Abstract: TiO$_2$ nanotube layers (TNTs) decorated with Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$ are investigated as a negative electrode for 3D Li-ion microbatteries. Homogenous nanosheets decoration of MoS$_2$, sandwiched between Al$_2$O$_3$ coatings within self-supporting TNTs was carried out using atomic layer deposition (ALD) process. The structure, morphology, and electrochemical performance of the Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-decorated TNTs were studied using scanning transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and chronopotentiometry. Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-decorated TNTs deliver an areal capacity almost three times higher than that obtained for MoS$_2$-decorated TNTs and as-prepared TNTs after 100 cycles at 1C. Moreover, stable and high discharge capacity (414 µAh cm$^{-2}$) has been obtained after 200 cycles even at very fast kinetics (3C).

Keywords: TiO$_2$ nanotube; MoS$_2$; Al$_2$O$_3$; atomic layer deposition; Li-ion microbatteries

1. Introduction

Nowadays, microelectrochemical systems are key devices for providing power for micro/nanoelectromechanical devices (M/NEMS) in the fields of bio/medical engineering, aerospace, and intelligent sensors [1–3]. The microelectrochemical systems can be classified based on their power source as rechargeable Li-ion microbatteries (µLIBs) [4–6], microsupercapacitors [7], microfuel cells [8], and microthermoelectric batteries [9]. The two main requirements for selecting power sources for M/NEMS devices are high energy/power densities and long lifetime [10,11]. Planar 2D µLIBs energy and power densities have an intrinsically inverse correlation, i.e., microbatteries with thick electrodes deliver a high-energy and a low-power density, while the reverse is true for thin electrodes [12]. Hence, the development of 3D µLIBs forms a viable alternative to planar 2D µLIBs to overcome the tradeoff between power and energy [13,14]. Nanomaterials such as nanopillars, nanorods, nanowires,
and nanotubes are widely explored as potential electrode materials for 3D µLIBs due to their short ion diffusion distances, high aspect ratio, and small foot print [15–18].

Self-supported TiO₂ nanotube (TNT) layers have been extensively explored as anodes for 2D/3D µLIBs due to their unique one-dimensional architecture, high self-ordering degree, short Li⁺ diffusion distance, fast electron transport, safety (high lithiation potential ~1.7 V vs. Li/Li⁺), low self-discharge rate, and nontoxic nature [18–22]. However, their low theoretical capacity (168 mAh g⁻¹) and poor electronic conductivity pose a major obstacle for practical application [20,23,24].

To overcome these problems, surface modification of the TNT layers by coating, decorating, and doping with various materials have been extensively explored [6,25–38]. Because of the low volumetric expansion and high porosity, the surface modified TNT layers deliver high capacity, while keeping the mechanical stability of the nanostructured electrode. In our recent work, we showed, for the first time, TNT layers homogenously decorated with ultrathin MoS₂ nanosheets using atomic layer deposition (ALD) process that can be used as anode for 3D µLIBs [6]. The MoS₂-decorated TNT layers deliver superior electrochemical performance in comparison to their pristine counterparts. However, the capacity fades continuously during cycling due to the formation of thick solid electrolyte interphase (SEI) on the surface of the electrode and the loss of active material [6].

In the present study, we report the remarkable electrochemical properties obtained for the reversible insertion of Li ions in Al₂O₃/MoS₂/Al₂O₃-decorated TNT layers. The capacity fading is strongly attenuated by protecting the MoS₂ nanosheets with Al₂O₃ sandwich coating, produced before and also after the MoS₂ ALD process. The 3D multilayers deliver excellent areal capacities with good stability up to 200 cycles even at very fast kinetics, making the Al₂O₃/MoS₂/Al₂O₃-decorated TNT layers a potential candidate as a negative electrode for high performance µLIBs.

