Highly Uniform Atomic Layer-Deposited MoS$_2$@3D-Ni-Foam: A Novel Approach To Prepare an Electrode for Supercapacitors

Dip K. Nandi,† Sumanta Sahoo,‡ Soumyadeep Sinha,§ Seungmin Yeo,‖ Hyungjun Kim,‖ Ravindra N. Bulakhe,‖ Jaeyeong Heo,§ Jae-Jin Shim,‖ and Soo-Hyun Kim*†§

†School of Materials Science and Engineering and ‡School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Republic of Korea
§Department of Materials Science and Engineering, and Optoelectronics Convergence Research Center, Chonnam National University, Gwangju 61186, Republic of Korea
‖School of Electrical and Electronic Engineering, Yonsei University, Seodaemun-gu, Seoul 120-749, Republic of Korea

Supporting Information

ABSTRACT: This article takes an effort to establish the potential of atomic layer deposition (ALD) technique toward the field of supercapacitors by preparing molybdenum disulfide (MoS$_2$) as its electrode. While molybdenum hexacarbonyl [Mo(CO)$_6$] serves as a novel precursor toward the low-temperature synthesis of ALD-grown MoS$_2$. H$_2$S plasma helps to deposit its polycrystalline phase at 200 °C. Several ex situ characterizations such as X-ray diffractometry (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and so forth are performed in detail to study the as-grown MoS$_2$ film on a Si/SiO$_2$ substrate. While stoichiometric MoS$_2$ with very negligible amount of C and O impurities was evident from XPS, the XRD and high-resolution transmission electron microscopy analyses confirmed the (002)-oriented polycrystalline h-MoS$_2$ phase of the as-grown film. A comparative study of ALD-grown MoS$_2$ as a supercapacitor electrode on 2-dimensional stainless steel and on 3-dimensional (3D) Ni-foam substrates clearly reflects the advantage and the potential of ALD for growing a uniform and conformal electrode material on a 3D-scaffold layer. Cyclic voltammetry measurements showed both double-layer capacitance and capacitance contributed by the faradic reaction at the MoS$_2$ electrode surface. The optimum number of ALD cycles was also found out for achieving maximum capacitance for such a MoS$_2$@3D-Ni-foam electrode. A record high areal capacitance of 3400 mF/cm$^2$ was achieved for MoS$_2$@3D-Ni-foam grown by 400 ALD cycles at a current density of 3 mA/cm$^2$. Moreover, the ALD-grown MoS$_2$@3D-Ni-foam composite also retains high areal capacitance, even up to a high current density of 50 mA/cm$^2$. Finally, this directly grown MoS$_2$ electrode on 3D-Ni-foam by ALD shows high cyclic stability (>80%) over 4500 charge−discharge cycles which must invoke the research community to further explore the potential of ALD for such applications.

KEYWORDS: plasma-enhanced atomic layer deposition, molybdenum hexacarbonyl, molybdenum sulfide, supercapacitor, areal capacitance

1. INTRODUCTION

Ever-growing demand for energy in this 21st century facilitates the urge for energy storage devices in proportion which mainly includes rechargeable batteries and electrochemical capacitors commonly known as supercapacitors. The revolutionary discovery of portable electronic gadgets and their overwhelming popularity make them the all-time need for almost everyone in every sphere of life. This fact alone brings a paradigm shift in the industrial market of rechargeable energy storage. Because of their high power/energy density, very fast charge−discharge capabilities, and extremely long cyclic stability, supercapacitors are considered as a better alternative to Li-ion batteries in the fields of high-power density electronic devices and plug-in electric vehicles.¹ Supercapacitors can store and release the energy in two different ways: either in the form of a double-layer capacitor where the energy is stored in the form of a charge separation at the electrode and electrolyte interface or in the form of faradic redox reaction with the electrode materials.¹,²

The transition-metal binaries are one of the most favored classes of electrode materials for this application because of their contribution of faradic capacitance in addition to their
fundamental role as an electrical double-layer capacitor (EDLC). Among several transition-metal binary compounds, transition-metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS$_2$), tungsten disulfide (WS$_2$), and so forth are considered as a unique class of materials because of their graphitelike layered structures that find a lot of applications in recent energy generation and storage applications. particul-
arily, MoS$_2$ can be considered as one of the most researched TMDs and is widely used in several renewable-energy-related applications which include solar cells, solar water splitting, and Li-ion storage. In recent time, MoS$_2$ has also been successfully investigated by a handful number of research groups as an electrode in supercapacitors. The layered structure of MoS$_2$ can contribute to the double-layer capacitance from its interlayer charge storage in addition to its intralayer charge storage. Similar to RuO$_2$, MoS$_2$ can also provide additional capacitance from the faradic reaction at the Mo center with its multiple oxidation states ranging from $+2$ to $+6$. Moreover, the 2-dimensional (2D) layer of MoS$_2$ provides a better electron transport as well as a higher ionic conductivity compared to the oxides. All of these above-mentioned points truly attract several researchers to explore this material as a potential candidate for supercapacitors. Unfortunately, most of the earlier works have adopted some wet chemical syntheses such as hydrothermal process and further combined active electrode material with some 3-dimensional (3D) scaffold layers such as graphene oxide (GO), multiwalled carbon nanotube (MWCNT), or polyaniline (PANI) to fabricate a hybrid composite to obtain the enhanced capacitance from it. In general, a wide range of synthesis processes have been tried out for the preparation of the electrode material for supercapacitors. Among all kinds of such processes, hydrothermal synthesis has always been the major stakeholder, as seen for the case of MoS$_2$ as well. The other relatively less implemented wet chemical processes to prepare MoS$_2$ electrodes include the chemical bath deposition and successive ionic layer adsorption and reaction (SILAR). On the other hand, there are also gas-phase deposition techniques such as chemical vapor deposition (CVD) which can also be found to grow a thin film of MoS$_2$ for this application. Such gas-phase deposition techniques usually have more control over the deposited material, which generally includes the stoichiometry, crystallinity, and so forth, compared to the wet chemical synthesis processes. Moreover, these deposition techniques involve a single step to deposit the desired material, whereas hydrothermal processes require longer synthesis time (ca. 24–48 h or more), followed by rigorous filtrations steps.

