Three-Dimensional MoS₂ Nanodot-Impregnated Nickel Foam Electrodes for High-Performance Supercapacitor Applications

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ABSTRACT: An economical and binder-free electrode was fabricated by impregnation of sub-5 nm MoS₂ nanodots (MoS₂ NDs) onto a three-dimensional (3D) nickel substrate using the facile dip-coating method. The MoS₂ NDs were successfully synthesized by controlled bath sonication of highly crystalline MoS₂ nanosheets. The as-fabricated high-surface area electrode demonstrated promising electrochemical properties. It was observed that the as-synthesized NDs outperformed the layered MoS₂ peers as the electrode for supercapacitors. MoS₂ NDs exhibited an excellent specific capacitance (Cₚ) of 395 F/g at a current load of 1.5 A/g in a three-electrode configuration. In addition, the fabricated symmetric supercapacitor demonstrated a Cₚ value of 122 F/g at 1 A/g and a cyclic performance of 86% over 1000 cycles with a gravimetric power and energy density of 10,000 W/kg and 22 W h/kg, respectively. Owing to its simple and efficient fabrication and high surface area, such 3D electrodes show high promise for various energy storage devices.

INTRODUCTION

Recently, with ever-growing energy concerns, the quest for high-performance multifunctional materials that display high performance toward energy storage and conversion with effective usage is on high demand. On this front, supercapacitors, owing to its ability to outburst power instantaneously, high specific energy, fast charge/discharge rates, and source of green energy have attracted a great deal of interests.¹,² Supercapacitors, otherwise electric double layer capacitor (EDLC), possess excellent energy and power density that opens portal for myriad applications in industries such as consumer electronics, hybrid automobiles, military devices, industrial power, and memory backup systems.³,⁴ Therefore, development of high-performance supercapacitors always remains a thrust area of research in the scientific community. In general, supercapacitors can be categorized into pseudo and double-layer capacitor, respectively, based on their charge storage mechanism. In a pseudocapacitor, energy storage occurs primarily via redox mechanism on the periphery of electrode materials such as transition metal oxides and hydroxides, conducting polymers such as PANI, polypyrrole, and EDOT, and so forth are typical electrode materials in pseudo-capacitors.⁵–⁷ However, in EDLC charge separation occurs at the interface of electrode and electrolyte; usually carbon materials like graphene, CNTs, carbon nanospheres, and activated carbon are utilized as the electrode material.⁸–¹⁰ In addition to metal oxides and conducting polymer-based pseudocapacitors, metal organic frameworks, conductive metal sulfides such as WS₂, MoS₂, CoS, NiS, SnS₂, and ZnS and their hybrids have also emerged as distinctive materials for supercapacitor applications.¹¹–¹⁸ Amongst, molybdenum disulfide (MoS₂) possess a unique S−Mo−S trilayer atomic structure that is restrained by weak van der Waals forces, analogous to that of graphene.¹⁹,²⁰ Also, due to its high electrical conductivity, and unique layered morphology, MoS₂-based materials offer better prospects as an electrode material for high-performance supercapacitor compared to metal oxides and graphitic materials. Similarly, nanostructured MoS₂ can be synthesized via simple and economical processes such as hydrothermal, sono-chemical, and chemical vapor deposition techniques.²¹–²³ Nowadays, MoS₂ has also attracted plenty of recognition in electrochemical energy storage devices attributed to its innate ionic conductivity and higher theoretical capacity than graphite, owing to its graphene analogous structure.²⁴,²⁵ The aforementioned characteristics of MoS₂ make them excellent electrode material compared to metal oxides and graphite. However, adorned with such fascinating properties, the studies that explore pseudocapacitive nature of MoS₂ electrodes are still limited and mostly focus nanostructured MoS₂ and its composites. Soon and Loh reported MoS₂ micro-supercapacitor with an areal capacitive value of 8 mF/cm².²⁶ Similarly, Sun et al. fabricated a tubular C/MoS₂ electrode material with a Cₚ value of 210 F/g at 1 A/g.²⁷ Huang et al. reported high-performance supercapacitor with polyaniline/
graphene equivalent MoS₂ as electrode material.²⁸ Kim et al. reported MoS₂ nanostuctures obtained via hydrothermal reaction and utilized as negative electrode material in 1 M Na₂SO₄ electrolyte and maximum capacitive performance of 92 F/g was observed at a current load of 0.5 mA/cm².¹¹ A flower-like MoS₂ structure was communicated by Ma et al. with a Cₛₑ value of 122 F/g at 1 A/g.²⁹ Wang et al. also reported flower like morphology with an improved Cₛₑ value of 168 F/g at 1 A/g.³⁰ Karade et al. illustrated MoS₂ nanoflakes prepared via chemical bath deposition with a high Cₛₑ value of ~210 F/g at 1.5 A/g.³¹ Apart from this, MoS₂/carbon composites such as MoS₂/graphene, MoS₂/graphene oxide, and MoS₂/MWCNT electrode materials are also reported.³¹,3²

