ALD growth of MoS₂ nanosheets on TiO₂ nanotube supports

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ABSTRACT

Two-dimensional MoS₂ nanostructures are highly interesting and effective in a number of energy-related applications. In this work, the synthesis of ultra-thin MoS₂ nanosheets produced by the thermal Atomic Layer Deposition (ALD) process is reported for the first time using a previously unpublished set of precursors, namely bis(t-butylimido)bis(dimethylamino)molybdenum and hydrogen sulfide. These nanosheets are homogenously deposited within one-dimensional anodic TiO₂ nanotube layers that act as a high surface area conductive support for the MoS₂ nanosheets. The decoration of high aspect ratio TiO₂ nanotube layers with MoS₂ nanosheets over the entire nanotube layer thickness is shown for the first time. The homogeneous distribution of the MoS₂ nanosheets is proved by STEM/EDX. This resulting new composite is employed as anode for Li-ion microbatteries. The MoS₂-decorated TiO₂ nanotube layers show a superior performance compared to their counterparts without MoS₂. Compared to electrochemical performance of pristine TiO₂ nanotube, a more than 50% higher areal capacity and a coulombic efficiency of 98% are obtained on the MoS₂ decorated TiO₂ nanotube layers, demonstrating clear synergic benefits of the new composite structure.

1. Introduction

In the last 15 years, anodic self-organized TiO₂ nanotube (TNT) layers have attracted considerable interest motivated by their wide range of applications, such as solar cells, sensors or batteries [1-5]. The advantage of TNT layers compared to other nanostructures, e.g. nanoparticles or fibers, is their high self-ordering degree and the straight vertical alignment on the Ti substrate and in general a very high available surface area. Meanwhile, the anodic TNT layers can be produced with distinct dimensions, i.e. nanotube diameter and layer thickness, using well-established anodization protocols [1,3]. To improve their performance and increase the range of functionality for different applications TNT layers are often decorated [4], filled [5,6] or coated [7,8] with secondary materials. Such modifications can lead for instance to a shift of light absorption from UV to VIS light [7] or to an improved stability and performance in batteries [8]. These modifications can be carried out by a variety of different methods, such as electrodeposition [5,6], sputtering [9,10], chemical bath decoration [11,12], spincoating [13,14], vapor deposition [15], etc. However, all these methods suffer from inhomogeneous coating of high aspect ratio TNT layers. Recently, Atomic Layer Deposition (ALD) was introduced as a technique being able to uniformly coat even extremely high aspect ratio TNT layers with controllable coating composition and thickness [7,16-18].

MoS₂, a transition metal dichalcogenide (TMDC) featuring a two-dimensional covalently bonded triplet layered S-Mo-S structure (graphene-like) that is held together along the third dimension by weak van-der-Waals forces [19,20], is well-known as an electrocatalyst for hydrogen evolution reaction [21,22]. However, it is an interesting anode material for lithium ion microbatteries (μLIBs). The weak interlayer interaction of MoS₂ allows Li⁺ to intercalate between the layers without a significant volumetric expansion [23,24]. The first report on the Li⁺ intercalation into MoS₂ dates back to 1959 [25]. However, as the bulk MoS₂ does not offer exciting electrochemical properties for lithium storage, the application has not been very successful. In the recent years, huge attention has been focused on nanostructured MoS₂ [26]. The MoS₂ nanostructures, such as nanoflakes [27], nanosheets [28-34], nanobelts [35], or MoS₂ nano-composites [36,37], are mainly prepared via hydrothermal synthesis [28-30,32,34,35] and have to be mixed with a conducting agent and a binder to be fixed on a copper foil.
to be used as electrode for Li-ion batteries (LIBs). Alternatively, MoS2 nanosheets, grown via ALD on conductive substrates [38–47], can be used as binder free anodes in LIBs [38,39]. However, in these two reports [38,39] relatively thick ALD MoS2 layers were used, i.e. 40 nm and 70 nm, respectively, while some recent reports [29,31] show that already few-layered MoS2 nanosheets can show good performances in LIBs. Few-layered MoS2 nanosheets, with many active side edges (electrochemically active) [21,48–50], deposited on large surface area substrates, such as TNT layers, could, therefore, be excellent anodes in µLIBs.