In recent time, atomic layer deposition (ALD) is considered as one of the most efficient techniques to deposit thin films of materials for energy storage applications which include both secondary batteries and supercapacitors. ALD is a gas-phase, two-stage, thin-film deposition technique where the precursors are dosed into the ALD reactor sequentially separated by a purging of inert gases such as Ar or N$_2$. This sequential dosing of the precursors leads to a self-limiting growth of the film which makes ALD unique from the rest of the deposition techniques. Though it finds usage in several types of rechargeable batteries including Li- and Na-ion batteries and Li–O$_2$ and Li–S batteries, unfortunately, this technique has been vastly applied only to Li-ion batteries. In this context, it is interesting to notice that, not only in the case of Li-ion battery but also for Li–S and Na-ion battery, the most of attempts are limited to surface engineering of the active electrode by depositing a very thin protecting layer which helps to increase the cyclic stability of the battery. However, ALD is also successfully demonstrated to grow the active anode materials for such applications. The most interesting thing to notice for the ALD-grown active electrode material is that when it is combined with a porous and conducting 3D-scaffold layer as a base material. Such a unique combination of conformally and uniformly coated ALD materials on a 3D-structure truly can establish this technique as a most preferred deposition tool for energy storage applications. There are very few attempts made to apply this process for growing supercapacitor electrode materials. ALD-grown TiO$_2$, V$_2$O$_5$, NiO, and Co$_3$S$_4$ are among few of them which were successfully demonstrated as an active electrode material for supercapacitors. The earliest studies on ALD-grown metal oxides (VO$_2$, and TiO$_2$) as electrodes were carried out by Boukhalfa et al. and by Sun et al. Both of these studies used graphene (G) and MWCNT as substrates to deposit the active electrode material to achieve high specific capacitance. One of the most recent study on ALD-grown Co$_3$S$_4$ showed very promising results toward this application which reflected the potential of this technique to deposit the sulphide materials for supercapacitor electrode fabrication. A critical issue of such thin films to be used as an electrode in electrochemical storage devices is associated with their extremely low mass loading of the active material. In most of these cases, the active material lies in the range of few micrograms which would eventually yield into an overestimated specific capacitance (per kilogram or even per gram). Therefore, it is preferable to calculate the areal capacitance (F/cm$^2$), especially for an extremely thin-film (on the order of nanometers) electrode grown by a technique like ALD. Nevertheless, ALD has already been extensively studied and established as a tool to grow an active electrode material conformally on several 3D-scaffold layers. In this regard, Ni-foam is commonly considered as an efficient 3D-current collector for supercapacitor applications. Moreover, Ni-foam further provides an advantage of direct deposition of the electrode material by ALD, avoiding any additional step which is essential in the cases of other 3D-scaffolds such as rGO, MWCNT, or PANI.

In this article, we take an effort to further establish ALD as a very efficient tool to fabricate the electrode for supercapacitors. For this purpose, MoS$_2$ was directly grown on 2D-stainless steel (SS) foil and on 3D-Ni-foam by plasma-enhanced ALD (PEALD) for the first time and was used as an electrode without any further modifications. Molybdenum hexacarbonyl (Mo(CO)$_6$), a novel emerging precursor for low-temperature ALD synthesis, was used to deposit MoS$_2$. Previously, a halide precursor (MoCl$_5$) and H$_2$S molecules as a reactant were used to deposit MoS$_2$ films at a temperature of 300 °C. However, the relatively high temperature of deposition and HCl as a byproduct during deposition might hinder this process to deposit MoS$_2$ films on fragile Ni-foam. Therefore, here, we prefer to adopt the hexacarbonyl precursor and H$_2$S plasma as the reactant. After the detailed investigations of the properties of the material and the unique growth of it on 3D-Ni-foam, the electrochemical studies were carried out to realize the potential of PEALD-grown MoS$_2$ as an electrode in asymmetric supercapacitors. Thickness-dependent electrochemical properties were studied, and an optimized number of ALD cycles for such applications were found out.
2. EXPERIMENTAL SECTION

2.1. Material Synthesis. MoS₂ thin films were deposited using a Mo(CO)₆ (UP Chemical Inc., Korea) precursor and a H₂S plasma reactant by PEALD in a showerhead-type ALD reactor (Lucida-M1000, NCD Technology) at a deposition temperature of 200 °C. Mo(CO)₆ is in the solid state at room temperature (white powder), the precursor was kept at a temperature of 40 °C to achieve a minimum amount of vapor pressure (ca. 0.8 Torr) and to prevent the precursor from condensation, and the line was heated up to 60 °C. In addition to the heating of the Mo(CO)₆ precursor, high-purity Ar was used as a carrier gas at a flow rate of 50 sccm (standard cubic centimeter per minute), enabling proper chemical transfer, as well as a purging gas at a flow rate of 200 sccm in between the sequential exposure of the precursor and the reactant. A radio frequency power of 100 W was applied to the showerhead to ignite the corresponding plasma during the H₂S pulsing. Thermally grown SiO₂ (∼100 nm) on Si (henceforth written as Si/SiO₂) substrates were used to deposit the MoS₂ films for material characterizations. For the electrochemical studies of PEALD-grown MoS₂ as an electrode in supercapacitors, the material was directly grown on 2D-SS-foil and on 3D-Ni-foam under self-limiting deposition condition.