In further advancement, the recent reports show the synthesis of zero-dimensional nanodots (NDs) of MoS₂ which are expected to possess different electronics and physico-chemical properties than their 2D nano and bulk counterparts, owing to modulated size confinements and edge effects.³³ Currently, the MoS₂ NDs are being investigated for applications such as electrocatalysts.³⁴ However, no literary reports investigating the MoS₂ NDs supercapacitive performance has been noted so far.

Hence, in the present report we have attempted to investigate the electrochemical and supercapacitor performance of MoS₂ NDs impregnated on the 3D nickel foam. The uniformly sized MoS₂ NDs were synthesized from controlled bath sonication of crystalline MoS₂ nanosheet in isopropanol at ambient temperature. The resulting NDs were successfully surface impregnated on Ni foam using a simple and facile dip-coating method. Subsequently, the electrochemical performance of MoS₂ NDs@Ni foam was evaluated using galvanostatic charge/discharge, chrono-potentiometry (CD), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) in a basic electrolyte (6 M KOH). Moreover, the supercapacitor performance of electrode material was also evaluated in a symmetric two-electrode configuration using MoS₂ ND-doped electrode material as cathode and anode, respectively. The resulting electrochemical properties suggest that the 3D MoS₂ NDs/Ni foam exhibit superior supercapacitive performance and cyclic efficiency compared to the bulk and nanostructured MoS₂ and its hybrid materials.

**RESULTS AND DISCUSSION**

**Experimental Section. Chemical and Materials.** Ammonium tetraethiomolybdate (ATTM) (99.97% pure), potassium hydroxide (ACS Reagent, >85%), and isopropanol was procured from Sigma-Aldrich and was utilized as received. High grade nickel foam (99.8% purity) was purchased from High Purity Metals, and was utilized as received. Hydroxide (ACS Reagent, >85%), and isopropanol was purchased from Sigma-Aldrich and was utilized as received. The resulting NDs were successfully surface impregnated on Ni foam using a simple and facile dip-coating method. Subsequently, the electrochemical performance of MoS₂ NDs@Ni foam was evaluated using galvanostatic charge/discharge, chrono-potentiometry (CD), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) in a basic electrolyte (6 M KOH).

**Fabrication of 3D MoS₂ NDs/Ni Foam Electrodes (3D MoS₂ NDs/NF).** First, uniformly distributed MoS₂ NDs were synthesized by top-down approach and by ultrasonication of a nanocrystalline MoS₂ in isopropanol. The MoS₂ was freshly prepared by thermal annealing of ATTM at 600 °C for 2 h inside the tube furnace and under a continuous flow of argon. After sonication, a color change of the dispersion to yellowish-green was observed. Further, the resulting dispersion was subjected to centrifugation at 4000 rpm for 1 h, which enabled the separation of highly dispersed MoS₂ NDs and large-sized MoS₂ particles. Thus the resulting MoS₂ NDs dispersion was recovered and used for further structural and electrochemical characterizations. In the second step, 3D Ni foam was coated with MoS₂ NDs by simple repetitive dip-coating into the as-obtained MoS₂ ND dispersion with known concentration. Pale yellow NDs impregnated Ni Foam was dried at 80 °C under vacuum and used for further studies. The active material loading (0.02 mg) was calculated using the weight difference of nickel foam before and after coating by high precision weighing balance which is accurate up to 0.0001 mg. A detailed synthesis mechanism is shown schematic illustration presented in Figure 1. The areal volumetric loading of MoS₂ QD on 3D nickel foam of dimension 0.8 cm × 0.5 cm × 0.1 cm was 0.5 mg/cm³.

