging fields such as energy storage, sensing, and next-generation electronics.

Synthesis of single-layer or few-layer MoS_2 can be achieved by either top-down exfoliation techniques or bottom-up growth approaches, each offering unique advantages and limitations [6]. Top-down methods are essential for scalable exfoliation, reducing bulk MoS_2 to thin layers for advanced applications [7]. Mechanical exfoliation [8], liquid phase exfoliation (LPE) [9], and ion intercalation [10] are commonly used methods. Mechanical exfoliation is straightforward and yields high-quality monolayers, yet its labor-intensive nature and low yield limit its viability for large-scale production. LPE offers a more scalable alternative by using sonication in a solvent to exfoliate MoS_2. However, this method often produces layers of varying thicknesses and is highly dependent on solvent choice, affecting exfoliation yield and quality. Ion intercalation introduces ions to weaken the van der Waals forces between MoS_2 layers, facilitating exfoliation. Despite its effectiveness, this method can leave behind chemical residues that may compromise material purity, making it less suitable for sensitive applications.

Bottom-up methods, such as chemical vapor deposition (CVD) and hydrothermal synthesis, allow for precise construction of MoS_2 layers from atomic or molecular precursors, ensuring control of layer thickness, composition, and uniformity [11,12]. This precision makes them suitable for high-performance electronics and optoelectronic devices. However, high-temperature setups and complex equipment in these methods increase production costs and limit scalability [13]. While bottom-up methods benefit laboratory-scale studies and specialized applications, they are less practical for large-scale industrial production [14,15].

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In this study, we propose a novel top-down approach employing the quenching process to induce exfoliation in MoS_2. Quenching, a technique widely used in metallurgy, involves rapid cooling from elevated temperatures, creating thermal stress that leads to micro-cracking and interlayer separation [16,17]. This process benefits from the anisotropic thermal expansion of MoS_2: while the in-plane direction is stabilized by strong covalent bonds and exhibits a low coefficient of thermal expansion (CTE), the out-of-plane direction – dominated by weak van der Waals forces – responds with a much higher CTE [18,19]. Such anisotropy enables effective thinning through thermal shock without compromising structural integrity. Our results indicate that an optimized quenching protocol facilitates the delamination of MoS_2, weakening interlayer interactions and yielding few-layer structures. This scalable and cost-effective method preserves the intrinsic properties of the material and offers tunability for specific application needs. Structural and morphological changes were confirmed using X-ray diffraction (XRD) and atomic force microscopy (AFM), with AFM offering quantitative measurements of sheet thickness. This strategy effectively bridges laboratory-scale exfoliation and industrial-level production, broadening the practical applications of MoS_2 in areas such as energy storage and catalysis.

2. Experimental

2.1. Preparation of Exfoliated MoS_2 materials

Initially, 5 g of bulk molybdenum disulfide (MoS_2) powder was prepared. The powder, purchased from Sigma-Aldrich (≥95% purity), was used as received without further purification. It was placed in a drying oven and subjected to heat treatment at 100°C, 125°C, and 175°C for 2 hours. The room temperature (RT) sample was used in its as-prepared state, without any thermal or quenching treatment. After heat treatment, the powder samples were rapidly cooled by immersion in 300 mL of liquefied nitrogen until complete evaporation.

2.2. Materials and characterizations

MoS_2 was purchased from Sigma Aldrich, Germany. The crystallographic structure of the samples before and after exfoliation was analyzed using a Bruker X-ray diffractometer (XRD). Additionally, the surface morphology and nanostructural features of the samples were evaluated using a Veeco Nanoscope Multimode IVa Atomic Force Microscope (AFM).