2.2. Material Characterizations. Several ex situ characterization techniques were adopted to study the PEALD-grown MoS₂ in detail. Grazing incident angle X-ray diffraction (GIAXRD, PANalytical X’Pert PRO MRD, incident angle: ∼3°) with a Cu Kα source was used within 2θ of 10°–70° to study the crystalline nature of the deposited films. Raman spectroscopy was carried out to find out the Raman active modes in the PEALD-grown MoS₂ films. A 500 nm laser source was used as an incident excitation energy for this purpose. X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XPS spectrometer) with an Al Kα source was adopted to investigate the presence of elements and the oxidation states of them in the grown material. Plan-view and cross-sectional-view transmission electron microscopy (TEM, Tecnai F20 equipped with a 200 kV accelerating voltage and a field emission gun) was performed to show the crystal lattice, its corresponding planes, and the uniform and conformal deposition of the film grown by PEALD. Energy-dispersive spectroscopy (EDS) analysis was also performed to detect the elemental distribution of MoS₂ on 3D-Ni-foam during scanning TEM (STEM) analysis. A plan-view scanning electron microscope (Hitachi, S-4800) was used to show the uniform deposition and the surface morphology of the film on the 3D-Ni-foam.

2.3. Electrochemical Measurements. The electrochemical studies were carried out in a conventional three-electrode configuration where the PEALD-grown MoS₂ on 2D-SS-foil or on 3D-Ni-foam was directly used as a working electrode without any additive or binder. The active electrode area adopted for the working electrode was 1 cm × 1 cm for both SS and Ni-foam substrates. Pt and Ag/AgCl were served as the counter and reference electrodes, respectively. KOH aqueous solution (1 M) was used as an electrolyte. The cyclic voltammetry (CV) and the galvanostatic charge–discharge cycling measurements were performed in a potentiostat (PGSTAT302N with Nova 1.10 software, Autolab, Netherlands). Electrochemical impedance spectroscopy (EIS) was further carried out within the frequency range of 10⁻² to 10⁶ Hz using the same Autolab instrument to realize the electrical behaviors of the electrode–electrolyte interface.

3. RESULTS AND DISCUSSION

ALD differs from the rest of the material synthesis techniques that include wet chemical synthesis as well as gas-phase thin-film deposition techniques by its unique feature of self-limiting growth of the material. A similar self-limiting growth condition with 10 s pulsing of both Mo(CO)₆ as well as H₂S plasma with Ar purging of 10 s in between the alternate exposure of these two was used to deposit the MoS₂ thin films as obtained in our previous study.²² A detailed study on the self-limiting ALD reaction and linear growth with ALD cycles could also be found in that study.²² The two half ALD surface reactions during the PEALD of MoS₂ can be written as follows

\[
\text{Mo(CO)}_6 + \text{H}_2\text{S} \rightarrow \text{Mo-SH}^* + \text{H}_2(\text{g}) + \text{CO}(\text{g}) \quad (1)
\]

\[
\text{MoSH}^* + \text{Mo(CO)}_6 \rightarrow \text{Mo-S-Mo(CO)}_6^* + \text{H}_2(\text{g}) + \text{CO}(\text{g}) \quad (2)
\]

where * denotes the surface species.

GIAXRD analysis of the as-grown MoS₂ film deposited by 200 ALD cycles on the Si/SiO₂ substrate is shown in Figure 1. The three distinct XRD peaks (at 2θ = 14.37, 32.67, and 39.54°) confirm the polycrystalline nature of the PEALD-grown MoS₂ films. These peaks can be assigned to the (002), (100), and (103) planes of hexagonal 2H-MoS₂, respectively (space group $P6_3/mmc$; JCPDS ref. 00-037-1492).¹⁺¹⁶⁺¹⁸⁺²² Predominantly (002)-oriented growth on the Si/SiO₂ substrate might be expected because of the presence of a much higher intense XRD peak at 14.37° compared to the other two planes, as revealed by this XRD measurement.¹⁺¹⁶⁺²² However, as mentioned earlier, the films were deposited on SS-foil and Ni-foam for supercapacitor applications. Therefore, we have also performed the characterizations of the film deposited on both the SS and the Ni-foam. The XRD pattern of the as-grown MoS₂ film on the SS-foil (Figure S1a) shows three less intense peaks along the (002), (101), and (110) planes at 14.3, 33.5, and 58.9°, respectively, corresponding to the same 2H-MoS₂. Unfortunately, we were not able to detect any XRD peaks of MoS₂ on Ni-foam, which might be due to the complex structure of the substrate, presence of high-intense peaks of bare Ni-foam, and low mass content of the target material (Figure S1c). Yet, they do not completely discard the crystalline growth of the film on the Ni-foam, as shown and discussed later in this article. Therefore, it might be said that the growth and the crystalline nature of the film might depend on the substrate to some extent but gives a similar polycrystalline MoS₂ on different substrates as well. Here, it is interesting to notice that an earlier study on thermal ALD of MoS₂ produced the amorphous film using the same precursor [Mo(CO)₆] as a source for Mo.²⁶ Therefore, it could be inferred that the H₂S plasma as a reactant facilitates the formation of crystalline MoS₂ at a relatively low deposition temperature of 200 °C. This deposition temperature is also considerably lower compared to 300 °C for ALD of MoS₂ using a MoCl₅ precursor.²¹ Unlike MoCl₅, the usage of Mo(CO)₆ would further help to avoid the formation of the corrosive HCl byproduct which must affects...
the MoS$_2$ film itself as well as the substrate during the growth. Therefore, it could be concluded that Mo(CO)$_6$ served as a better precursor from both deposition-temperature and reaction-byproduct points of view. The crystalline nature of such PEALD-grown MoS$_2$ will certainly help to ease the electron as well as ion transport (for faradic intercalation—deintercalation reaction) when it is used as an electrode in supercapacitors.