2. Materials and Methods

2.1. Synthesis of TNTs and ALD-Decorated TNTs

Self-organized TNT layers with a thickness of ~20 µm and an inner diameter of ~110 nm were produced via anodization of thin Ti foils (127 µm thick, Sigma-Aldrich) according to the previous published work [39]. In brief, the Ti foils were anodized in an ethylene glycol-based electrolyte containing NH₄F (170 mM) and 1.5 vol % H₂O at 60 V for 4 h. Prior to anodization the Ti foils were degreased by sonication in isopropanol and acetone for 60 s, respectively, and dried in air. The anodization setup consisted of a high-voltage potentiostat (PGU-200 V; Elektroniklabor GmbH) in a two-electrode configuration, with a Pt foil as a counter electrode and the Ti foil as a working electrode. The samples were coated using atomic layer deposition (ALD) (Beneq TFS-200) with 15 cycles MoS₂ (henceforth referred as Al₂O₃/MoS₂/Al₂O₃-TNTs). The coating of MoS₂ was carried out as described in our previous work with bis(t-butylimido)bis(dimethylamino) molybdenum (Strem, 98%) and hydrogen sulfide (99.9%) as molybdenum and sulphur precursors, respectively [6]. The MoS₂ was deposited within the TNT layers by applying 15 ALD cycles at a temperature of 275 °C with N₂ (99.9999%) as carrier gas at a flow rate of 500 standard cubic centimeters per min (sccm). The molybdenum precursor was heated up to 75 °C to increase its vapor pressure. Under these deposition conditions, one growth ALD cycle was defined by the following sequence: Bis(t-butylimido)bis(dimethylamino) molybdenum pulse (4 s)—Bis(t-butylimido)bis(dimethylamino) molybdenum exposure (45 s)—N₂ purge (90 s)—H₂S pulse (2.5 s)—H₂S exposure (45 s)—N₂ purge (90 s).

The coating of Al₂O₃ on the TNT layers was prepared using trimethylaluminum (TMA, Strem, 99.999+%) and deionized water (18 MΩ) as aluminum and oxygen precursors, respectively [29,39]. Under these conditions, one ALD Al₂O₃ growth cycle was defined by the following sequence:
TMA pulse (500 ms)—TMA exposure (5 s)—N₂ purge (10 s)—H₂O pulse (500 ms)—H₂O exposure (5 s)—N₂ purge (10 s). All processes were carried out at a temperature of 150 °C, using N₂ (99.9999%) as the carrier gas, at a flow rate of 400 sccm. The ALD process of 9 cycles Al₂O₃ corresponds to a nominal thickness of 1 nm Al₂O₃, as shown in our previous work [29].

2.2. Materials Characterization

The morphology and chemical composition of the fresh and cycled electrodes were characterized by a field emission electron microscope (FE-SEM JEOL JSM 7500F, JEOL, Tokyo, Japan) and a transmission electron microscope (Titan Themis 60–300, Thermo Fisher Scientific, Eindhoven, Netherlands) operated at 300 keV and equipped with a high angle annular dark field detector for scanning transmission electron microscopy (STEM-HAADF) and Super-X energy dispersive X-ray (EDX) spectrometer with 4 × 30 mm² windowless silicon drift detectors. All the EDX elemental maps are shown in net intensities, which represent the count intensities according to the background corrected and fitted model performed by Velox 2.9 software. Cross section views were obtained from mechanical bended TNTs. Dimensions of the layers were measured and statistically evaluated using proprietary Nanomeasure software.

The surface chemical state of MoS₂ was monitored by X-ray photoelectron spectroscopy (XPS) (ESCA25R, Scienta-Omicron, Taunusstein, Germany) using a monochromatic Al Kα (1486.7 eV) X-ray source operated with 250W and 12.5kV. The binding energy scale was referenced to adventitious carbon (284.8 eV).

2.3. Electrochemical Characterization

The electrochemical performance tests were performed using standard two-electrode Swagelok cells that were assembled in a glovebox filled with high purity argon (Ar). The half-cells consist of as-prepared TNTs, MoS₂-TNTs, or Al₂O₃/MoS₂/Al₂O₃-TNTs as the working electrode and Li foil (1 mm in thickness and 9 mm in diameter) as the reference electrode. The two electrodes were separated by a Whatman glass microfiber soaked in organic liquid electrolyte solution (0.35 mL) composed of 1M LiPF₆ dissolved in a 1:1 vol.% mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC).

