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# Surface modification of silicon nanowires via drop-casting for high-performance Li-ion battery electrodes: SiNWs decorated with molybdenum oxide nanoparticles

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### ABSTRACT

The functionalization of molybdenum oxide (MoO<sub>3</sub>) nanoparticles is presented as a method to significantly enhance the cycling stability of lithium-ion battery (LIB) anodes based on silicon nanowire (SiNW) arrays. Transition-metal oxides have emerged as promising candidates for advanced anode materials in modern Li-ion batteries. In this study, we explore a novel approach involving the deposition of MoO3 nanoparticles via unique drop-casting technique onto pre-fabricated SiNW arrays, fabricated using a straightforward one-step metal-assisted chemical etching (MACE) process. The primary objective is to assess their potential suitability as anode materials for Li-ion batteries. Our methodology entails the top-down synthesis of binder-free hybrid electrodes, achieved by depositing Mo oxides nanostructures onto SiNW arrays through a combination of dropcasting and thermal annealing processes. The resulting MoO3@SiNWs hybrid structure exhibits distinctive and specialized attributes, including exceptional structural resilience, diminutive particle dimensions, and a porous configuration. These features effectively enhance electron and ion accessibility at the electrode-electrolyte interface

Electrochemical assessments reveal that the MoO<sub>3</sub>@SiNWs hybrids exhibit superior lithium storage performance compared to bare SiNW electrodes. Particularly under high current densities, MoO3 nanoparticles deposited via drop-casting technique demonstrate improved cycling stability and increased capacity. The enhanced electrochemical characteristics are primarily ascribed to the synergistic effects between the MoO<sub>3</sub> nanoparticles and SiNW arrays. The findings of this study strongly suggest that the MoO3@SiNWs hybrid structure holds substantial promise as anode materials for high-performance energy storage devices.

## 1. Introduction

The rapid expansion of electric vehicles and portable electronic devices has ushered in a substantial surge in the demand for lithium-ion (Li-ion) batteries, renowned for their high energy density and robust cycling stability. Currently, conventional Li-ion batteries employ graphite as the anode material and LiCoO<sub>2</sub> as the cathode material, resulting in an energy density to approximately 150 Wh·kg<sup>-1</sup> (375  $Wh \cdot L^{-1}$ ) [1]. However, this configuration falls short of meeting the burgeoning requirements of long-range electric vehicles due to the inherent constraints associated with the C-LiCoO<sub>2</sub> chemistry. These limitations pose formidable obstacles to further augmenting areal capacity and energy density. Consequently, it has become paramount to explore alternative approaches, with a specific focus on novel electrode materials capable of affording enhanced capacity and energy density for Li-ion batteries.

Silicon (Si) has garnered substantial interest as a highly promising material for negative electrodes. This enthusiasm stems from its remarkably high theoretical capacity, which stands at 4200 mA·h·g<sup>-1</sup>, nearly tenfold greater than that of graphite (372 mA·h·g<sup>-1</sup>) [2]. Specifically, silicon nanowires (SiNWs) have gained considerable attention as an electrode material. SiNW arrays offer several distinct advantages, such as their one-dimensional electron transport characteristics and extensive surface area, rendering them highly suitable for deployment as electrode materials. [3] In contrast to the vapor-liquid-solid growth technique, SiNWs can be conveniently fabricated through a

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straightforward one-step metal-assisted chemical etching (MACE) method. This method presents notable advantages, including cost-effectiveness and the potential for large-scale production [4–6].

Recent times have witnessed a surge in interest in SiNW arrays produced via the MACE method, owing to their versatile applications as electrode materials in diverse array of devices, encompassing supercapacitors, [7], Li-ion batteries, [8], solar cells [9], and sensors [10]. Moreover, these SiNWs grow directly onto the silicon substrate and possess the inherent capacity to serve as the current collector, obviating the need for additional binders [11]. In light of these multifaceted benefits, SiNW arrays synthesized using the MACE method were chosen as the electrode material in the research endeavor elucidated in this article. However, the use of SiNWs as electrodes in Li-ion batteries is not without its challenges, as documented in various reports. These challenges enccompasss intrinsic limitations in electronic and ionic conductivity, substantial volume fluctuations (approximating 420 %), and the progressive formation of a thick solid electrolyte interface (SEI) film during cycling, culminating in diminished cycling lifespan [12,13]. To overcome these challenges, various surface modification techniques have been extensively explored to improve the electrochemical performance of SiNW electrodes. These techniques include Magnesiothermic reduction method [14], Electrospinning method [15], Spin-coating [16], Atomic layer deposition [17] and RF-magnetron sputtering [11,14,17–23]. Among these techniques, drop-casting has emerged as a subject of considerable interest due to its simplicity, cost-effectiveness, and compatibility with large-scale fabrication processes [24]. By introducing a functional material onto the surface of SiNWs, drop-casting facilitates tailored modifications aimed at augmenting electrode performance. Transition-metal oxides have exhibited remarkable potential for Li-ion intercalation at the nanoscale [25,26]. In this context, MoO<sub>3</sub> has garnered particular attention as a prospective anode material for Liion batteries. MoO<sub>3</sub> exists in three distinct forms: orthorhombic  $\alpha$ -MoO<sub>3</sub>, monoclinic  $\beta$ -MoO<sub>3</sub>, and hexagonal h-MoO<sub>3</sub> [27]. In the [010] direction, the  $\alpha$ -phase exhibits a dual-layered structure characterized by covalent bonds within the dense layer and van der Waals forces between doublelayers [27,28]. The exceptional performance of  $\alpha$ -MoO<sub>3</sub> as an anode material for Li-ion batteries can be attributed to its anisotropic layered structure and the capability of molybdenum ions to alter their oxidation states. Theoretical calculations indicate a capacity of 1117 mA·h·g<sup>-</sup> allowing for the accommodation of six lithium ions per mole of MoO<sub>3</sub> [29].