Once XRD proved the crystalline growth of the PEALD-grown MoS$_2$ with its most favorable and preferential direction of (002), we further carried out Raman spectroscopy to investigate the material in more detail. Raman spectrum was obtained for the as-grown MoS$_2$ film deposited on the Si/SiO$_2$ substrate. Two distinct peaks were observed at the frequencies of $\sim$383 and $\sim$408 cm$^{-1}$, corresponding to the two typical first-order Raman active vibrational modes, that is, E$_{2g}$ and A$_{1g}$ respectively, within the S–Mo–S layer, as shown in Figure 2a. These are similar to the frequency values found in bulk MoS$_2$.

The peak at $\sim$520 cm$^{-1}$ was obtained from the Si substrate. The vibrational peak for E$_{2g}$ is associated with the planer vibration, whereas the A$_{1g}$ peak indicates the vibration along the out-of-plane direction of the sulfides, as represented in the schematic Figure 2b. Similarly, two distinct peaks corresponding to those in-plane and out-of-plane vibrational modes, as shown in Figure S1b, were also obtained for the MoS$_2$ film deposited on the 2D-SS substrate.

XPS was performed further to confirm the constituent element, chemical composition, and the oxidation state of Mo in the MoS$_2$ film by determining the corresponding binding energies of Mo and S electrons, as shown in Figure 2c,d. The XPS data were taken after the etching ca. 10 nm of the film from the surface to avoid the presence of O and C in the spectrum that may arise from the surface. The doublet of Mo 3d electrons at the binding energies of ca. 229 and 232.3 eV (Figure 2c) can be assigned, respectively, to the 3d$_{3/2}$ and 3d$_{5/2}$ electronic states of Mo in the Mo–S bond. These binding energies of Mo 3d orbital electrons in the as-grown film also indicate the Mo$^{+4}$ oxidation state of Mo, confirming the chemical composition as MoS$_2$. On the other hand, the XPS spectrum corresponding to the 2p binding energies of S is shown in Figure 2d. The peaks at binding energies of 162 and 163.2 eV, as obtained after the XPS peak fitting, are attributed to the S 2p$_{1/2}$ and S 2p$_{3/2}$ electronic states, respectively, for the divalent sulfide ions (S$^{2-}$) present in the film. In addition to these S 2p peaks, an additional S 2s peak was also detected (Figure 2c) at 226.8 eV in the energy range of Mo peaks, which also confirms the binding state of S in MoS$_2$. The full survey of the XPS spectrum of the MoS$_2$ film without surface etching on the Ni-foam substrate in the binding energy range of 0–1350 eV with the constituent elemental peaks is given in the Supporting Information of this article (Figure S2a). The presence of Mo 3d, S 2p, and Ni 2p peaks in the spectrum confirms the successful deposition of MoS$_2$ on the 3D-Ni-foam. Figure S2b–d shows the further deconvolution of the individual XPS spectra of Ni 2p (2p$_{3/2}$, 2p$_{1/2}$, and the satellite peaks), Mo 3d (3d$_{3/2}$ and 3d$_{5/2}$), and S 2p (2p$_{3/2}$ and 2p$_{1/2}$), respectively, at their corresponding binding energies, which proves our claim beyond any doubt. The presence of an O 1s peak at $\sim$532 eV indicates the hydroxide formation due to the absorbed oxygen on the film surface after air exposure which can also be observed in other sulfide materials.

The crystallinity of the as-deposited MoS$_2$ thin films was further verified by using TEM analysis. Figure S3a shows the plan-view TEM image of the film on the Si/SiO$_2$ substrate. Figure S3b represents the magnified view of a small portion from Figure S3a. From the lattice fringes of Figure S3a,b, the interplanar spacing was mostly found to be about 0.60–0.62 nm, which corresponds to the (002) plane of the hexagonal structure of MoS$_2$ (JCPDS ref: 00-037-1492). The lattice image clearly shows the highly oriented MoS$_2$ thin film with a preferential orientation along the [002] direction, which was
also obtained from the XRD pattern, as shown in Figure 1. The cross-sectional-view TEM images of the as-grown MoS2 films using 200 ALD cycles on the Si/SiO2 substrate and the trench structure (top opening width of ~100 nm) are shown in Figure S3c,d, respectively. The cross-sectional-view TEM images thus prove the uniform and conformal deposition ability of PEALD which will encourage us to deposit the material on a porous 3D-Ni substrate for electrode fabrication. Further cross-sectional TEM analysis of the MoS2@Ni-foam composite was also performed and discussed in detail in the later section of this article.