3. Results and discussion

XRD analysis was performed to evaluate the structural changes in MoS_2 following the quenching process. As shown in Fig. 1, distinct diffraction peaks were observed at approximately $2\theta = 14.4°$ and 39.6°, corresponding to the (002) and (103) planes of the 2H phase, respectively, based on JCPDS Card No. 77-1716. This indicates that the crystal structure of MoS_2 remained in the 2H phase after quenching, without transitioning to the 1T or 3R phases [20]. The semiconducting 2H phase is highly suitable for electronic and optoelectronic applications, as it supports stable charge transport and enhances catalytic activity in energy-related fields. Furthermore, Fig. 1 shows that the intensity of the (002) peak significantly decreased after quenching, whereas the (103) peak remained relatively unchanged. This suggests that exfoliation predominantly occurred along the (002) planes, which are held together by weak van der Waals forces, while the (103) planes, stabilized by stronger covalent bonds, were less affected. This directional exfoliation behavior is likely attributed to the asymmetric thermal stress generated during the quenching process. MoS_2 exhibits anisotropic thermal expansion depending on the crystallographic direction. The in-plane direction, governed by covalent bonding, has a relatively low coefficient of thermal expansion (CTE) of approximately 4.5×10^{-6} K^{-1}, whereas the out-of-plane direction, dominated by van der Waals interactions, shows a significantly higher CTE exceeding 12.0×10^{-6} K^{-1}. This thermal expansion anisotropy enables efficient exfoliation along specific crystallographic planes when thermal shock is applied during quenching. Although theoretical models suggest that MoS_2 becomes thermally stabilized around 400 K [21], the highest exfoliation efficiency in this study was observed at 150°C. At this temperature, the van der Waals interactions were sufficiently weakened to promote interlayer separation, while the overall structural integrity of the crystal was preserved. In contrast, at higher temperatures, recrystallization may occur, which could reduce exfoliation efficiency.

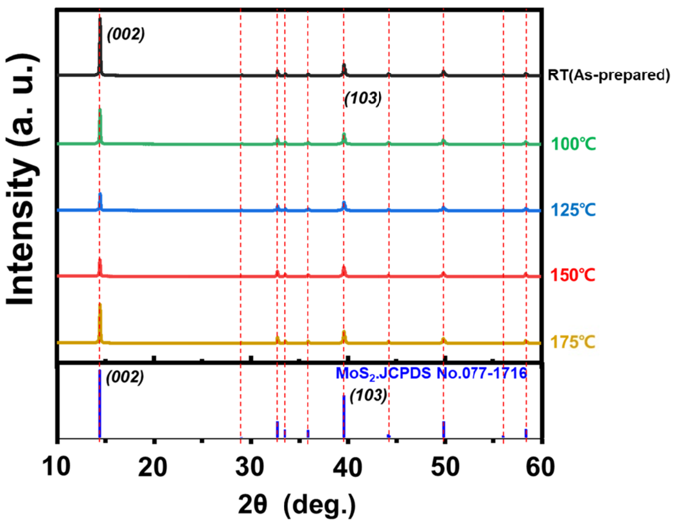

Fig. 1. XRD Analysis of Exfoliated MoS_2 by Quenching Method

Fig. 2 presents a quantitative evaluation of the exfoliation degree of MoS_2 as a function of quenching temperature. Fig. 2(a) shows normalized XRD patterns based on the (002) peak, allowing for a visual comparison of relative diffraction intensities between samples. However, due to the normalization, absolute