In this study, we introduce an innovative technique involving dropcasting to modify the surface of silicon nanowires, with the overarching objective of enhancing the efficiency of electrodes based on SiNW arrays and thereby elevating the performance of Li-ion batteries for highdemand applications. Our specific focus centers on the functionalization of SiNWs with molybdenum oxide nanoparticles (MoO<sub>3</sub>). Collectively, this research serves as a pivotal milestone in the field of energy storage materials and lays the groundwork for the real-world integration of SiNW-based electrodes in high-performance Li-ion batteries.

### 2. Experimental procedure

### 2.1. Preparation of metal-assisted etched SiNWs

The experiment employed commercially available p-type borondoped silicon wafers (resistivity: 0.01–0.02  $\Omega \cdot cm$ ) sourced from Si-Mat Germany. The silicon wafers (100) underwent a rigorous cleaning process as follows: Initially, a 10-min ultrasonic rinse in acetone was conducted for the 2.5 × 2.5 cm<sup>2</sup> silicon wafers, followed by another 10-min ultrasonic rinse in ethanol. Subsequently, the wafers were immersed in a boiling solution of H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> for a period ranging from 10 to 30 min. Following this, thorough cleaning was performed using deionized water, and the wafers were dried under an inert gas environment.

The fabrication process consisted of two main steps. The first step involved the deposition of silver nanoparticles (AgNPs) onto the silicon wafer's surface. This was achieved by using an aqueous solution composed of 0.02 M AgNO<sub>3</sub> and 5 M HF, mixed in a volume ratio of 1:10 ( $\nu$ /v), with the deposition process lasting for 1 min. In the second step, the silicon wafer coated with Ag nanoparticles was immersed in an etching solution. This solution comprised 5 M HF and 30 % H<sub>2</sub>O<sub>2</sub> in a volume ratio of 10:1 ( $\nu$ /v), and the immersion was carried out for 30 min at room temperature. During this step, anisotropic etching occurred within the HF/H<sub>2</sub>O<sub>2</sub> solution, resulting in the formation of SiNW arrays. Subsequently, the SiNW arrays underwent several rinses with deionized water and were left to air-dry at room temperature.

To eliminate the silver nanoparticles located on the bottom of the SiNWs, the SiNW arrays underwent a treatment involving concentrated 65 % nitric acid (HNO<sub>3</sub>) for a duration of 10 min. Following this, the samples were immersed in a 2 % hydrofluoric acid (HF) solution to remove the oxide layer that had formed during previous treatments involving nitric acid (HNO<sub>3</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Finally, the samples underwent a washing process using deionized water and were subsequently dried under a stream of inert gas at room temperature.

### 2.2. Deposition of Mo oxides on SiNWs via drop-casting

The fabrication process for SiNWs decorated with Mo oxides is schematically depicted in Fig. 1. To enhance the hydrophilicity of the SiNW array surface, a brief  $O_2$  plasma treatment was applied. This treatment involved an  $O_2$  flow rate of 13 sccm and an RF power of 40 W. The procedure was conducted at a pressure of 400 mTorr for a duration of 30 s. In a typical experimental procedure, 18.7 mg of molybdenum (V) chloride (MoCl<sub>5</sub>, Merck) were dissolved in 100 ml of deionized water, ensuring complete dissolution through agitation using a magnetic stirrer. The resultant MoCl<sub>5</sub> solution was homogeneous and devoid of any undissolved particles.

For the drop-casting process, the cleaned SiNW array substrate was positioned in a suitable container. Approximately 50 drops (2 ml) of the  $MoCl_5$  solution were carefully dispensed onto the SiNW array substrate to ensure complete coverage. The container was allowed to stand for a specific duration, promoting the formation of  $MoO_3$  particles on the SiNW array surface. After drop-casting, the container was left undisturbed, and the solvent was left to naturally evaporate overnight at room temperature. Once the solvent had completely evaporated, the SiNW array substrate was transferred to a furnace for annealing. The annealing process lasted 15 min for all samples, while maintaining a pressure of 70 mTorr in a pure oxygen atmosphere. Various annealing temperatures such as 500 °C, 600 °C, and 700 °C were employed to perform the oxidation of the samples under identical atmospheric conditions. The system was then cooled down, and the sample was retrieved for characterization.