Figure 3a−d shows the plan-view scanning electron microscopy (SEM) images of the MoS2 film deposited on the 3D-Ni-foam with different magnifications where the inset of Figure 3c shows the SEM image of bare Ni-foam with the same magnification as 3(c). The SEM images show uniform film deposition on the entire 3D-substrate surface, which again confirms the conformal film deposition by PEALD process. Further, Figure S4a shows the SEM image of the MoS2-coated 3-D Ni-foam at very low magnification where it is clear that the film growth was extremely uniform and conformal over a large area of this 3D-substrate. The MoS2 film grown with 400 ALD cycles also retains uniform microporosity throughout the surface of the film. A nanocauliflower-like morphology (Figure S4b) can be observed from the SEM image of the MoS2 film on the 3D-Ni-foam which is quite different from the film morphology obtained from the SEM images (Figure S5) of the 2D-SS substrate with a uniform film deposition. Therefore, there are some differences observed in the surface morphologies of the MoS2 grown by the same number of ALD cycles on the SS and on the 3D-Ni-foam. It is also true that the morphology considerably affects the performance of electrochemical storage devices. However, in this case, the performance was predominantly determined by the dimensionality of the substrate. The porous 3D-Ni-foam provides much higher active surface area compared to the 2D-SS substrate, which enables the deposition of more materials with the same number of ALD cycles. On the other hand, the morphology changes drastically when the film was grown on the Ni-foam using 500 ALD cycles. The plan-view SEM images (Figure S6) clearly show that the porosity of the MoS2 films was lost to a great extent as we increased the number of ALD cycles beyond the optimum number. This affects further the performance when they were used as an electrode in supercapacitors. The elemental distribution mapping of EDS analysis for the MoS2 film on the 3-D Ni-foam is illustrated in Figure 3e−g. The presence of two constituent elements (Mo and S) is indicated by two different color representations which show the uniform distribution of the elements throughout the Ni-foam captured in the frame due to the uniform and conformal deposition by ALD. Figure 4a,b shows the schematics of the two-step ALD of MoS2 using Mo(CO)6 and H2S plasma, followed by its growth on the 2D-SS as well as 3D-Ni-foam substrates, respectively. From this schematic (Figure 4b), it is clear that the conformal and uniform coating by ALD on the 3D-substrate (Ni-foam for this case) will provide higher mass loading by orders of magnitude for the same number of ALD cycles.

Figure 5 shows the cross-sectional-view TEM images and the elemental mapping of the MoS2@Ni-foam composite grown by 500 ALD cycles. We prefer this condition to perform TEM as it makes this analysis easier for the composite almost without any porosity as observed by the plan-view SEM images of the same.
Figure 5a,b clearly shows the uniform and conformal coating of the material on a complex 3D-Ni-foam structure. Unlike the samples grown by 400 ALD cycles, here, the surface of the Ni-foam substrate got covered completely by a 2D thick film of MoS$_2$ (Figure 5b) without any surface porosity as observed in the case of the former. Two different layers could further be observed for this sample, mainly because of the surface oxidation of the sample under considerable amount of exposure to the ambient. A catalytic ALD growth adjacent to the Ni surface might also cause a more dense film deposition at the beginning. High-resolution TEM (HRTEM) images (Figure 5c,d) clearly show the polycrystalline lattice grains in the films. The $d$-spacing measurements further reveal the (100) and (103) planes of h-MoS$_2$ with interplanar spacings of 2.74 and 2.27 Å, respectively (JCPDS ref: 00-037-1492). STEM–EDS mapping of this MoS$_2$@Ni-foam composite (Figure 5e–h) clearly reflects the uniform distribution of the elemental Mo (Figure 5g) and S (Figure 5h) on Ni (Figure 5f). Therefore, this cross-sectional-view TEM along with STEM analysis univocally proves the formation of polycrystalline MoS$_2$ on the 3D-Ni-foam. Conformal and uniform deposition by ALD on the 3D-Ni-foam structure is also evident from this analysis which is extremely rare in the existing literature to the best of our knowledge.

Electrochemical analysis of the PEALD-grown MoS$_2$ as a supercapacitor electrode was performed in 1 M KOH aqueous solution. CV measurements were carried out within a potential window of 0–0.6 V to study the capacitive response of these MoS$_2$ electrodes. For this purpose, CV of the 400-cycle-PEALD-grown MoS$_2$ on the 2D-SS-foil was first tested (Figure S5) for five different voltage scan rates from 5 to 50 mV/s. The current response of MoS$_2$@2D-SS-foil was increased with...
Figure 5. (a–d) Cross-sectional-view TEM images of MoS$_2$@Ni-foam grown by 500 ALD cycles and the corresponding HRTEM images showing the polycrystalline grains in the MoS$_2$ film and (e–h) the STEM elemental mapping confirming the uniform distribution of Mo and S on Ni.