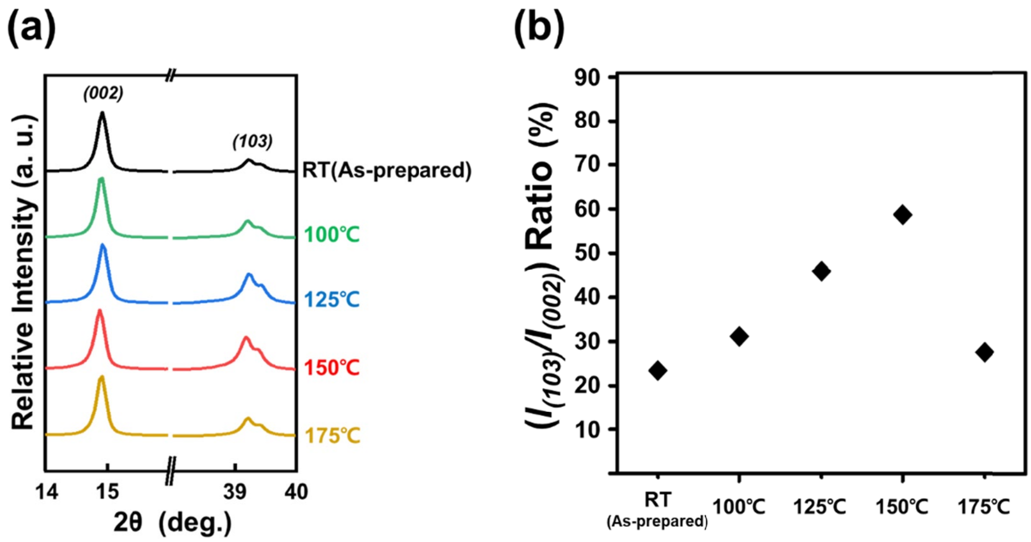

Fig. 2. (a) Relative Intensity of XRD Peaks of Exfoliated MoS_2, (b) The Intensity Ratio ($I_{(103)}/I_{(002)}$) of Exfoliated MoS_2 XRD peaks

intensity reductions in the (002) peak cannot be directly identified. Therefore, to more accurately assess the exfoliation behavior, the intensity ratio of $I_{(103)}/I_{(002)}$ was calculated and plotted in Fig. 2(b). This ratio was determined using the original relative intensity data from the XRD patterns shown in Fig. 1. Since the (002) peak decreases with exfoliation while the (103) peak remains relatively stable, the $I_{(103)}/I_{(002)}$ ratio provides a reliable indication of exfoliation efficiency. The results show that this ratio gradually increases with quenching temperature, reaching its maximum at 150°C, suggesting that exfoliation is most effective under this condition. These findings are consistent with the structural changes discussed in Fig. 1 and further confirm that quenching at 150°C is the most favorable condition for achieving effective interlayer exfoliation of MoS_2.

AFM analysis, presented in Fig. 3, shows the thickness distribution of MoS_2 samples at RT and 150°C. The RT sample,