Anodic TNT layers have been decorated and coated with MoS2 by different techniques, such as via photocalytic reduction of (NH4)2MoS4 into MoS2 nanoparticles [51], electrodeposition [52,53], hydrothermal routes [54,55], sputtering [10], or physical and chemical vapor deposition [15]. However, all these reports use either relatively thin, low aspect-ratio TNT layers, i.e. with thicknesses below 1 µm [15,51,53], or show incomplete coating of higher aspect ratio TNT layers [10,52,54,55]. Furthermore, the coated or decorated TNT layers were only employed for (photo-)catalysis [10,15,51–53,55] or for alcohol sensing [54]. Only one report can be found in the literature on the use of a TNT@carbon@MoS2 heterostructure in LIBs [56]. However, in this report several days were needed to produce the modified TNTs via a multi-step synthesis. Another disadvantage of this procedure is the fact that the obtained TNTs are not ordered and have to be deposited with a binder on a Cu foil.

In this paper, for the first time the homogenous decoration of high aspect-ratio anodic TNT layers with ultra-thin MoS2 nanosheets using ALD is reported. For this, a new combination of a non-halide Mo precursor (i.e. to avoid the use of MoCl5, which corrodes the ALD tool) and H2S, which can be used at low temperatures and has no detrimental effect on the TNT layers during the ALD process and on the ALD tool itself, was used. The homogenous decoration of the TNT layers over their entire thickness and available surface area is shown using STEM/EDX, and the composition of the MoS2 nanosheets is evaluated by XPS. It is also shown that the MoS2-decorated TNT layers are promising materials as negative electrodes for µLIBs. They show a superior electrochemical performance in comparison to their pristine counterparts. The state of art in the utilization of the TiO2-MoS2 nanostuctures for Li-ion batteries is significantly moved forward.

2. Material and methods

Self-organized TiO2 nanotube layers (TNTs) with a thickness of ~20 µm and a diameter of ~110 nm (yielding an aspect ratio of ~180) were produced by electrochemical anodization of thin Ti foils (Sigma-Aldrich, 127 µm thick, 99.7% purity) according to the previously published work [57]. In brief, prior to anodization the Ti foils were degreased by sonication in isopropanol and acetone and dried in air. The anodization was carried out at 60 V for 4 h in an ethylene glycol based electrolyte containing 170 mM NH4F and 1.5 vol% H2O. The electrochemical cell consisted of a high voltage potentiostat (PGU-200 V; Metrohm Autolab B.V., Nova 1.10 software) in a three-electrode set-up, with Ag/AgCl reference electrode, a Pt wire as counter electrode, and the TNT layers as working electrode.

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The electrochemical performance tests (cyclic voltammetry (CV) and 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 0.5 mV s−1. Galvanostatic tests were performed at 1C in the potential window of 0.01–3 V. C/n means the battery is fully charged or discharged up to its total storage capacity in n hours. In line with the literature on the Li-ion microbatteries [58,59], areal capacities were used, instead of the gravimetric capacities. The surface area of the both blank and MoS2-decorated TNT layers was considered as a macroscopic surface area (0.79 cm2) used for the microbattery with a diameter of the active area of 1 cm.

The structure and morphology of the pristine and MoS2-decorated TNTs were characterized by field-emission scanning electron microscopy (FE-SEM JEOL JSM 7500F) and a high-resolution transmission electron microscope (FEI Titan Themis 60–300, operated at 60 keV) equipped with a high angle annular dark field detector for scanning transmission electron microscopy (HAADF-STEM) and SUPER-X energy dispersive X-ray (EDX) spectrometer with 4 × 30 mm2 windowless silicon drift detectors. All the presented EDX maps are shown in atomic % calculated from measured intensities by k-factor method implemented in used software Velox 2.5. Cross section views were obtained from mechanical bended TNTs.

