Metallic 1T Phase MoS$_2$ Nanosheets for Supercapacitor Application

K.M. Sarode, D.R. Patil*
Nanomaterial Research Laboratory, R.C. Patel Arts, Commerce and Science College, Shirpur – 425 405, Maharashtra, India.

1. Introduction

Nowadays, stable and high-performance energy-storage device has been paid tremendous research interest with the enhancing requirement of sustainable energy [1-3]. Supercapacitor is an updated kind of energy storage device, which possesses multiple strengths including, long cycle life, excellent power density, environment-friendly, fast charge/discharge rate and better safety [4-7]. However, to date, most commercial electrical double layer capacitors (EDLCs) employ carbonaceous materials with large surface areas as electrode materials. Furthermore, carbon materials have some other drawbacks, such as low energy density and instability in aqueous electrolyte [8-10]. Thus, a growing attention has been focused on the development of redox-active materials such as conducting polymers [11] and metal oxide [12, 13] for pseudocapacitors.

Two-dimensional transition-metal dichalcogenides (2D TMDs) such as MoS$_2$ have recently attracted worldwide attention in various fields, such as sodium-ion batteries [14], lithium-ion batteries [15-17], electrochemical capacitors (ECs) [18-21], solid lubricants [22, 23], and catalysts [24, 25] benefiting from their distinct chemical and structure properties. MoS$_2$ has layered structure consisting of covalently bonded S-Mo-S, separated by a relatively weak van der Waals gap [26, 27]. Hence, it is easy to peel MoS$_2$ layers from the bulk [28, 29]. Nevertheless, MoS$_2$ usually exhibits the extremely low conductivity between two adjacent Van der Waals bonded layers which would significantly suppress their overall electrochemical performance [30]. To solve this problem, adjusting the microcrystal morphology or connecting with other materials is an effective way.

Herein, we synthesized MoS$_2$ NS by lithium intercalation and exfoliation method. The physical Property and electrochemical performance of the as-obtained MoS$_2$ NS are evaluated in detail. The MoS$_2$ NS-based electrodes were found to deliver a capacitance of 148 Fg$^{-1}$ at 1 mV/s or 142 Fg$^{-1}$ at 1 Ag$^{-1}$ with excellent long-term cycling stability over 1000 cycles in 1 M KCl. The result indicates that the MoS$_2$ NS can be served as a promising electrode material for electrochemical supercapacitor.

2. Experimental Methods

2.1 Synthesis of MoS$_2$ NSs

The MoS$_2$ NSs were prepared by lithium intercalation and exfoliation method [31]. In a typical synthesis, 1.0 g of bulk MoS$_2$ powder was dispersed in 10 mL of 1.6 M butyllithium solution in hexane in a flask filled with N$_2$ gas. The mixture was soaked at room temperature for 48 h, and the obtained Li$_x$MoS$_2$ was centrifuged and washed with hexane to remove excessive lithium and organic residues. Exfoliation was achieved by sonicating the Li$_x$MoS$_2$ slurry in DI water for 1 h. The obtained aqueous suspension of MoS$_2$ NSs was centrifuged at 3,000 rpm for 25 min to discard the precipitates, and the supernatant was again centrifuged at 8,000 rpm for 25 min. The mixture was re-dispersed in DI water and re-centrifuged for several times and dried at 60 °C in vacuum. Finally, black MoS$_2$ crystalline powder was obtained.

2.2 Material Characterization

The crystalline structures of bulk MoS$_2$ and MoS$_2$ NSs were characterized by X-ray diffraction (XRD) (EMPYREAN with Cu Kα radiation, λ = 1.5418 Å). The morphology was observed by field emission scanning electron microscopy (FESEM, Zeiss/ Ultra 55). A Raman spectrometer (Renishaw inVia, excitation 514.5 nm) was also used to characterize the synthesized materials.

2.3 Electrochemical Characterization

All electrochemical measurements were tested in a conventional three-electrode system using an electrochemical workstation; 1 M KCl solutions were used as the electrolyte. The working electrodes were prepared by mixing the as-prepared active material, acetylene black and polyvinylidene difluoride (PVDF) with a mass ratio of 8:1:1, followed by the addition of N-methylpyrrolidone (NMP) to form homogenous slurry. The obtained slurry was then coated onto a stainless steel plate with NMP and dried at 60 °C in vacuum. Finally, black MoS$_2$ electrolyte powder was obtained.

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2.4 Property and Electrochemical Performance of the as-obtained MoS$_2$ NSs

The electrochemical performance of the as-obtained MoS$_2$ NSs was evaluated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS). The CV curves were recorded at various scan rates (0.5 to 0.2 V) in a potential window of 0.5 to 0.2 V. The GCD curves were obtained at various current densities (1, 2, 3, and 5 Ag$^{-1}$) in a potential window of 0.5 to 0.2 V.