**Material Characterization.** The scanning electron microscopy (SEM) images were taken with a Quanta- FEG-250 scanning electron microscope. X-ray diffraction (XRD) patterns were obtained on X’Pert PRO Powder Diffractometer with Cu Kα radiation. A Raman spectrum of MoS₂ NDs was collected using a Jobin Yvon HORIBA LabRAM spectrometer with back-scattered confocal configuration using a HeNe laser (633 nm). Transmission electron microscopy (TEM) images were obtained using FEI Tecnai G20 with 0.11 nm point resolution operated at 200 kV using Gatan digital camera.

**Electrochemical Measurements.** Electrochemical behavior of 3D MoS₂ NDs/NF was studied via CV, charge–discharge (CD), and impedance (EIS) using a potentiostat–galvanostat (VMP-300, BioLogic) instrument. In a three-electrode configuration, a 3D MoS₂ NDs/Ni electrode was utilized as a working electrode, and platinum wire (pt) and saturated calomel electrode (SCE) were employed as counter and reference electrode, respectively. The electrochemical analysis was carried out in 6 M KOH electrolyte for scan rates 10–100 mV/s, current densities 1–20 A/g, and frequency ranging from 100 kHz to 1 Hz, respectively. The specific capacitance of 3D MoS₂ NDs/NF was evaluated from discharge curve (CD) by using eq 1

\[
C_p = \frac{I \times \Delta t}{m \times \Delta V}
\]

where \(C_p\) is the specific capacitance in F/g, \(I\) is the current in mA, \(\Delta t\) is the discharge time in seconds, \(m\) is the amount of
active material in mg, and $\Delta V$ (V) is the operational window. Also, the supercapacitor performance of the electrode material was evaluated by fabricating a symmetric supercapacitor device using 3D MoS$_2$ NDs/NF as a positive and negative electrode. Whatman filter paper, cat no.: 1441 110, soaked in 6 M KOH was used as a separator. Specific capacitance, power density (W/kg) and energy density (W h/kg) of fabricated supercapacitor was estimated using the following equations eqs 2−4.\(^{35}\) EIS was performed from 1 Hz to 100 kHz for a sinusoidal voltage of 10 mV.

$$C_{sp} = \frac{2I \times \Delta t}{m \times \Delta V} \quad (2)$$

$$E_{cell} = \frac{0.5 \times C_{sp} \times (\Delta V)^2}{3.6} \quad (3)$$

$$P_{cell} = \frac{E \times 3600}{t} \quad (4)$$

The synthesis protocol was schematically demonstrated in Scheme 1. The highly crystalline as-obtained MoS$_2$ nanosheets were subjected to the controlled bath sonication in iso-propanol suspension for 1 h. After the stipulated time, a stable yellowish-green dispersion of the sub-5 nm monodisperse MoS$_2$ NDs were obtained. The forces exerted by ultrasonic vibration vibrate the planar MoS$_2$ nanosheets and ultrasonic vibration vibrate the planar MoS$_2$ nanosheets. Here, sonication parameters were controlled by high-resolution TEM (HRTEM) images provided in Figures 1, and S1 respectively. Figure 1a shows the TEM image of highly crystalline MoS$_2$ nanosheets obtained after thermal annealing of ATTM precursor at 600 °C for 2 h, which clearly shows a characteristic layered structure of MoS$_2$. Upon sonication treatment, the layered MoS$_2$ was disintegrated into well-dispersed sub—5 nm NDs was observed (Figure 1b).