### 2.3. Characterization

A comprehensive array of analytical techniques was employed to thoroughly characterize the samples. X-ray diffraction (XRD) analysis was carried out using a PANalytical XPert PRO MPD Bragg-Brentano powder diffractometer with a radius of 240 mm. The XRD analysis employed Co K $\alpha$  radiation ( $\lambda = 1.789$  Å). The measurements involved scanning the 2 $\theta$  angle over a range from 4 to 99°, with a step size of 0.17° and a measuring time of 200s per step. Morphological assessments were conducted using field emission scanning electron microscopy (FE-SEM) with a JEOL J-7100 instrument and transmission electron microscopy (TEM) with a JEOL 2100 instrument. The nanostructures were transferred onto a Cu grid by applying gentle pressure with a cutter to detach them from the growth substrate. Image J and Digital Micrograph software were employed for image processing and analysis. X-ray photoelectron spectroscopy (XPS) measurements were conducted utilizing a PHI 5500 Multi-Technique system from Physical Electronics, Chanhassen, MN, USA. An aluminum Ka X-ray source with a photon energy of 1486.6 eV and a power of 350 W was utilized for the analysis. The



Fig. 1. Schematic representation summarizing the synthesis of SiNW arrays, the procedures of deposition and oxidation of nanostructured Mo oxides on SiNW arrays.

instrument was calibrated using Ag as a reference, with a full width at half maximum (FWHM) of 0.8 eV. Spectra were acquired with a pass energy of 187.5 eV and a step size of 0.8 eV per step for general spectra. For spectra involving different elements, a pass energy of 11.75 eV and a step size of 0.1 eV per step were employed. The analyzed area had a diameter of 0.8 mm. Peak positions and widths were determined by fitting the spectra using a mixed Gaussian-Lorentzian (GL) function, and a Shirley background was subtracted using the Casa XPS Software.

### 2.4. Electrochemical analyses

Electrochemical analyses were conducted using the AutoLab PGSTAT30 potentiostat/galvanostat system from Eco Chemie B.V. All experiments took place within the glove box filled with nitrogen to maintain an inert environment. A three-electrode electrochemical cell configuration was employed, utilizing a 1 M solution of LiClO<sub>4</sub> in 1:1 w/w ethylene carbonate and propylene carbonate, as the electrolyte. Lithium rods served as both the counter and reference electrodes, while the working electrode consisted of SiNW arrays decorated with Mo oxides nanoparticles. The electrochemical cell employed had a window hole, exposing an approximate area of 0.57 cm<sup>2</sup>. For cyclic voltammetry experiments, the SiNW arrays decorated with Mo oxides nanoparticles electrodes were cycled against a Li/Li<sup>+</sup> reference electrode within a voltage window ranging from 0.0 to 2.0 V. To evaluate the long-term cycling stability of the SiNW arrays decorated with Mo oxide nanoparticles, galvanostatic charge-discharge tests were conducted at various current densities, specifically at 100  $\mu$ A·cm<sup>-2</sup>. The tests covered a selected voltage range from 0.1 V to 2.0 V, with  $\text{Li}/\text{Li}^+$  as the reference electrode serving as the reference standard.

### 3. Results and discussion

### 3.1. Identification of Mo oxides via X-ray diffraction

X-ray diffraction (XRD) analysis was used to ascertain the presence of Mo oxide nanoparticles on the silicon nanowire (SiNW) arrays. Fig. 2 displays the XRD patterns of the bare SiNW arrays and SiNW arrays decorated with Mo oxides nanoparticles via drop-casting technique. These arrays were subjected to distinct annealing temperatures of 500 °C, 600 °C, and 700 °C for 15 min in an  $O_2$  atmosphere.

The XRD patterns unveil various crystallographic orientations. The characteristic peaks of Si, located at 28.8° and 69.1°, correspond to the (111) and (400) crystallographic planes (JCPDS No. 00-027-1402) [6]. Additional XRD peaks at approximately 25.4°, 34.2°, 45.5°, 47.0°, 49.2°, 53.4°, and 57.3° (Fig. 2) are attributed to the diffractions from the (040), (140), (160), (210), (002), (221) and (180) planes of orthorhombic  $\alpha$ -MoO<sub>3</sub> phase [30,31]. Notably, Mo oxide is detected in all diffraction spectra with orientations of orthorhombic  $\alpha$ -MoO<sub>3</sub> phase. Two distinct



**Fig. 2.** XRD patterns of as-synthesized SiNW arrays and SiNW arrays decorated with Mo oxide nanoparticles annealed at different temperatures (500  $^{\circ}$ C, 600  $^{\circ}$ C, and 700  $^{\circ}$ C, for 15 min, in O<sub>2</sub> atmosphere).

peaks at angles of  $18.6^{\circ}$  and  $31.6^{\circ}$  indicate the presence of the (-101) and (101) crystal planes of Monoclinic phase of MoO<sub>2</sub> (JCPDS NO. 00-32-0671). It is noted that as annealing temperature increases, the diffraction peaks intensify, indicating an improvement in the overall crystalline structure of the Mo oxides nanoparticles [32,33]. No additional peaks corresponding to silver nanoparticles (AgNPs) used in the preparation of the SiNW arrays during MACE were detected, demonstrating the complete removal of AgNPs from the bottom of SiNW arrays. Furthermore, after annealing, no impurity-related peaks were detected, confirming that the resultant product solely comprises Mo oxides. This series of crystallographic examinations underscore the successful preparation of SiNWs decorated with MoO<sub>3</sub> nanoparticles using the drop-casting technique and subsequent heat treatment.