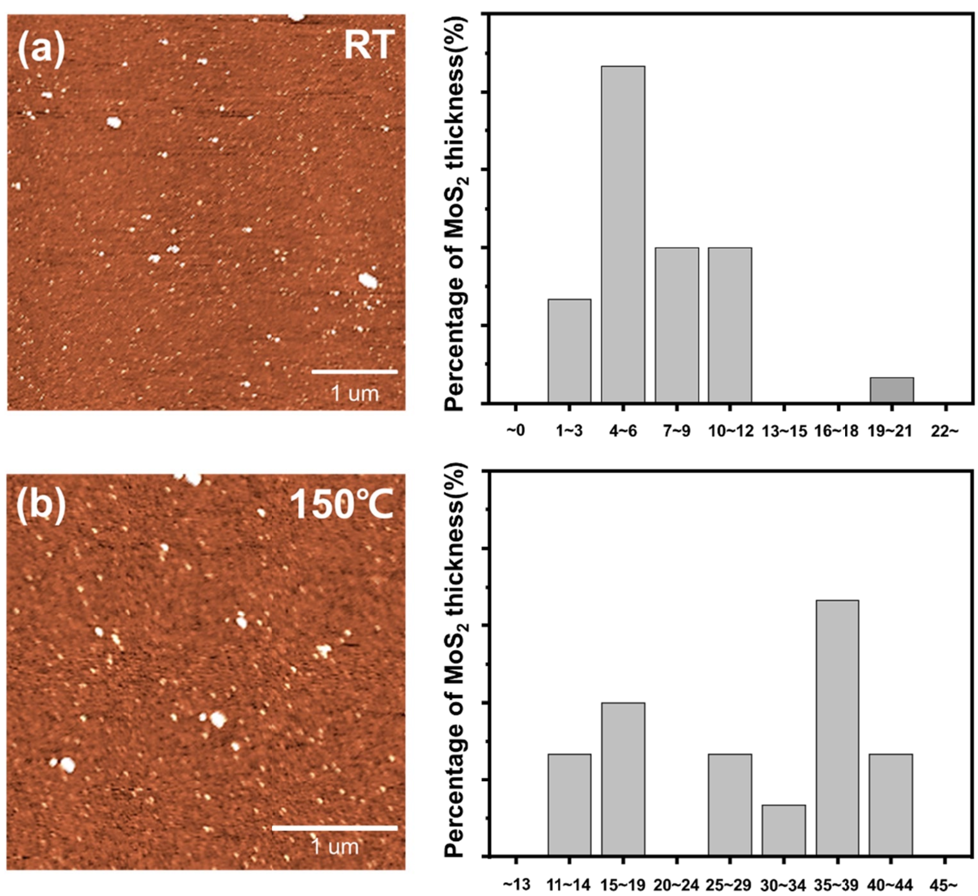

Fig. 3. Thickness Distribution Comparison of MoS_2 Samples: (a) As-prepared (No Quenching), (b) Quenched at 150°C

used as a control without undergoing the quenching process, had a thickness concentrated within the 35-39 nm range, typical of bulk MoS_2, where the van der Waals forces remained intact, preventing exfoliation. In contrast, the 150°C sample displayed a much thinner, more uniform nanoflake structure. The majority of flakes in the 150°C sample measured between 4-6 nm, indicating successful exfoliation. Quenching-induced thermal stress weakened van der Waals forces, producing uniform, thin nanoflakes while preserving structural integrity.

As summarized in TABLE 1, the quenching exfoliation method demonstrates stable efficiency when compared to other methods. The quenching method yields 4-6 nm flakes, demonstrating competitive and scalable exfoliation performance.

TABLE 1

Comparison of Thicknesses by MoS_2 Exfoliation Methods

Exfoliation Method	Exfoliation Strategy	Exfoliated MoS_2 Thickness (nm)	References
Cathodic Exfoliation	Top-down	3-6	[22]
Hydrothermal-Assisted Ball Milling	Top-down	5-7	[23]
Electric Field Exfoliation	Top-down	4-5	[24]
Liquid Exfoliation (Water-based)	Top-down	6-10	[25]
Quenching Exfoliation	Top-down	4-6	My Work

Furthermore, the exfoliation efficiency of MoS_2 was quantitatively evaluated by comparing the average and median thickness values before and after exfoliation. Before exfoliation, the average thickness of the MoS_2 flakes was 28.8 nm, and the median thickness was 32.0 nm. After the quenching process at 150°C, the average thickness decreased to 7.86 nm, and the median decreased to 6.5 nm. These results indicate that MoS_2 layers were successfully exfoliated, with an average reduction of 20.94 nm and a median reduction of 25.5 nm. This confirms that the size and thickness of the nanoflakes were very uniformly reduced, proving the high efficiency of the exfoliation process.

This exfoliation process plays a key role in significantly enhancing the electrocatalytic performance of MoS_2. Thinner nanoflakes have a higher surface-area-to-volume ratio, which allows for more exposure of active sites. Reduced thickness enhances electron conductivity, which improves electrocatalytic performance by increasing reactivity and efficiency. The improved electron conductivity of thinner nanoflakes may further enhance the electrocatalytic performance of MoS_2 by increasing both reactivity and efficiency. Therefore, the quenching process at 150°C effectively reduces the thickness of MoS_2 layers, greatly improving its material properties for catalytic and energy-related applications. The scalability of this method, along with its consistent results in exfoliation efficiency, positions it as a highly promising technique for large-scale production of MoS_2 nanoflakes.

4. Conclusions

This study demonstrated that the quenching process is an effective top-down strategy for exfoliating MoS_2, offering a scalable and cost-efficient method. XRD confirmed the preservation of the 2H crystal structure after thermal treatment, with exfoliation primarily along the (002) plane due to weakened van der Waals interactions. The anisotropic thermal expansion of MoS_2 induced directional exfoliation, with stress applied more effectively out-of-plane. AFM results showed that the sample quenched at 150°C had significantly reduced thickness, forming uniform nanoflakes in the 4-6 nm range, compared to the untreated sample's 35-39 nm. Unlike other methods, quenching produced competitive thicknesses without chemical intercalants or complex setups. These structural changes are expected to improve the electrocatalytic potential of MoS_2 by increasing surface area and enhancing electron transport. Overall, the quenching-based exfoliation approach provides a promising and scalable route for producing few-layer MoS_2, bridging the gap between lab-scale processing and industrial implementation in next-generation 2D materials.

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