Previously, Gopalakrishnan et al. reported the growth of MoS$_2$ nanoparticles distributed within the in MoS$_2$ nanosheets via bath and probe sonication of bulk MoS$_2$ for hydrogen evolution kinetics study.\(^{36}\) However, the average sizes of MoS$_2$ nanoparticles were not informed. Herein, we report much smaller dimensions and uniform distribution of MoS$_2$ NDs. This could be attributed to the controlled bath sonication subjected to highly crystalline MoS$_2$ nanosheets. Henceforth, the controlled bath sonication facilitated very precise scission of MoS$_2$ nanosheets and their impregnation on to 3D Nickel Foam. Also, the absence of any visible diffraction spots or rings which further support the amorphous nature of these NDs. Also, these results confirm the simple dip-coating facilitated good adherence between NDs and nickel foam. This can be due to weak van der Waals force between NDs and the nickel substrate. Additionally, the nickel substrate will provide good conductive pathway and bulk level interaction for electron/ion transportation during oxidation/reduction reaction due to its high conductivity and foam structure, respectively. The Raman study reveals the formation of nanoscopic MoS$_2$. The characteristic Raman peaks (Figure 2a) near 378 and 407 cm$^{-1}$ associated with E$_{2g}^{1}$ and A$_{1g}$ active modes, respectively, ascertains the presence of MoS$_2$ nanostructure.\(^{37−39}\) The additional Raman peak near 450 cm$^{-1}$ is associated with oxidation of MoS$_2$ to MoO$_3$ in the presence of laser light. Generation of hetero-dimensional MoS$_2$ NDs can be attributed to the sonication assisted scission of MoS$_2$ nanosheets. Here, sonication parameters were controlled to obtain MoS$_2$ NDs. The standing waves induced during ultrasonic vibration vibrate the planar MoS$_2$ nanosheets and prolonged sonication resulted in the formation of NDs, as observed in TEM images (Figure 1b,d). Hence, a simple bath sonication over a prolonged time led to the formation of MoS$_2$ NDs. The XRD pattern of 3D MoS$_2$ NDs/NF foam was shown in Figure 2b,c. It can be seen that the no characteristic peaks associated with MoS$_2$ diffraction was observed and only peaks associated with Ni foam are present. This indicates that the existence of noncrystalline nanodots of MoS$_2$ successfully impregnated on the Ni foam substrate. Moreover, the absence

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c01045)
of any MoS\textsubscript{2} specific peaks in short-range XRD (Figure 2c) indicates the existence of amorphous MoS\textsubscript{2} NDs. For comparison, the XRD data of crystalline MoS\textsubscript{2} and pristine MoS\textsubscript{2} NDs are presented in Figure S2, indicating highly crystalline MoS\textsubscript{2} nanosheets and amorphous MoS\textsubscript{2} NDs. Similarly, the X-ray photoelectron spectroscopy and SEM−energy-dispersive X-ray spectrometry characterization indicates that the precursor MoS\textsubscript{2} crystalline starting material is free from contamination (Figures S3 and S4). Furthermore, an amorphous material possesses low lattice energy and therefore enhances the utility ratio of active material. This allows easy de-intercalation process, which is beneficial in electrochemical performance of the electrode material.

**Electrochemical Studies.** Under three electrode configuration, the CV curves were obtained for scan rates varying from 10 to 100 mV/s. As observed in Figure 3a, presence of redox shoulder in CV plots indicates the redox reaction occurring between strong basic electrolyte, (KOH), and MoS\textsubscript{2} NDs. During the faradaic charge transfer process, the ions such as H\textsuperscript{+} and K\textsuperscript{+} distribute into the stacked layer of MoS\textsubscript{2} structure resulting in a reaction mechanism as shown in eq 5.

\[
\text{MoS}_2 + K^+ + e^- \leftrightarrow \text{MoS} - 5K^+ \tag{5}
\]

However nonfaradaic nature is exhibited along the electrode/electrolyte interface, as shown in eq 6.

\[
(\text{MoS}_2)_{\text{surface}} + K^+ + e^- \leftrightarrow (\text{MoS}_2 - K^+)_{\text{surface}} \tag{6}
\]