Figure 6. (a) CV plots of bare Ni-foam and MoS$_2$@3D-Ni-foam grown by 200, 400, and 500 ALD cycles at a scan rate of 5 mV/s, (b) CV curves at different scan rates for the MoS$_2$@3D-Ni-foam electrode grown by 400 ALD cycles, (c) charge–discharge profiles at a current density of 3 mA/cm$^2$ for the above three MoS$_2$@3D-Ni-foam electrodes, (d) charge–discharge profiles at different current densities for MoS$_2$@3D-Ni-foam grown by 400 ALD cycles, (e) areal capacitances at different current densities for the three different electrodes, and (f) their corresponding CEs.
increasing scan rate, which can be confirmed by the enhancement in the area under the CV curve (or the current). The faradic capacitance was realized from the distinct peaks in the CV curve of MoS$_2$@SS-foil at a 50 mV/s voltage scan rate. The peaks at ca. 0.34 and 0.46 V during the cathodic and anodic sweeps, respectively, confirm such redox reactions in the MoS$_2$ electrode in supercapacitors. However, the area under the CV curve and the proportional maximum current yielded even for the highest voltage scan rate (50 mV/s) were truly negligible. The reason for such a low capacitive response in this case is the less mass loading by ALD on a flat 2D substrate (SS-foil). On the contrary, ALD is best known for its uniform and conformal coating on any randomly shaped 3D-substrate. Therefore, it gives further avenue to deposit this material on the 3D-Ni-foam which can provide much more surface to deposit MoS$_2$, leading to a reasonable mass loading. Figure 6a shows the CV curves of bare Ni-foam and MoS$_2$@3D-Ni-foam deposited with 200, 400, and 500 ALD cycles at a 5 mV/s scan rate. The manifold increase in the area under the CV curve compared to the bare Ni-foam clearly confirmed the high capacitive nature of this composite. The capacity increased considerably when the number of ALD cycles was increased from 200 to 400 cycles. The highest capacitive response was observed for the electrode grown with 400 ALD cycles. Further increase in the ALD cycles (MoS$_2$@3D-Ni-foam electrode grown by 500 ALD cycles) increases the resistivity of the composite as the MoS$_2$ films became thicker. The porosity of the electrode was also lost to a great extent which could be observed from the plan-view SEM images of this sample (Figure S6). As a result, the current response in the CV curves and hence the capacitance for this electrode were decreased drastically. Thus, the optimum number of 400 ALD cycles was identified to achieve the maximum capacity for the MoS$_2$@3D-Ni-foam electrode. However, the nature of the CV curves for both 200- and 400-ALD-cycle grown composites remained almost unaltered. The faradic reactions in the MoS$_2$ electrode are clear from the prominent redox reactions during both anodic and cathodic sweeps in CV. The reduction peak during the discharge cycle (anodic sweep) for both MoS$_2$@3D-Ni-foam composites grown by 200 and 400 ALD cycles in the CV curve and the proportional maximum current yielded even from the CV curves when the voltage scan rate was increased. The opposite phenomena during the cathodic sweep (during charging, higher potential corresponds to higher energy supply) could also be seen from the CV curves (Figure 6b). During cathodic sweeps, the faradic reactions even almost disappeared at 50 and 100 mV/s scan rates which did not allow enough time for the faradic reversible reaction to take place. Though such a faradic capacitance for the MoS$_2$ electrode was not observed in most of the earlier reports where the hydrothermal synthesis route was adopted, few others have reported CV curves similar to the one observed in this study. It is interesting to notice that when MoS$_2$ was prepared in the form of a thin film by CVD or by SILAR (a wet chemical synthesis route to deposit thin films layer by layer and therefore could be considered as a method analogous to ALD) method, prominent faradic reactions were observed along with the EDLC behavior. It is usually expected for transition-metal binary compounds to undergo a reversible faradic reaction (intercalation and deintercalation), similar to rechargeable secondary batteries (e.g., Li- or Na-ion batteries) along with the double-layer capacitance. The capacitance added from such faradic reactions therefore should be considered as an advantage for this PEALD-grown MoS$_2$ electrode for this case. Therefore, in this context, we find that ALD-grown films could be a true alternative to grow the active electrode material.

Once the electrochemical response (both pseudocapacitance and electrical double-layer capacitance) was investigated, the galvanostatic charge–discharge properties of the PEALD-grown MoS$_2$@3D-Ni-foam at different current densities were investigated in detail within a potential window of 0–0.45 V. Figure 6c shows such charge–discharge profiles of MoS$_2$@3D-Ni-foam grown by 200, 400, and 500 ALD cycles at a current density of 3 mA/cm$^2$. Similar to the CV curves of these three different electrodes, the charge–discharge time for the electrode grown by 400 ALD cycles increased considerably compared to the electrode grown by 200 cycles. Moreover, the charge–discharge time decreased drastically when the ALD cycles were increased further to 500 cycles for depositing MoS$_2$ on the Ni-foam which is in complete line with the response obtained during the CV measurements. Such deterioration in the electrochemical property might be caused by two simultaneous factors: (a) more number of ALD cycles beyond a point makes the MoS$_2$@3-D Ni-foam more resistive and (b) the loss of the porosity of the film. However, all of these three electrodes showed a similar trend during both charge and discharge profiles. Unlike the linear charge–discharge profiles for pure EDLC, the prominent plateau in between 0.2 and 0.3 V during the discharge process confirmed the faradic reaction for this ALD-grown MoS$_2$@3-D Ni-foam electrode. The plateau in the charge–discharge profiles is thus in well agreement with the CV measurements. The charge–discharge profiles were performed for a wide range of current densities up to 50 mA/cm$^2$. Figure 6d shows the charge–discharge profiles for 400 ALD cycles carried out with current densities of 3–18 mA/cm$^2$. Similar stable profiles with much less charge–discharge time were also observed for higher current densities (20, 30, 40, and 50 mA/cm$^2$) (Figure S8a). Thus, this study shows that this ALD-grown electrode can well-withstand a high current density and can be applied to any high-energy density device in future.

The corresponding areal capacitances with increasing current density for 200-, 400-, and 500-ALD-cycle MoS$_2$@3D-Ni-foam electrodes were plotted and shown in Figure 6e. The areal
The areal capacitance drastically falls (0.22 F/cm²) when the MoS2@Ni-foam composite acted as a hybrid supercapacitor with the optimum porosity and resistivity of the composite assembly. As electrode materials, which includes MoS2 as well.17,50 several other areal capacitances reported earlier for different potential differences (0.45 V), and A is the area of the electrode (1 cm²).