The electrochemical performance tests (cyclic voltammetry, CV, galvanostatic charge−discharge) were performed using a VMP3 potentiostat (Bio Logic, France). The CV curves were recorded in a potential window of 0.01−3 V at a scan rate of 1 mV s⁻¹. Galvanostatic tests were performed at multiple C-rate in the potential window of 0.01−3 V. The current was applied based on TNTs assuming a porosity of 70.5%. The porosity calculation is based on the amount of the TNTs per cm² and should be noted that it is only an estimated value (see supplementary materials for the calculations). C/n means the battery is fully charged or discharged up to its total storage capacity in n hours (for this work 1C = 340 µA cm⁻²). As the surface area of the as-prepared and ALD-decorated TNTs are macroscopic (0.82 cm²), the obtained capacities are given in areal capacities (mAh cm⁻²).

3. Results and Discussion

The highly ordered TNT layers were 20 µm thick, and the nanotubes had an inner diameter of ~110 nm resulting in an aspect ratio of 180, as shown in our previous publication [6]. As the amount of MoS₂ decorated on the TNT layers by 15 ALD cycles is very low, it was not possible to visualize it by using SEM. However, as proved previously by STEM-EDX, already 2 ALD cycles of MoS₂ led to a decoration of the TNT layers with small MoS₂ sheets [6].

Figure 1 shows a STEM-HAADF image of the edge of TNT decorated with 9 cycles Al₂O₃—15 cycles MoS₂—9 cycles Al₂O₃ and the corresponding EDX maps (see Figure S1a for the EDX spectrum). These maps reveal a homogenous distribution of Mo and S as well as of Al on the TNT wall. In comparison with our previous publication, the MoS₂ nanosheets appear smaller [6]. This can be explained by the different chemical nature of the surfaces that MoS₂ was deposited on: herein, the MoS₂ was deposited on the Al₂O₃ layer, while in our previous publication the MoS₂ was deposited directly...
on the TNT walls [6]. The initial ALD growth of MoS$_2$ is different on different surfaces, and, thus, MoS$_2$ nanosheets observed herein are smaller than if they are directly grown on TiO$_2$.

Figure 1. STEM-HAADF image in high magnification and the STEM EDX elemental maps showing the distribution of Mo, S, and Al on the surface of the TiO$_2$ nanotube layers (TNTs).

XPS survey spectra of TNT layers decorated with 15 cycles MoS$_2$ and with 9 cycles Al$_2$O$_3$—15 cycles MoS$_2$—9 cycles Al$_2$O$_3$ are shown in Figure 2a. For 15 cycles MoS$_2$ sample, Ti 2p and O 1s signals stem from the underlying TNT layer. In the case of the sandwich sample it is observed that the intensity of the O 1s signal increases and the Ti 2p decreases, due to the presence of the Al$_2$O$_3$ layers; therefore most of the O 1s comes from the Al$_2$O$_3$. The C species detected on both TNT layers are related to adventitious carbon. Figure 2b shows the corresponding Mo 3d high-resolution spectra (HR) along with the S 2s signal. As can be seen, the HR signals on both samples are relatively broad. This can be explained by the very thin MoS$_2$ decoration as on the TiO$_2$/MoS$_2$ interface, as well as on the Al$_2$O$_3$/MoS$_2$ some Mo-O bonds might be built. When higher ALD MoS$_2$ cycle numbers were applied (results not shown), the signals became narrower due to thicker MoS$_2$ nanosheet decorations, and the XPS spectra showed pure MoS$_2$ [6]. Considering this, Mo 3d HR spectra of both samples show their corresponding spin–orbit Mo 3d$_{5/2}$/Mo 3d$_{3/2}$ and were deconvoluted into three doublets. The first one (red), centered
at ~229.0/232.1 eV, is assigned to Mo\(^{4+}\) belonging to the MoS\(_2\) lattice [40,41]. The second one (blue), located at ~229.9/233.0 eV, is attributed to Mo bonded with oxygen to form MoO\(_2\) [42]. The last doublet (orange) at ~232.5/235.6 eV corresponds to MoO\(_3\) [43,44]. It is notable that in the sandwich sample the signals corresponding to MoS\(_2\) decrease, while molybdenum oxide signals increase. This could be due to the interaction of MoS\(_2\) with the water used as a precursor for the synthesis of Al\(_2\)O\(_3\). Besides, S 2s peaks of the 15 cycles MoS\(_2\) sample, centered at ~226.6 (MoS\(_2\)) (dark cyan) and 229.5 eV (SH—thiol groups) (purple), respectively, and S 2s peaks of the sandwich sample, located at 226.8 (MoS\(_2\)) (dark cyan) and 234.2 (SO\(_4^{2-}\)) (green), respectively, agree well with the chemical species observed in S 2p.