In addition, the CV curve area increases proportionally for scan rates 10−100 mV/s, implying the capacitive nature of the electrode. Besides, the shape of the CV plot more or less remains the same even at higher scan rates indicating good rate and capacitive performance of MoS\textsubscript{2} NDs. Figure S5 provides a qualitative comparison between CV plots obtained for pristine nickel and MoS\textsubscript{2} ND impregnated nickel foam. It can be concluded that the charge storage mechanism primarily happens in MoS\textsubscript{2} ND-doped nickel foam and electrochemical inertness of utilized nickel foam. Figure 3d shows the change in specific capacitance for different current densities. The decrease in capacitance was observed with increase in current densities, which can be associated with an internal resistance of electrode material. MoS\textsubscript{2} NDs demonstrated excellent \(C_p\) value of 395 F/g at 1.5 A/g. Several researchers have reported capacitive behavior of MoS\textsubscript{2} nanostructures. Recent studies that include MoS\textsubscript{2} nanoflakes reported by Karade et al.\textsuperscript{2} reported a specific capacitance of 576 F/g at 5 mV/s. Ilanchezhiyan et al.\textsuperscript{12} reported a capacitance value of 122 F/g at 5 mV/s in the 1 M Na\textsubscript{2}SO\textsubscript{4} electrolyte. Ramadoss et al.\textsuperscript{13} reported spherical aggregates of MoS\textsubscript{2} nanostructures with a specific capacitance of 403 F/g at 1 mV/s. Linear relation obtained for cathodic and anodic peak current for the corresponding square root of scan rate (Figure 3b) indicates the diffusion-controlled behavior on the MoS\textsubscript{2} ND electrode surface.\textsuperscript{40} The latter behavior is observed very often in the presence of strong basic electrolytes (6 M KOH). The CD curves were obtained at varying current load (1.5, 2, 2.5, 3, 5, and 10 A/g) and showed triangular and symmetrical behaviour indicating good capacitive behavior of electrode material. The specific capacitance of the MoS\textsubscript{2} ND electrode was obtained using eq 5, from CD curve shown in Figure 3c. Specific capacitance \((C_p)\) of MoS\textsubscript{2} NDs obtained are 395, 147, 106, 86, 62, and 47 F/g for current loads 1.5, 2, 2.5, 3, 5, and 10 A/g, respectively (Figure 3d). Observed specific capacitance of MoS\textsubscript{2} NDs (1.5 A/g) is significantly large than that of pure MoS\textsubscript{2} (1 A/g) reported earlier 40, 98, 122, and 168 F/g, respectively.\textsuperscript{25−30} This indicates that the MoS\textsubscript{2} NDs exhibited superior performance compared to the aforementioned MoS\textsubscript{2} peers. The observed high capacitance for MoS\textsubscript{2} NDs was primarily attributed due to pseudo behavior in the presence of a strong basic electrolyte (6 M KOH), facilitated by MoS\textsubscript{2} NDs uniformly impregnated on the surface of the nickel substrate via simple dip coating. In addition, nickel substrate provides a better conductive pathway for intercalation/de-intercalation of ions during redox reaction. Previously reported capacitive behavior of MoS\textsubscript{2} electrode materials along with present work are tabulated in Table S1.
The EIS studies were performed to understand the charge transfer process occurring between the MoS₂ ND electrode and electrolyte interface and resistance developed within the system (Figure 4a). The semicircle in the higher frequency region accommodates the electrode/electrolyte charge transfer resistance and electrolyte resistance.

![Figure 4](image)

**Figure 4.** (a) Nyquist plot of electrode material inset showing the equivalent circuit (b) assembly of symmetric supercapacitor and charge storage mechanism, schematics.

The linear line accounts for the diffusive resistance, known as Warburg impedance. The obtained slope is greater than 45°, suggesting good capacitive nature of the electrode material. The Nyquist plot obtained was fitted with an equivalent circuit (Figure 4a, inset) containing R and C components. An equivalent series resistance (Rₛ) ~1.19 Ω was obtained from the intercept on real axis. Semi arc in the high-frequency region can be associated with double-layer capacitance C_d and charge-transfer resistance, Rₜ ≈ 3.75 Ω at the electrode/electrolyte interface. The presence of the Cₜ component implies the faradaic charge-transfer process occurring in the alkaline medium. Similarly, the performance of the resulting 3D MoS₂ NDs/NF was compared with the previously reported MoS₂-based electrode materials for supercapacitor application and tabulated in Table 1.