The areal capacitance is increased considerably from 1.4 to 3.4 F/cm² corresponding to the 200- and 400-cycle MoS2 respectively, at a current density of 3 mA/cm². On the other hand, the areal capacitance drastically falls (0.22 F/cm²) when the ALD cycles were further increased to 500 cycles. This observation is in well agreement with the earlier CV and discharge time, (Figure 6f). Excellent CE (~100%) was found for the optimized electrode assembly (400-cycle MoS2) from 8 mA/cm² current density and beyond.

Table 1. Areal Capacitances of Different Electrodes Reported Earlier along with That in This Work

<table>
<thead>
<tr>
<th>sr. no.</th>
<th>supercapacitor electrode materials</th>
<th>material growth process</th>
<th>areal capacitance</th>
<th>cycling stability</th>
<th>refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoS2@CNT/RGO</td>
<td>hydrothermal</td>
<td>1.29 mF/cm²</td>
<td>94.7% after 10000 cycles</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>NiS@Ni-foam</td>
<td>electrochemical deposition</td>
<td>2.60 mF/cm²</td>
<td>95.7% after 2000 cycles</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>PANi/carbon cloth</td>
<td>electropolymerization</td>
<td>3.00 mF/cm²</td>
<td>91% after 5000 cycles</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>FeCo3O4@Ni-foam</td>
<td>chemical deposition</td>
<td>1.88 mF/cm²</td>
<td>92.7% after 1000 cycles</td>
<td>69</td>
</tr>
<tr>
<td>5</td>
<td>MoS2/Co3O4@Ni-foam</td>
<td>hydrothermal</td>
<td>1.425 mF/cm²</td>
<td>92.7% after 1000 cycles</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>monolayer 1H-MoS2@oleylamine</td>
<td>hot-injection thermolysis</td>
<td>5.05 mF/cm²</td>
<td>240% after 5000 cycles</td>
<td>71</td>
</tr>
<tr>
<td>7</td>
<td>NiCO3-SiSi nanosheet@NiCo2O4 nanowire arrays on a Ti plate</td>
<td>hydrothermal followed by electrodeposition</td>
<td>1.86 mF/cm²</td>
<td>87.6% after 10000 cycles</td>
<td>72</td>
</tr>
<tr>
<td>8</td>
<td>NiCo2O4@Ni-foam</td>
<td>solvothermal followed by calcination</td>
<td>0.925 mF/cm²</td>
<td>75.8% after 6000 cycles</td>
<td>73</td>
</tr>
<tr>
<td>9</td>
<td>NiO/MnO2@carbon cloth</td>
<td>hydrothermal followed by chemical deposition</td>
<td>0.286 mF/cm²</td>
<td>89% after 2200 cycles</td>
<td>74</td>
</tr>
<tr>
<td>10</td>
<td>MoS2--graphene composite</td>
<td>ultrasonication</td>
<td>0.11 mF/cm² at 5 mV/s scan rate</td>
<td>~250% after 10000 cycles</td>
<td>50</td>
</tr>
<tr>
<td>11</td>
<td>MoS2 thin films</td>
<td>CVD</td>
<td>0.71 mF/cm² at 1 mV/s scan rate</td>
<td>95% after 7000 cycles</td>
<td>17</td>
</tr>
<tr>
<td>12</td>
<td>rGO/NiCo2O4</td>
<td>hydrothermal followed by calcination</td>
<td>2.370 mF/cm² at 2 A/g</td>
<td>&gt;100% throughout 7500 cycles</td>
<td>75</td>
</tr>
<tr>
<td>13</td>
<td>MoS2@3D-Ni-foam</td>
<td>ALD</td>
<td>3.400 mF/cm² at 3 mA/cm²</td>
<td>82% after 4500 cycles</td>
<td>this work</td>
</tr>
</tbody>
</table>

The areal capacitances of these electrodes could be obtained from the discharge curve of these charge–discharge profiles from the following equation:

\[ C_A = \frac{I_t A}{V V A} \]  

where \( I \) is the current density, \( t_d \) is the discharge time, \( V \) is the working potential difference (0.45 V), and \( A \) is the area of the electrode (1 cm²).
The CE for this electrode at current densities 3 and 5 mA/cm² was also as high as over 95%. Such a relatively lower CE at a low current density is a common observation because of the slower discharge kinetics compared to the charge kinetics. Less values of CE were observed for the 200- and 500-cycle electrodes which was in good agreement with other observations. The comparatively higher fluctuations in CE obtained for different current rates in the case of the 500-cycle electrode further support the large thickness and the absence of porosity in the film which resulted in abrupt/random charge–discharge properties under continuous operation.