In Figure 2c, the deconvoluted HR S 2p spectra of both samples confirm the presence of MoS\(_2\) with the doublet S2p\(_{3/2}/S2p_{1/2}\) (dark cyan) and 234.2 (SO\(_4^{2-}\)) (green), respectively, agree well with the chemical species observed in S 2p. In Figure 2c, the deconvoluted HR S 2p spectra of both samples confirm the presence of MoS\(_2\) with the doublet S2p\(_{3/2}/S2p_{1/2}\) (dark cyan), centered at ~161.9/163.1 eV, which corresponds to the S\(^{2-}\) state from the MoS\(_2\) lattice [45]. However, each sample presented two different additional chemical species. 15 cycles MoS\(_2\) sample show another doublet (purple) at ~163.6/164.8 eV attributed to SH that remained on the surface after the MoS\(_2\) deposition [46]. The sandwich sample displayed its doublet (green) at ~167.8/169.0 eV, assigned to SO\(_4^{2-}\) (sulfate) [46], possibly due to the interaction of sulfur with the water used in Al\(_2\)O\(_3\) synthesis.

![Figure 2. (a) X-ray photoelectron spectroscopy (XPS) survey spectra, (b) Mo 3d high resolution spectra and (c) S 2p high resolution spectra for TNT layers decorated with 15 cycles MoS\(_2\) and with 9 cycles Al\(_2\)O\(_3\)—15 cycles MoS\(_2\)—9 cycles Al\(_2\)O\(_3\).](image)

Figure 3a–c shows the cyclic voltammetry curves obtained for as-prepared TNTs, MoS\(_2\)-TNTs and Al\(_2\)O\(_3\)/MoS\(_2\)/Al\(_2\)O\(_3\)-TNTs recorded at a scan rate of 1 mV s\(^{-1}\) in the potential window of 0.01–3 V vs. Li/Li\(^{+}\). All the CV curves obtained exhibit a cathodic peak at 1.7 V vs. Li/Li\(^{+}\) and anodic peak at 2.2 V vs. Li/Li\(^{+}\) associated to the reversible insertion/extraction of Li\(^{+}\) into/from anatase according to Equation (1) [5,18,47,48]. However, the first insertion peak for Al\(_2\)O\(_3\)/MoS\(_2\)/Al\(_2\)O\(_3\)-TNTs is shallow and shifts to the lower potential because of the Al\(_2\)O\(_3\) insulating coating which slows down
the Li-diffusion [29]. This behavior is not observed in the subsequent cycles due to the formation of a conductive Al-O-Li phase.

\[
\text{TiO}_2 + x\text{Li}^+ + xe^- \rightleftharpoons \text{Li}_x\text{TiO}_2 \quad 0 \leq x \leq 1,
\]  

(1)

**Figure 3.** Cyclic voltammograms of (a) as-prepared TNTs, (b) MoS$_2$-TNTs and (c) Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs recorded at a scan rate of 1 mV s$^{-1}$

In comparison to as-prepared TNTs, the CV curves show additional peaks for the MoS$_2$-TNTs (Figure 3b) and Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs (Figure 3c). These peaks are attributed to the multistep reaction of Li$^+$ with MoS$_2$. During the first discharge (lithiation), the two cathodic peaks at 1.25–1.75 V and 0.5 V vs. Li/Li$^+$ are attributed to phase transformation of MoS$_2$ in to Li$_x$MoS$_2$ and the subsequent complete reduction of Mo$^{4+}$ to Mo$^0$ and Li$_2$S, respectively, according to Equations (2) and (3) [49,50]. Upon the charge (delithiation) process, the shallow peak at 1.9 vs. Li/Li$^+$ associated with retrieval of Li$_x$MoS$_2$ from Mo is dwarfed by the broader and more prominent peak at 2–2.75 V vs. Li/Li$^+$ which correspond to the oxidation of Li$_2$S to S according to Equations (3) and (4), respectively [49,50]. This phenomenon is more pronounced for MoS$_2$-TNTs because of the absence of the protective Al$_2$O$_3$-coating layer.