**Symmetric Supercapacitor.** To further investigate electrochemical properties of MoS₂ ND as an electrode material, a symmetrical supercapacitor was fabricated as shown in Figure 4b. The charge storage mechanism is also illustrated in the schematics provided in Figure 4b. A 6 M KOH soaked filter paper was used as electrolyte and separator, respectively. The operational voltage of symmetrical supercapacitor was determined by investigating the CV plots of negative and positive MoS₂ ND electrode material in a three electrode configuration (Figure 5a). As observed in Figure 5a, MoS₂ ND electrodes exhibited nearly rectangular shape except toward the extreme potential, where instability of electrode material was pronounced. This can be attributed to hydrogen and oxygen evolution reaction, thereby narrowing the operating voltage. Hence, the determined operating potential of 0.6 V was used for carrying out electrochemical analysis in a symmetric supercapacitor. The CV plot obtained for symmetric supercapacitor at 30 mV/s with the determined operational voltage is shown in Figure 5b. As observed, nearly a rectangular curve was obtained in a two-electrode configuration, confirming the capacitive nature of MoS₂ ND supercapacitor.

![Figure 5](image)

**Figure 6a** shows the CV curves of MoS₂ ND symmetric supercapacitor for scan rates 20–100 mV/s, with an operational window of 0.6 V. As seen in **Figure 6a,** all of the curves are identical and exhibited an approaching rectangular shape indicating good rate capability of the two-electrode supercapacitor. **Figure 6b** shows the capacitance (Cᵣ) obtained for MoS₂ ND supercapacitor for different scan rates. Specific capacitance from CV plots was calculated using eq 7.

\[
2 \times \int_0^{0.6} I(V) \, dV 
\]

where \(I(V)\,dV\) is the area enclosed in CV curves, \(ν\) is the scan rate in V/s, and other units were as stated elsewhere in the text.

Specific capacitances obtained are 105, 100, 104, 102, and 100 F/g for scan rates 20–100 mV/s. The electrode material demonstrated excellent rate capability as there was a capacitance retention of 95% for varying scan rates (Figure 6b). Galvanostatic charge–discharge plots were obtained for MoS₂ ND symmetric supercapacitor as shown in Figure 6c. A voltage drop of ~0.25 Ω can be observed. The specific capacitances obtained using eq 6 is 122, 98, 82, 80, and 48 F/g for current loads 1, 1.5, 2, 2.5, and 10 A/g, respectively (Figure 6d). MoS₂ ND symmetric supercapacitor exhibited 65% of capacitance retention for current loads varying from 1 to 2.5 A/g.

**Figure 7**, illustrates the cyclic stability and Coulombic efficiency of MoS₂ ND supercapacitor for an input load of 2.5 A/g. As seen in **Figure 7a,** as-assembled symmetric supercapacitor demonstrated a capacitance retention of ~100% in the first 300 cycles and then begins to flatten. The electrode material demonstrated a capacitance retention of ~86% over 1000 cycles. CD curve obtained in first and last few cycles are shown in **Figure 7a,** inset. Similarly, the MoS₂ NDs displayed an excellent Coulombic efficiency of 100% at the end of 1000 CD cycles, which further highlights the advantage of the MoS₂ ND electrode. Hence, we can conclude that the MoS₂ ND symmetric supercapacitor exhibits good reversibility of energy storage. The Ragone plot obtained for the MoS₂ ND supercapacitor is shown in **Figure 7b**. As observed, the fabricated supercapacitor exhibited high energy density without comprising much power density. A high energy density and power density of 22 W h/kg and 1300 W/kg were obtained for a current load of 1 A/g. The fabricated supercapacitor exhibited gravimetric energy and power density of 2.4 W h/kg and ~10,000 W/kg, respectively, though the