All of the previous electrochemical studies (CV curves and rate capability) univocally proved that the 400 ALD cycles was the optimum number to grow the MoS₂ electrode on the 3D-Ni-foam that yielded the highest capacitance. Therefore, the cyclic stability of the MoS₂@3D-Ni-foam electrode grown by 400 ALD cycles was further investigated by carrying out 4500 charge–discharge cycles. The capacity retention over the cycles and the corresponding CE for 4500 cycles were plotted, as shown in Figure 7. Reasonably good capacity retention of ca. 82% was achieved for this composite at the end of the 4500th discharge cycle with an excellent CE over 90% throughout the cycling which reached beyond the value of 95% after first 2000 cycles of charge–discharge. The cycling performance also revealed that there was no fading in the capacitance retention (or in the areal capacitance) for the last ca. 2500 cycles (after 2000) which eventually indicated the stability of this ALD-grown MoS₂@3D-Ni-foam electrode even beyond 4500 cycles. The capacity fading in the initial 2000 cycles could be attributed to the slow collapsing of the layered structure of the ALD-grown MoS₂ which might cause the predominant loss in the faradic capacitance upon cycling. In addition, the loss of the electrode materials to some extent from the external surface of the electrode also leads to such a capacity fading during the initial period of the cycling. However, a highest stable areal capacitance over 2700 mF/cm² could be achieved as per the best of our knowledge at the end of 4500 cycles. The stability could be further realized from the unaltered nature of the last few charge–discharge cycles which are also shown in the inset of Figure 7. Such an excellent stability could be attributed to the uniform and conformal coating of polycrystalline MoS₂ with an optimum microporosity. This study therefore establishes the feasibility and potential of ALD toward the application of supercapacitors where the electrochemistry is surface-dominant, and therefore ALD can lead to the optimization of the fabrication of an electrode in a most efficient way.

EIS was further carried out for the three different electrodes to understand the kinetics of the electrochemical reactions, and the corresponding Nyquist plots were shown and explained with the help of an equivalent circuit. Figure S10 shows the Nyquist and Bode plots and the schematic of the corresponding equivalent circuit of these three electrodes. Typical Nyquist plots observed for supercapacitors were also found for this ALD-grown electrode material. However, MoS₂@3D-Ni-foam grown by 500 ALD cycles exhibited much higher Warburg impedance than the other two electrodes. Complementary information could also be drawn from the corresponding Bode analysis. Thus, these analyses clearly reflect the drastic fall in the capacitance for the electrode grown by 500 ALD cycles. A more detailed discussion on the EIS measurements could be found in the Supporting Information of this article.

The robustness and the strong bond between MoS₂ and 3D-Ni-foam composite were further revealed by plan-view SEM analysis of the electrode after 4500 charge–discharge cycles, as shown in Figure 8. The SEM images proved that the ALD-grown morphology undergoes considerable agglomeration/aggregation (Figure 8b) during the large cycling process. Nevertheless, the similar nanospherical morphologies could be still realized for MoS₂@3D-Ni-foam grown by 400 ALD cycles (Figure 8a) which were observed before the cycling. Thus, this postcycling analysis established the potential of ALD toward a very efficient and direct growth of an electrode material on a 3D-scaffold layer. Therefore, the enhanced electrochemical performance of this MoS₂@3D-Ni-foam grown by ALD can be attributed to these three factors: (1) the porous nanostructure of the active material allowed superior ion and electron transport during electrochemical test in aqueous electrolyte, (2) the strong attachment of the active materials on the 3D-Ni-
foam substrate allowed the electrode to achieve good mechanical strength and prevented major structural deformation during cycling, and (3) both EDLC and Faradic reactions of MoS$_2$ synergistically contributed toward the capacitive response. We believe that further research can truly bring ALD into the field of supercapacitors in a similar way it has already been showcased for Li-ion batteries.

4. CONCLUSIONS

Molybdenum disulfide (MoS$_2$) was successfully deposited by PEALD using a molybdenum hexacarbonyl [Mo(CO)$_6$] precursor and H$_2$S plasma at a relatively low temperature of 200 °C. The thin films of MoS$_2$ deposited on Si/SiO$_2$, SS-foil, and Ni-foam substrates were thoroughly characterized by XRD, Raman spectroscopy, XPS, and TEM analyses. Stoichiometric and polycrystalline MoS$_2$ with preferential (002)-directional growth was evident for the as-grown films. MoS$_2$ was further coated uniformly on the 2D-SS-foil and conformally on the 3D-Ni-foam by PEALD for the first time and tested as an electrode in supercapacitors. The potential of ALD technique to fabricate a unique and conformal MoS$_2$@3D-Ni-foam composite electrode was revealed clearly. The 3D-composite electrode showed manifold increase in capacity compared to its 2D-applications. We believe that this work will facilitate the further exploration of the ALD technique for supercapacitor applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b12248.

Detailed characterizations (XRD, Raman spectroscopy, and XPS) of MoS$_2$ grown on SS-foil and Ni-foam substrates; TEM analysis of the as-grown MoS$_2$ on the Si/SiO$_2$ substrate; SEM images of MoS$_2$ grown on SS-foil and on Ni-foam using 500 ALD cycles; CV curves of the MoS$_2$@SS electrode; charge–discharge profiles at high current densities; and detailed Trasatti and impedance analyses of the optimized MoS$_2$@Ni-foam composite electrode (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: soohyun@ynu.ac.kr.

ORCID

Hyunjun Kim: 0000-0003-2256-8046
Jaeyeong Heo: 0000-0002-2602-6538
Jae-Jin Shim: 0000-0002-8027-9886
Soo-Hyun Kim: 0000-0003-3748-2755

Author Contributions

*Authors contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by Mid-career Researcher Program through the National Research Foundation of Korea (NRF) (2015R1A2A2A04004945), the Priority Research Centers Program through the NRF funded by the Ministry of Education (2014R1A6A1031189), and Korea Basic Science Institute under the R&D program (project no. D37700) supervised by the Ministry of Science, ICT and Future Planning, Republic of Korea.

REFERENCES

(2) Sun, X.; Wang, G.; Sun, H.; Lu, F.; Yu, M.; Jian, L. Morphology controlled high performance supercapacitor behaviour of the Ni-Co binary hydroxide system. J. Power Sources 2013, 238, 150–156.
Layer-controlled precise fabrication of ultrathin MoS2 films by atomic layer deposition. *NanoTechnology* 2017, 28, 195605.