\[
\text{MoS}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{MoS}_2, 
\]

(2)

\[
\text{Li}_x\text{MoS}_2 + (4 - x) \text{Li}^+ + (4 - x) e^- \rightleftharpoons \text{Mo} + 2\text{Li}_2\text{S},
\]

(3)

\[
\text{Li}_2\text{S} \rightleftharpoons 2\text{Li}^+ + \text{S} + 2e^-.
\]

(4)

Compared to the CV curves of as-prepared TNTs and Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs, the MoS$_2$-TNTs shows broader peaks and larger surface area under the CV curve. This is attributed to the MoS$_2$-decoration contributing to the total capacity and modification of the electrode structure. However, the peak intensity and area under the CV curve diminish with cycling. In our previous work, we reported that electrochemical performance of MoS$_2$-TNTs is affected by the dissolution of S combined to the formation and growth of a SEI layer [6]. In contrast, reversible and stable CV curves are obtained for Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs owing to the ALD-deposited Al$_2$O$_3$ thin layers. The surface modification results in the improved stability of the electrode by limiting the S dissolution and the growth of the SEI layer through the formation of a stable Al-O-Li composite [29].

The electrochemical performance was evaluated through the examination of the charge/discharge profiles obtained by galvanostatic cycling tests. Figure 4a–c, shows the galvanostatic charge/discharge profiles for as-prepared TNTs, MoS$_2$-TNTs, and Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs at a current density of 340 μA cm$^{-2}$ (1C) in the potential window of 0.01–3 V vs. Li/Li$^+$. The charge/discharge profiles are in agreement with the electrochemical behaviors observed from the CV plots. For as-prepared TNTs and MoS$_2$-TNTs, the obtained capacity fades with cycle number unlike to the Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs. This is attributed to the beneficial effects of the Al$_2$O$_3$-coating on the TNTs, which are in agreement with works reported in the literature [25,29,51,52].
Figure 4. Galvanostatic charge/discharge profiles of (a) as-prepared TNTs, (b) MoS$_2$-TNTs, and (c) Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs at 1C.

Figure 5a shows the discharge capacity vs. cycle number for as-prepared TNTs, MoS$_2$-TNTs, and Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs cycled at 1C. The first cycle delivers a discharge capacity of 652 µAh cm$^{-2}$, 1286 µAh cm$^{-2}$, and 729 µAh cm$^{-2}$ for the as-prepared TNTs, MoS$_2$-TNTs, and Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs, respectively. The higher capacity obtained for the decorated-TNT electrodes are attributed to the contribution of MoS$_2$ coating. The irreversible capacity observed after the first cycle is attributed to the side reactions of Li$^+$ with water molecule traces and the structural defects of the TNTs, and additionally, the dissolution of S and the formation of the SEI layer in the case of MoS$_2$-TNTs [6,53,54]. It is clearly apparent that the Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs have superior cyclability as-prepared TNTs and MoS$_2$-TNTs with a reversible capacity of 640 µAh cm$^{-2}$ obtained, whereas only 222 µAh cm$^{-2}$ and 220 µAh cm$^{-2}$ was retained after 100 cycles for the as-prepared TNTs and MoS$_2$-TNTs, respectively. It is remarkable that the areal capacities increase with the number of cycles. This is attributed to the formation of microcracks as the result of Li$^+$ reaction with MoS$_2$, which expose additional pore channels. In addition, the presence of Al$_2$O$_3$ decoration bestows the TNT electrodes with enhanced chemical properties. Figure 5b shows the coulombic efficiency (CE) at 1C for 100 cycles. The CE obtained for Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs at the first cycle was 62% and reached more than 99% just after three cycles. In comparison, as-prepared TNTs and MoS$_2$-TNTs have a first cycle CE of 64% and 74% and reaching the 98% only after 15 and 85 cycles, respectively. These values indicate relatively more stable SEI formation on the surface of the Al$_2$O$_3$-coated electrode even after long-term cycling. It is remarkable that the beneficial effect of the Al$_2$O$_3$ coating is also evidenced at very fast kinetics (3 C) over 200 cycles as shown in Figure 5c. Indeed, the Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNT electrode is able to maintain a capacity of 414 µAh cm$^{-2}$, whereas the as-prepared TNTs and MoS$_2$-TNTs retain only 130 µAh cm$^{-2}$ and 195 µAh cm$^{-2}$, respectively. The main electrochemical results of the as-prepared and ALD-decorated TNTs in comparison with literature are shown in Table 1.
Figure 5. Long-term cycling tests of as-prepared TNTs, MoS$_2$-TNTs, and Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs: (a) at 1C for 100 cycles, and (b) the corresponding coulombic efficiency vs. cycle number and (c) at 3C for 200 cycles.