### 3.2. Morphological insights into Mo oxide-decorated SiNW arrays

The morphology of SiNW arrays decorated with Mo oxide nanoparticles was investigated to provide deeper insights into the formation of MoO<sub>3</sub>@SiNWs hybrid structures. Side-view field-emission scanning electron microscopy (FE-SEM) images are presented in Fig. 3(a–d), with corresponding higher magnifications in the upper right corner (insets). Figs. 3(e–h) showcase top-view FE-SEM images of both bare SiNW arrays



**Fig. 3.** FE-SEM images of (a–d) side-view of bare SiNW arrays and SiNW arrays decorated with Mo oxides nanoparticles and their corresponding higher magnification as an inset in the right upper corner, (e–h) top-view of bare SiNW arrays and SiNW arrays decorated with Mo oxides nanoparticles with different annealing tempratures (500 °C, 600 °C, and 700 °C, for 15 min, in  $O_2$  atmosphere) along with illustrations of the resulting Mo oxides nanoparticles.

and SiNW arrays decorated with Mo oxides nanoparticles, each obtained at different annealing temperatures (500 °C, 600 °C, and 700 °C, for 15 min, in an  $O_2$  atmosphere). These illustrations are accompanied by representations of the resulting Mo oxides nanoparticles.

The vertical nanowire arrays with the average length of around (20  $\mu m \pm 0.26)$  long have diameter of average (381.2 nm  $\pm$  110.4) and the adequate spacing (in the range of 50-100 nm) were prepared on the silicon substrate, offering advantages for the uniform loading of active materials. In Fig. 3 (a) (side-view) and (e) (top-view), the vertically aligned bare SiNWs are depicted, along with their higher magnification inset image, obtained through the Metal-Assisted Chemical Etching (MACE) method. Despite employing a consistent amount of aqueous MoCl<sub>5</sub> solution for Mo deposition in all samples, the resulting nanoparticle structures exhibit significant variations. At the lowest annealing temperature of 500 °C, small Mo oxides nanoparticles on average size of (~44.5 nm  $\pm$  6.3) form and adhere to the SiNW sidewalls (Fig. 3(b,f)). This is evident in the higher magnification inset image of Fig. 3(b). Additionally, the Mo oxides nanoparticles cover the entire length of the SiNWs. A detailed examination of these nanoparticles by EDX and TEM will be addressed in the upcoming sections.

At a moderate annealing temperature of 600 °C, Mo oxide nanoparticles develop into larger grain on average size of (~169.5 nm  $\pm$ 23.1) structures deposited along the SiNW sidewalls (Fig. 3(c)). The increased size of the grain structure is clearly visible in the top-view image (Fig. 3(g)) and the inset of Fig. 3(c). In the highest annealing temperature of 700 °C, Mo oxide nanoparticles merge to form even larger agglomerates of grain on average size of (~513 nm  $\pm$  153.2) structures Fig. 3(d). The top-view image (Fig. 3(h)) clearly shows the enlarged grain structure of Mo oxide nanoparticles. The grain size of Mo oxides nanoparticles increases with rising annealing temperature. Fig. 3 (f–h) provide clear evidence that by increasing the annealing temperature from 500 °C to 600 °C, and then 700 °C, the grain size is also increased due to enhanced coalescence occurring between the MoO<sub>3</sub> particles [34]. The illustrations showcasing the resultant nanostructures are provided in Fig. 3(a–d) to aid in comprehending their morphologies. When analyzing the results obtained through FESEM characterization, it is anticipated that the electrochemical properties will be superior in the case of smaller particles attached densely on the SiNWs, as depicted in the SEM image Fig. 3(a). Consequently, our subsequent analysis concentrates exclusively on the sample involving SiNW arrays decorated with Mo oxide nanoparticles (annealed at 500 °C temperature). This preference may be attributed to the remarkably high specific surface area of the MoO<sub>3</sub> nanoparticles, which are affixed to the SiNWs [34].

# 3.3. Surface elemental mapping and TEM characterization of Mo oxide nanoparticles

Surface elemental mapping analysis using X-ray energy-dispersive spectroscopy (EDS) was carried out on the SiNW arrays decorated with Mo oxide nanoparticles annealed at 500 °C in an oxygen atmosphere. Fig. 4(a) illustrates a backscattered electron (BSE) image of the cross-sectional view of SiNW arrays decorated with Mo oxide nanoparticles. Additionally, Fig. 4(b-d) depict elemental mappings acquired through energy-dispersive X-ray spectroscopy (EDX) for silicon, molybdenum, and oxygen, respectively. The results reveal a homogeneous distribution of Mo and O atoms on the SiNWs surface. Notably, there were no signals indicative of Ag or Cl during the EDX analysis, corroborating the XRD findings. The signals of O and Mo exhibit a strong correlation and intensify along the length of SiNW arrays, indicating the comprehensive coverage of Mo oxide nanoparticles on the SiNWs sidewalls. This observation emphasizes the remarkable ability of Drop-Casting technique to uniformly coat the entire length of SiNWs with nanoparticles.