**Table 1. Comparison of 3D MoS₂ ND Performance with Preciously Reported MoS₂ Electrode Materials**

| sample description | synthesis method | specific capacitance | electrolyte | references |
|--------------------|------------------|----------------------|------------|------------|
| MoS₂ NDs bath sonication/probe sonication | 395 F/g @ 1 A/g | 6 M KOH | present work |
| MoS₂/graphene hydrothermal, in cysteine solvent | 243 F/g @ 1 A/g | 1 M Na₂SO₄ | 42 |
| MoS₂/chemically modified graphene hydrothermal reduction reaction | 268 F/g @ 0.5 A/g | 1 M Na₂SO₄ | 43 |
| edge oriented MoS₂ nanoporous film oxidation of Mo foil by sulfur vapors | 15 mF/cm² @ 1 mA/cm² | 1 M LiOH | 44 |
| flower like MoS₂ nanostructure hydrothermal | 168 F/g @ 1 A/g | 1 M KCl | 45 |
| MoS₂ thin film electrode physical deposition | 330 F/cm² @ 17 mA/cm² | 0.5 M H₂SO₄ | 46 |
input current load was 10 A/g. The energy and power characteristics obtained in the present work were compared to previously reported work as shown in Figure 7b. As illustrated in Figure 7b, present work demonstrated better energy density compared to Krishamoorthy et al., Javed et al., and Patil et al. EIS was also performed on supercapacitor for a frequency range of 100 kHz to 1 Hz. Nyquist plot obtained before and after 1000 cycles is shown in Figure 7c. As observed, the Nyquist plot obtained exhibited a similar trend even after 1000 cycles. The slope of the linear curve in lower frequency that accounts for diffusive resistance (Warburg impedance) is greater than 45°, indicating the capacitive behavior. An equivalent circuit for the same is provided in Figure 7c (inset). An equivalent series resistance (R_s) of ≈4.01 Ω was observed for supercapacitor before and after 1000 cycles, demonstrating the stability of fabricated supercapacitor.

Bode plot shown in Figure 7d indicates, at lower frequencies phase angle (Φ) is closer to 90°, exhibiting the behavior of an ideal capacitor (C_d). However, a deviation from the ideal capacitive behavior is associated with faradic charge transfer process occurring as shown in eq 6. The presence of C_f component in the equivalent circuit shown in Figure 7c; inset ascertains the redox nature of the symmetric supercapacitor.

### CONCLUSIONS

In this preliminary study, we have demonstrated the fabrication of 3D MoS2 ND-impregnated Ni foam as binder-free electrode for supercapacitor applications. The sub-5 nm MoS2 NDs were successfully synthesized by controlled bath sonication of 2D nanocrystalline MoS2 sheets that were obtained via thermal annealing of the ATTM precursor. The fabrication of the electrode was achieved by simple and economical dip-coating procedure. The morphological and structural characterizations confirmed the formation NDs as well as successful deposition of MoS2 NDs on the 3D nickel substrate. The resulting electrode material exhibited a superior capacitance value (C_sp) 395 F/g for an input load of 1.5 A/g compared to bulk and nano MoS2 based electrodes in a three-electrode configuration. In addition, a symmetric supercapacitor was also fabricated and successfully evaluated the supercapacitive performance of the electrode material. The latter demonstrated promising values (C_sp = 122 F/g at 1 A/g) and a cyclic performance of 86% over 1000 runs. Furthermore, a high energy and power density of 22
W h/kg and 10,000 W/kg were achieved, respectively. Overall, the presented approach can be extended to the large-scale production of economical binder-free electrode based on MoS2 NDS for various energy storage applications.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01045.

Literature comparison table, HRTEM images, XRD pattern, and CV plots pristine MoS2 NDS (PDF)