Table 1. Comparison of the electrochemical performance of as-prepared and atomic layer deposition (ALD)-decorated TNTs with TNTs coated with various materials.

| Working Electrode | First Discharge Capacity (µAh cm$^{-2}$) at C-Rate | Discharge Capacity after (n) Cycle (µAh cm$^{-2}$) | Coulombic Efficiency (%) after (n) Cycles |
|-------------------|-----------------------------------------------|-----------------------------------------------|------------------------------------------|
| as-prepared TNTs  | 1C-652                                        | 222 (100)                                     | ~98% (100)                               |
|                   | 3C-952                                        | 130 (200)                                     | ~98% (200)                               |
| MoS$_2$-TNTs      | 1C-1286                                       | 220 (100)                                     | ~98% (100)                               |
|                   | 3C-1520                                       | 195 (200)                                     | ~98% (200)                               |
| Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs | 1C-729                                       | 640 (100)                                     | >99% (100)                               |
|                   | 3C-887                                        | 414 (200)                                     | >99% (200)                               |
| SnO$_2$@TNTs [55] | 2C-469.8                                      | 113 (50)                                      | >94% (50)                                |
| Co$_3$O$_4$@TNTs [56] | 1C-200                                      | 103 (25)                                      | NA                                       |
| TNTs@Fe$_2$O$_3$ [57] | 100 mA cm$^{-2}$-570                       | 680 (50)                                      | 100% (50)                                |

Post-mortem analysis was carried out to provide further evidence for the positive contribution of the Al$_2$O$_3$ decoration on the electrochemical properties. Figure 6a–c shows the SEM images of the as-prepared TNTs, MoS$_2$-TNTs, and Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs after 200 charge/discharge cycles at 3C, respectively. A very thick (ca. 6 µm) and rough SEI layer has been grown on MoS$_2$-TNTs (Figure 6b) in comparison to as-prepared TNTs that is around 2 µm thick (Figure 6a). Similar behavior was observed from our previous work on MoS$_2$-coated TNTs [6]. In contrary, the SEI formed on Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs is much thinner (ca. 1 µm) and smoother (Figure 6c) confirming the benefit of Al$_2$O$_3$ coatings. This effect is further evidenced by STEM-EDX elemental maps given in Figure 6d showing the homogenous distribution of Mo, S, and Al on the TNT walls after electrochemical tests (see Figure S1b for the EDX spectrum).
In this work, enhanced electrochemical performance of TNT was achieved by decorating the surface with nanosheets of MoS$_2$, sandwiched between Al$_2$O$_3$ coatings. ALD technique was used to homogenously deposit the MoS$_2$ nanosheets and the Al$_2$O$_3$ layers on the self-supporting TNT layers. The excellent capacity and stability of Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-decorated TNT is attributed to the mechanical and structural stability imported by Al$_2$O$_3$ decoration. The Al$_2$O$_3$ limits the formation and growth of SEI layer and loss of active material during cycling. As a result, the Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-decorated TNT deliver an areal capacity almost three times higher than that obtained for MoS$_2$-decorated TNT and as-prepared TNTs after 100 cycles at 1C.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-4991/10/5/953/s1. Calculation to determine the porosity of TNTs and Figure S1: EDX spectrum of Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs (a) before and (b) after 100 galvanostatic cycles.

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Figure 6. Cross sectional SEM images of (a) as-prepared TNTs, (b) MoS$_2$-TNTs, and (c) Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs after 200 cycles at 3C. Solid electrolyte interphase (SEI) layer thickness and surface roughness is indicated by a white line and red arrows. (d) High magnification STEM HAADF image and the STEM-EDX elemental maps showing the distribution of Mo, S, and Al on the surface of the TNT for Al$_2$O$_3$/MoS$_2$/Al$_2$O$_3$-TNTs.
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