TEM characterization of the sample annealed at 500 °C in an oxygen atmosphere provides insights into the dimensions of Mo oxide nanoparticles deposited on the SiNW sidewalls, as illustrated in Fig. 5. Fig. 5 (a) reveals the homogeneous deposition of particles on the SiNW sidewall, displaying a dense distribution. The nanoparticles were observed to form a relatively continuous coating on the SiNW surfaces, indicating that the total active surface area of Mo oxide in this sample is likely



Fig. 4. BSE image of SiNW arrays decorated with Mo oxides nanoparticles (annealed at 500 °C temperature) along with corresponding elemental mappings of (b) silicon, (c) molybdenum, and (d) oxygen.

greater than in samples resulting from longer annealing times. This observation could provide an explanation for the increased electrochemical activity of this sample, a topic to be further explored in subsequent sections of this article. Fig. 5(b) illustrates the anchoring of a Mo oxide nanoparticle on a SiNW sidewall, while Fig. 5(c) shows a highresolution image of the MoO<sub>3</sub> nanoparticle. Fast Fourier transform (FFT) analysis of the lattice spacing confirmed the existence of the (040) plane [35], a plane also identified in the XRD pattern. To verify the elements, present in the Mo oxides nanoparticles decorating the SiNWs, elemental mapping for the TEM images is shown in Figs. 5(d-g), confirming that the Mo oxide nanoparticles contain Mo and O elements homogeneously dispersed on the silicon nanowire.

# 3.4. Surface states of Mo compounds via X-ray photoelectron spectroscopy

Surface states of Mo compounds were examined by X-ray photoelectron spectroscopy (XPS), with results illustrated in Fig. 6. Fig. 6(a) shows the wide scan spectra of bare SiNW arrays (black line) and Mo oxide nanoparticles decorated on SiNW arrays (annealed at 500 °C in oxygen atmosphere) nanostructure (red line). In the bare SiNW arrays sample, the Si 2p and Si 2s peaks appear at 103.0 eV and 153.0 eV, respectively, with the O1s peak at 532.0 eV. No peak corresponding to silver nanoparticles, used in the preparation the SiNW arrays during MACE, was detected, affirming the complete removal of AgNPs from the SiNW arrays. In the MoO<sub>3</sub>@SiNWs hybrid nanostructure sample, peaks were detected at a binding energy of 284.0 eV for C1s, 532.0 eV for O1s, as well as the Mo3p1/2 peak at 397.0 eV, the Mo3p3/2 peak at 414.0 eV, and the Mo3d3/2 peak at 231.92 eV. No peak corresponding to Cl, used to deposit Mo nanoparticles via drop-casting using molybdenum chloride (MoCl<sub>5</sub>), was detected, confirming that all chloride was removed during annealing, consistent with our EDX results. Figs. 6(b,c,d) show the deconvoluted peaks of the Si 2p, O 1s and Mo 3d modes, respectively, for the sample annealed at 500 °C in an oxygen atmosphere. Analysis of the Si 2p peak reveals the Si peak centered at 98.9 eV (2p3/ 2), while SiO<sub>2</sub> exhibits peaks centered at 103.2 eV (2p3/2) and 103.9 eV (2p3/2), and SiO<sub>x</sub> displays a peak centred at 99.5 eV (2p) [36–38]. In Fig. 6(c), the main component of the O1s peak is centered at 532.6 eV, attributed to O—Si (1s), while weaker components are attributed to O—Mo (peak at 531.1 eV) and O—C (peak at 533.2 eV) [34,38]. Analysis of the Mo peak in Fig. 6(d) reveals the formation of oxide species, including MoO with peaks centered at 228.5 eV (3d5/2) and 231.6 eV (3d3/2), MoO<sub>2</sub> with peaks centered at 229.9 eV (3d5/2) and 233.1 eV (3d3/2), and MoO<sub>3</sub> with peaks centered at 232.3 eV (3d5/2) and 235.4 eV (3d3/2) [34].

# 3.5. Electrochemical performance of Mo oxides nanoparticles decorated on SiNW arrays for LIBs

### 3.5.1. Cyclic voltammetry analysis

To investigate the electrochemical performance of Mo oxide nanoparticles decorated on SiNW arrays (annealed at 500 °C in an oxygen atmosphere) during charging and discharging, cyclic voltammetry (CV) was employed. Fig. 7(a,c) show the cyclic voltammograms of the first ten cycles for both bare SiNW arrays and MoO<sub>3</sub>@SiNWs hybrids (annealed at 500 °C in oxygen atmosphere), using a scan rate of 0.1 mV·s<sup>-1</sup> over the potential range of 0–2 V.

In Fig. 7 (a), the voltage profile for bare SiNW arrays aligns with prior findings on silicon anodes. During the initial charging phase, a stable voltage plateau emerges, corresponding to the reaction between crystalline silicon and Li<sup>+</sup> ions, leading to the formation of amorphous Li<sub>x</sub>Si [39-41]. In Fig. 7 (c), significant differences appear between the CV graphs of bare SiNW arrays and MoO3@SiNWs hybrids, attributed to the decoration of Mo oxide nanoparticles. Two broad reduction peaks are evident at 0.4 and 1.2 V. The peak at 1.2 V in the first cathodic scan is associated with the amorphousization process of the MoO3 active material and the initial reaction of lithium-ion insertion into the layered structure of crystalline  $\alpha MoO_3$  [42], as represented by the equation  $MoO_3 + xLi^+ + xe^- \rightarrow Li_xMoO_3$  [43]. Upon the completion of the first cathodic conversion reaction, the crystal structure of the active material experiences a change into an amorphous state, contributing to lowered redox potentials during cycling [44,45]. The peak observed at a lower potential of 0.4 V can be attributed to reversible conversion reactions [42]. After the initial cycle, there is a slight shift in the cathodic



**Fig. 5.** TEM images of: (a) distribution of Mo oxides nanoparticles on the SiNW, (b) a Mo oxide nanoparticle anchored on a SiNW (c) high resolution TEM image of MoO<sub>3</sub> nanoparticle along with corresponding FFT, (d) the corresponding TEM/elemental mapping, images of the Mo oxide nanoparticles decorated on SiNW, presenting the distribution of (e) Si, (f) O, and (g) Mo elements.

conversion potential toward a lower potential, accompanied by a decrease in the cathodic peak current. These results reveal that both Mo oxide nanoparticles and SiNW arrays facilitate the insertion and extraction of  $\rm Li^+$  ions.