The specific capacitance of the as-prepared electrode was calculated from the cyclic voltammetry [Eq (1)]

$$C_s = \int \frac{I(V)dv}{vmdw} \quad \text{(Fg}^{-1})$$

and galvanostatic charge discharge curves [Eq (2)], according to the following equations:

$$C_m = \frac{1}{\Delta t} \Delta W \quad \text{(Fg}^{-1})$$

where $C_s$ is the specific capacitance (Fg$^{-1}$), $I(V)dv$ is the integrated area of the CV curve (Ah), $v$ is the scan rate (mV/s$^{-1}$), $m$ is the mass of the active material (g), $\Delta W$ is the potential window (V), $I$ is the discharge current (A), and $\Delta t$ is the discharge time (s).
3. Results and Discussion

3.1 Characterization of MoS₂ NS

Fig. 1 shows the FESEM images of the bulk MoS₂ and MoS₂ NSs. The bulk MoS₂ exhibited largely micrometer-sized inorganic nanosheets, which are tightly stacked. After lithiation-exfoliation, the morphology of MoS₂ NSs interestingly changed to highly scattered nanoflakes. It is also noted that the size and thickness of the nanosheets were significantly decreased relative to the bulk phase.

![Image](https://doi.org/10.30799/ijstl.108.18040301)

Fig. 1 FESEM images of (a) bulk MoS₂, (b) MoS₂ NSs

MoS₂ NSs possess a high degree of reversibility and superior rate capability. The specific capacitance as a function of the scan rate is shown in Fig. 4(c). At the scan rate of 1 mV s⁻¹, the specific capacitance values of the Bulk MoS₂ and MoS₂ NSs were 68 and 148 F g⁻¹ from the cyclic voltammetry measurements, when we increasing the scan rate from 2 mV s⁻¹ to 20 mV s⁻¹, around 55% of initial capacitance was retained, respectively.

Further, the supercapacitive behaviors of the prepared electrodes were analyzed using GCD tests. Fig. 4(d) shows the GCD curves of MoS₂ NSs electrodes at the increased current densities from 1 to 5 A g⁻¹. Fig. 4(e) shows the variation of the specific capacitance value calculated from the charge–discharge curves at different current densities. As can be seen in Fig. 4(d), the charge–discharge curves show a good triangle shape, which indicates the ideal supercapacitive characteristic of MoS₂ NSs electrode. The specific capacitance decays from 148 F g⁻¹ to 80 F g⁻¹ as the current density increases from 1 to 5 A g⁻¹, which shows the same tendency as CV measurement.

![Image](https://doi.org/10.30799/ijstl.108.18040301)

Fig. 2 X-ray diffraction patterns of bulk MoS₂ and MoS₂ NSs

The electrochemical performances of the as-prepared electrodes were first investigated in a three-electrode system by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests. Meanwhile, the electrochemical measurements were achieved in 1 M KCl electrolyte solution. Fig. 4(a) shows the CV curves of the Bulk MoS₂, MoS₂ NSs and stainless-steel current collector electrodes at a scan rate of 20 mV s⁻¹. The MoS₂ NSs present a pair of redox peaks, which states pseudocapacitive features. By comparison, one can find that the area surrounded by the CV curve of MoS₂ NSs electrode is larger than that of bulk MoS₂ and stainless-steel current collector respectively, suggesting a higher specific capacitance. The increased specific capacitance demonstrated superior electrochemical performance which might be due to the exfoliated layers to dynamically expand and intercalate the Li⁺ ions.

Fig. 4(b) shows the CV curves of MoS₂ NSs electrode at various scan rates. With the increase of scan rate, the integral area of CV curves and the peak current density are accordingly increased. Meanwhile, a pair of perfectly redox peaks is always retained in all the CV curves. These results indicate the MoS₂ NSs possess a rapid and reversible Faradic behavior and superior rate capability. The specific capacitance as a function of the scan rate is shown in Fig. 4(c). At the scan rate of 1 mV s⁻¹, the specific capacitance values of the Bulk MoS₂ and MoS₂ NSs were 68 and 148 F g⁻¹, from the cyclic voltammetry measurements, when we increasing the scan rate from 2 mV s⁻¹ to 20 mV s⁻¹, around 55% of initial capacitance was retained, respectively.

4. Conclusion

The MoS₂ NSs have been prepared as electrode materials for supercapacitors through a facile and efficient strategy. The morphology and structure of the MoS₂ NSs were analyzed by FESEM, XRD, and Raman analysis. Electrochemical measurements indicate that the MoS₂ NSs electrode exhibited a higher specific capacitance (148 F g⁻¹), as well as a better cyclic stability than the bulk MoS₂ electrode. It is concluded that
these MoS2 NSs with excellent electrochemical performance can be very promising for high performance electrode materials in supercapacitors and other energy-storage devices.

References