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S.P.L. and S.M.A. conceived the project idea and designed the experiment; A.M.A. and V.V.P. performed the experiments and data analysis. S.P.L. wrote the manuscript and S.M.A. revised it. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Pang, H.; Wang, S.; Shao, W.; Zhao, S.; Yan, B.; Li, X.; Li, S.; Chen, J.; Du, W. Few-layered Co(HPO4)2·3H2O ultrathin nanosheets for high performance of electrode materials for supercapacitors. Nanoscale 2013, 5, 5752−5757.
(2) Karade, S. S.; Dubal, D. P.; Sankapal, B. R. MoS2 ultrathin nanoflakes for high performance supercapacitors: room temperature chemical bath deposition (CBD). RSC Adv. 2016, 6, 39159−39165.
(3) Conway, B. Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications; Kluwer-Plenum, 1999.
(4) Liu, C.; Li, F.; Ma, L. P.; Cheng, H. M. Advanced materials for energy storage. Adv. Mater. 2010, 22, No. E28.
(5) Dubal, D. P.; Suarez-Guevara, J.; Tonti, D.; Enciso, E.; Gomez-Romero, P. A high voltage solid state symmetric supercapacitor based on graphene-polyoxometalate hybrid electrodes with a hydroquinone doped hybrid gel-electrolyte. J. Mater. Chem. A 2015, 3, 23483−23492.
(6) Ma, G.; Peng, H.; Mu, J.; Huang, H.; Zhou, X.; Lei, Z. In situ intercalative polymerization of pyrrole in graphene analogue of MoS2 as advanced electrode material in supercapacitor. J. Power Sources 2013, 229, 72−78.
(7) Zhai, Z.-B.; Huang, K.-J.; Wu, X. Superior mixed Co-Cd selenide nanorods for high performance alkaline battery-supercapacitor hybrid energy storage. Nano Energy 2018, 47, 89−95.
(8) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. Nat. Chem. 2013, 5, 263−275.
(9) Feng, J.; Sun, X.; Wu, C.; Peng, L.; Lin, C.; Hu, S.; Yang, J.; Xie, Y. Metallic few-layered VS2 ultrathin nanosheets: high two-dimensional conductivity for in-plane supercapacitors. J. Am. Chem. Soc. 2011, 133, 17832−17838.
(10) Shuai, H.; Ge, P.; Hong, W.; Li, S.; Hu, J.; Hou, H.; Zou, G.; Ji, X. Electrochemically Exfoliated Phosphorene–Graphene Hybrid for Sodium-Ion Batteries. Small Methods 2019, 3, 1800328.
process to form a nickel-based/carbon nanofoam composite supercapacitor electrode using Na$_2$SO$_4$ as an eco-friendly electrolyte. RSC Adv. 2016, 6, 15920−15928.

(49) Noce, R. D.; Eugénio, S.; Silva, T. M.; Carmezim, M. J.; Montemor, M. F. a-Co (OH)$_2$/carbon nanofoam composite as electrochemical capacitor electrode operating at 2 V in aqueous medium. J. Power Sources 2015, 288, 234−242.

(50) Javed, M. S.; Dai, S.; Wang, M.; Guo, D.; Chen, L.; Wang, X.; Hu, C.; Xi, Y. High performance solid state flexible supercapacitor based on molybdenum sulfide hierarchical nanospheres. J. Power Sources 2015, 285, 63−69.

(51) Krishnamoorthy, K.; Veerasubramani, G. K.; Pazhamalai, P.; Kim, S. J. Designing two dimensional nanoarchitectured MoS$_2$ 2 sheets grown on Mo foil as a binder free electrode for supercapacitors. Electrochim. Acta 2016, 190, 305−312.

(52) Patil, S.; Harle, A.; Sathaye, S.; Patil, K. Development of a novel method to grow mono-/few-layered MoS$_2$ films and MoS$_2$/graphene hybrid films for supercapacitor applications. CrystEngComm 2014, 16, 10845−10855.

(53) Pujari, R. B.; Lokhande, A. C.; Shelke, A. R.; Kim, J. H.; Lokhande, C. D. Chemically deposited nano grain composed MoS$_2$ thin films for supercapacitor application. J. Colloid Interface Sci. 2017, 496, 1−7.

(54) Augustyn, V.; Simon, P.; Dunn, B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. Energy Environ. Sci. 2014, 7, 1597−1614.

(55) Ma, X.-J.; Zhang, W.-B.; Kong, L.-B.; Luo, Y.-C.; Kang, L. VO$_2$: from negative electrode material to symmetric electrochemical capacitor. RSC Adv. 2015, 5, 97239−97247.