Furthermore, the electrochemical reactivity of both bare SiNW arrays and SiNW arrays decorated with molybdenum oxide nanoparticles was evaluated as anode materials for LIBs in the potential range of 0.1–2.0 V at a rate of 1C (100  $\mu$ A·cm<sup>-2</sup>) in the first ten cycles. Fig. 7(b,d) show the first ten discharge and charge profiles of the bare SiNW arrays and MoO<sub>3</sub>@SiNWs hybrids (annealed at 500 °C in an oxygen atmosphere) electrodes at a current density of 100  $\mu$ A·cm<sup>-2</sup>.

Fig. 7(b) highlights the substantial capacity of bare SiNWs, closely resembling previously reported findings [41,46]. The initial discharge duration is longer than subsequent discharges, indicating an irreversible loss of capacity, likely due to the formation of a solid electrolyte interface. However, both charge and discharge capacities exhibit minimal reduction in subsequent charge/discharge cycles, consistent with the CV measurements and previous research [46]. In contrast, MoO<sub>3</sub>@SiNWs hybrids exhibit distinct electrochemical characteristics. In Fig. 7 (d), the

first discharge capacity for Mo oxide nanoparticles decorated on SiNW arrays is  $1.34 \text{ mA}\cdot\text{h}\cdot\text{cm}^{-2}$ , significantly higher than the 0.35 mA·h·cm<sup>-2</sup> observed for bare SiNW arrays.

Notably, more distinct potential plateaus are observed at 1.5 V. The second cycle exhibits a maximum capacity of approximately 1.25 mA·h·cm<sup>-2</sup>, surpassing the capacity observed for bare SiNW arrays during its second cycle. Additionally, the presence of Mo oxide nanoparticles on the SiNW arrays significantly impacts the anode's stability. As depicted in Fig. 7 (d), the 2nd and 10th discharge profiles are nearly identical, with curves exhibiting much less dispersion compared to Fig. 7 (b). At this current density, the maximum capacities during the 10th cycle for the bare SiNW arrays and the MoO<sub>3</sub>@SiNWs hybrids were found to be 0.31 and 1.18 mA·h·cm<sup>-2</sup>, respectively. These results highlight the substantial capacity improvement achieved by incorporating Mo oxide nanoparticles on SiNW arrays.

### 3.5.2. Rate capability analysis

The rate capability of SiNW arrays, both bare and decorated with Mo oxide nanoparticles (annealed at 500  $^{\circ}$ C in an oxygen atmosphere), was



Fig. 6. (a) Wide scan spectra of bare SiNW arrays and Mo oxides nanoparticles decorated on SiNW arrays (annealed at 500 °C in Oxygen atmosphere time), (b, c, d) deconvoluted peaks of the Si<sub>2p</sub>, O<sub>1s</sub> and Mo<sub>3d</sub> modes, respectively, for Mo oxides nanoparticles decorated on SiNW arrays (annealed at 500 °C in Oxygen atmosphere time).

evaluated at different current densities (Fig. 8a). Current densities were incrementally increased to 10C after the electrode was tested at 1C for 10 cycles. At all current densities, the MoO<sub>3</sub>@SiNWs hybrid electrode exhibited superior capacities compared to bare SiNW arrays. The average reversible capacity of the Mo oxide nanoparticles decorated on SiNW arrays electrode was approximately 1.25, 1.03, 0.78, 0.60 and 0.44 mA  $h~cm^{-2}$  at current densities of 1C (100  $\mu A~cm^{-2}$ ), 2C (200  $\mu A$ cm<sup>-2</sup>), 4C (400  $\mu$ A cm<sup>-2</sup>), 8C (800  $\mu$ A cm<sup>-2</sup>) and 10C (1000  $\mu$ A cm<sup>-2</sup>), respectively. Upon a rapid transition from 10C to 1C, the capacity of Mo oxide nanoparticles decorated on SiNW arrays recovered to 1.18 mA·h·cm<sup>-2</sup>, underscoring the robustness and reversibility of the structure. This high-rate capability and good capacity retention are attributed to the embedded MoO<sub>3</sub> nanoparticles within the SiNWs, providing a large specific surface area that facilitates the transportation of electrons and Li<sup>+</sup>. This structure effectively buffers the volume expansion of Si during lithiation, ensuring stability [18,23]. Additionally, the hybrid architecture enhances electrical conductivity, expediting charge transfer. Consequently, the MoO<sub>3</sub>@SiNWs hybrid electrode demonstrates outstanding cycling performance even at high discharge rates.

### 3.5.3. Comparison with prior studies

Table 1. provides a comparative analysis of first discharge specific capacities obtained in this work with those from previous studies. K. Peng. et al. [46] explored large-area silicon nanowire (SiNW) arrays prepared by MACH as anode materials, achieving a first discharge

specific capacity of 0.55 mA·h·cm<sup>-2</sup>. H. Ohtsuka et al. [47] fabricated thin film batteries using the RF sputtering method with a MoO<sub>3</sub> cathode film, obtaining a first discharge specific capacity of 0.39 mA·h·cm<sup>-2</sup>. H. Chen et al. [48] prepared copper-coated SiNWs by the chemical vapor deposition and magnetron sputtering method, with a first discharge specific capacity of  $1.70 \text{ mA} \cdot \text{h} \cdot \text{cm}^{-2}$ . H. Chen et al. achieved the highest discharge specific capacity of 1.70 mA·h·cm<sup>-2</sup> using Cu-coated SiNWs. However, the use of Cu, compared to MoO<sub>3</sub>, may introduce instability to the electrode due to diffusivity of Cu and metal reactivity, such as with oxygen. Despite providing a lower discharge specific capacity of 1.34  $mA \cdot h \cdot cm^{-2}$ , it appears that MoO<sub>3</sub> is more stable. In this work, we achieved a relatively high initial specific capacity of 1.35 mA·h·cm<sup>-2</sup> by combining both SiNW arrays with MoO<sub>3</sub> nanoparticles. This improvement can be attributed to the substantially increased active surface area of Mo Oxide nanoparticles on SiNW arrays compared to thin films, as shown in Fig. 5(a) [34].

# 3.5.4. Cycling performance and Coulombic efficiency

Fig. 8(b) despicts the specific capacity and Coulombic efficiency of the bare SiNW arrays and Mo oxide nanoparticles decorated SiNW arrays (annealed at 500 °C in an oxygen atmosphere) at a current density of 100  $\mu$ A·cm<sup>-2</sup>. The capacity profiles remain almost flat after 70 cycles at discharging rates of 1C. Remarkably, the MoO<sub>3</sub>@SiNWs hybrid nanostructure shows better cycling stability and superior reversible capacity than bare SiNW arrays even after the 200 cycles, maintaining a



**Fig. 7.** Cyclic voltammograms of the electrodes based on (a) bare SiNW arrays, (c) Mo oxides nanoparticles decorated on SiNW arrays annealed at 500 °C in Oxygen atmosphere, for the first 10 cycles with the scanning speed of 0.1 mV/s between 0 and 2 V. Charge–discharge Voltage profiles of the electrodes based on (b) bare SiNW arrays, (d) Mo oxides nanoparticles decorated on SiNW arrays annealed at 500 °C in Oxygen atmosphere, at a current density of 100  $\mu$ Acm<sup>-2</sup> in the range of 0.001 to 2 V, for 10 cycles.



**Fig. 8.** Rate performance of (a) bare SiNW arrays and Mo oxides nanoparticles decorated on SiNW arrays annealed at 500 °C in oxygen atmosphere, electrodes at various current rates, (b) comparison of cyclic performance of bare SiNW arrays and Mo oxides nanoparticles decorated on SiNW arrays annealed at 500 °C in oxygen atmosphere and columbic efficiency of Mo oxides nanoparticles decorated on SiNW arrays annealed at 500 °C in oxygen atmosphere.

reversible specific capacity of  $1.34 \text{ mA}\cdot\text{h}\cdot\text{cm}^{-2}$  compared to the considerably lower 0.34 mA·h·cm<sup>-2</sup> capacity of bare SiNW arrays. The Coulombic efficiency for Mo oxide nanoparticles decorated on SiNW arrays starts at 96 % in the first cycle and progressively increases to a stable value of 99.4 % after the first 6 cycles. In contrast, the Coulombic efficiency for bare SiNW arrays starts at 95 % in the first cycle and progressively increases to a stable value of 97.4 % after the first 10 cycles. After 200 cycles, the electrode maintains a reversible specific capacity of 1.23 mA·h·cm<sup>-2</sup>, in contrast to the significantly lower 0.20 mA·h·cm<sup>-2</sup> capacity maintained by bare SiNW arrays. This enhanced capacity is likely due to the dual mechanism at play, leveraging contributions from both SiNWs and MoO<sub>3</sub> decorated on SiNWs. Additionally, the hybrid nanostructure exhibits good cycling stability.

# 3.6. Morphological insights into Mo oxide-decorated SiNW arrays after 200 cycles

Post mortem investigation were conducted to analyze the structural deformation characteristics of MoO<sub>3</sub>@SiNWs hybrid nanostructure after undergoing 200 cycles. As depicted in Fig. 9(a), the MoO<sub>3</sub>@SiNWs hybrid nanostructure remarkably maintained its original shape, remaining largely intact after the extensive cycling process. While the original morphology is preserved, subtle surface modifications are apparent when compared to the as-prepared MoO<sub>3</sub>@SiNWs hybrid nanostructure (refer to Fig. 3b). These modifications are likely attributed to the repetitive lithiation/delithiation processes of the MoO<sub>3</sub> oxide nanoparticles on the surface of SiNWs (Fig. 9b) and/or the minor

#### Table 1

A comparison table detailing the characteristics of various materials coated on SiNW-based anodes, as documented in the literature. Notably, our experimental conditions are emphasized for their favorable impact on the achievable areal capacity.

Materials	First discharge capacity (mA·h·cm $^{-2}$ )	Ref
Bare Silicon nanowire (SiNW)	0.55	[46]
MoO <sub>3</sub> thin cathode film	0.39	[47]
Copper-coated SiNWs	1.70	[48]
Sn-coated SiNWs	1.10	[11]
TiO <sub>2</sub> -coated SiNWs	0.48	[21]
Carbon-coated SiNWs	0.48	[49]
Pre-lithiated SiNWs	0.05	[50]
MoO <sub>3</sub> -coated SiNWs	1.34	This Work

deposition of a solid electrolyte interface after 200 cycles. [20] This observation underscores the efficacy of  $MoO_3$  oxides anchored on the SiNW surface in preserving the mechanical integrity of the SiNWs throughout the cycling process. In addition, Fig. 9(c) presents elemental mappings acquired through EDX for silicon, molybdenum, lithium and oxygen, respectively.

The drop-casting technique emerged as a simple vet effective method for decorating SiNW arrays with MoO<sub>3</sub> nanoparticles. The SiNWs arrays exhibited excellent compatibility with MoO3 nanoparticles, and the unique structure of Mo oxide nanoparticles on SiNW arrays electrodes significantly contributed to outstanding electrochemical performance, including good cycling stability, excellent rate performance, and high reversible capacity. Several key factors account for the exemplary electrochemical performance of the MoO3@SiNWs hybrid nanostructure electrode: i) the high aspect ratio facilitates achieving percolation limits with lower weights, ii) the vertical SiNWs structure provides a regular and porous path for ion diffusion, iii) SiNWs, acting as an active material themselves, ensure a large surface area for Li<sup>+</sup> ion insertion/extraction. iv) MoO<sub>3</sub> enhances the capacity of SiNWs by incorporating Li into the storage system, providing additional electrochemical reaction sites due to its large specific surface area, v) the total specific capacity is elevated by both MoO<sub>3</sub> and SiNW arrays, resulting in a high reversible capacity.

Furthermore, the presence of  $MoO_3$  nanoparticles on the SiNWs acts as a buffer, mitigating volume expansions resulting from repeated Li-ion intercalation/deintercalation, addresing a critical concern regarding volume expansions and material degradation [11].

#### 4. Conclusions

In summary, the present study has culminated in the successfully fabrication of a novel MoO<sub>3</sub>@SiNWs nanostructure. This achievement was realized through the application of a straightforward on-step metal-assisted chemical etching (MACE) method for the formation of SiNW arrays, followed by the deposition of Mo via a drop-casting technique. Subsequent FE-SEM analysis has provided crucial insights into the morphology of the Mo oxide nanoparticles, revealing their strong dependence on the annealing temperature. Specifically, the lowest annealing temperature of 500 °C resulted in the formation of Mo oxides with diminutive nanometric diameters, while increasing the annealing temperature to 600 °C and 700 °C led to the development of larger grain structures in the Mo oxide nanoparticles. Interestingly, TEM analyses showed well-dispersed and uniformly anchored MoO<sub>3</sub> nanoparticles on SiNWs, irrespective of the applied annealing temperature.

When evaluated as an anode material for Li-ion batteries, the Mo oxide nanoparticle-decorated SiNW arrays electrode exhibited superior electrochemical properties in comparison to the bare SiNW arrays electrode. Evidently, the MoO<sub>3</sub>@SiNWs hybrid electrode displayed an enhanced initial discharge capacity  $(1.34 \text{ mA} \cdot \text{h} \cdot \text{cm}^{-2})$  as opposed to the bare SiNW arrays electrode (0.35 mA·h·cm<sup>-2</sup>) at a scan rate of 1C. Moreover, the MoO<sub>3</sub>@SiNWs hybrid electrode consistently maintained a reversible specific capacity of 1.23 mA·h·cm<sup>-2</sup> even after undergoing 200 charge-discharge cycles, while the bare SiNW arrays electrode exhibited a significant lower capacity of 0.20 mAh cm<sup>-2</sup> under identical cycling conditions. Notably, the MoO<sub>3</sub>@SiNWs hybrid electrode showed a progressive enhancement in coulombic efficiency, transitioning from 96 % to 99.4 % over the initial five cycles, followed by stable performance thereafter. This exceptional electrochemical performance can be attributed to the dynamic interaction between MoO3 nanoparticles anchored on SiNW arrays.

In essence, our study has unveiled a promising avenue for the creation of highly efficient energy storage devices through the synthesis of diverse oxides@SiNWs hybrid structures, using the proposed synthesis process. This research not only advances our fundamental understanding of nanostructure fabrication but also holds substantial potential for the development of next-generation energy storage technologies.



Fig. 9. FE-SEM image of (a) side-view of SiNW arrays decorated with Mo oxide nanoparticles annealing at temperature (500 °C for 15 min, in  $O_2$  atmosphere) after 200 cycles. (b) zoomed FE-SEM image of the SiNW arrays surface, Scale bar is 1  $\mu$ m. c) EDS spectra of MoO<sub>3</sub>@SiNWs hybrid nanostructure after 200 cycles.

### CRediT authorship contribution statement

**Ghulam Farid:** Conceptualization, Formal analysis, Investigation, Validation, Writing – original draft. **Roger Amade-Rovira:** Funding acquisition, Supervision, Writing – review & editing. **Rogelio Ospina:** Formal analysis, Validation, Writing – review & editing. **Enric Bertran-Serra:** Funding acquisition, Supervision, Writing – review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

No data was used for the research described in the article.

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