The X-ray diffraction (XRD) patterns were measured on Panalytical Empyrean diffractometer using a Cu X-ray tube and a scintillation detector Pixel3D. The measurement were performed in the 20 range of 5–65°, the step size was 0.026°. The diffractometer was equipped with a xyz programmable stage, which allows to adjust height and position of the sample.

The composition of MoS2 was monitored by X-ray photoelectron spectroscopy (XPS) (ESCA25R, Scienta-Omicron) using a monochromatic Al Kα (1486.7 eV) X-ray source. The binding energy scale was referenced to adventitious carbon (284.8 eV). The quantitative analysis was performed using the elemental sensitivity factors provided by the manufacturer.

3. Results and discussion

3.1. Characterization of ALD MoS2-decorated TNTs

Fig. 1a and b show SEM images of the as-prepared anodic TNT layers. Obviously, the TNTs are highly ordered, closed packed and possess an internal diameter of ~110 nm. The thickness of the TNT layers was ~20 µm, giving an aspect ratio of ~180. It was not possible to observe the MoS2 nanosheets on the MoS2-decorated TNTs, due to their extremely small thickness (heights), since only 2 MoS2 ALD cycles...
were used herein. Nevertheless, when a considerably larger number of ALD cycles was used, it was possible to visualize larger MoS2 nanosheets. Fig. 1c shows a representative SEM image of a reference Ti foil for which 225 ALD cycles of the MoS2 process were used. The nature of the ALD grown MoS2 nanosheets is clearly observed, which fits to the typical morphology of this material (and other TMDCs), produced by various techniques [50,60]. Due to the extremely small size of the MoS2 nanosheets, scanning transmission electron microscopy (STEM) along with energy dispersive X-ray spectroscopy (EDX) was used to characterize the nanosheets in more details. Fig. 2a shows the STEM/EDX elemental maps of the chemical distribution of Mo and S elements on fragments of two adjacent TiO2 nanotubes in the cross-sectional view. These maps reveal that MoS2 was deposited within the TNT walls after 2 ALD cycles. However, individual MoS2 nanosheets could not be revealed by atomic high resolution imaging in STEM or TEM mode due to too thick TNT walls. However, a detailed view on the EDX maps in Fig. 2a reveals a MoS2 decoration at the edges of the TNT walls. Given the number of ALD cycles used in this work (i.e. 2 cycles), the principle of the ALD growth and the layered nature of 2D materials (including MoS2 [50]), the individual MoS2 nanosheets consist of 1–2 MoS2 layers at maximum. Given also the nanoscale dimensions of the TNT wall - MoS2 nanosheet interface and the high magnification during the STEM imaging (to be judged from the scale bar), the nanosheets are very likely thinner than 1 nm. Based on the TMDCs literature evidence, MoS2 follows the Volmer-Weber growth mode, which can be attributed to a dominant atom-to-atom interaction. This was studied and discussed in detail for PbTe and PbSe [61]. Thus, during the initial ALD cycles an island growth was observed, while for higher cycle numbers a homogenous MoS2 film consisting of MoS2 nanosheets was found (see Fig. 1c for comparison with the MoS2 ALD 225 cycle case). This phenomenon can also be found in the literature for ALD MoS2 produced with other precursors [41,62].

Fig. 2b shows a high angle annular dark field (HAADF) STEM image of a fragment of a TNT in the planar view and corresponding EDX maps. These data reveal the presence of numerous Mo- and S-rich nanosheets on the TNT walls, with rather irregular shape and a width of about 10–15 nm. By detailed inspection of the decorated TNTs, a homogenous and uniform decoration of the TNT layers with MoS2 nanosheets was revealed over their entire volume. These results are in good accordance with the previous studies of coating or decoration of 20 µm long TNT layers with secondary materials using ALD [57,63,64].

To obtain additional information on the crystalline structure and composition of the MoS2 nanosheets, XRD and XPS analyses were carried out. Fig. 3 shows the XRD patterns of the TNT layer decorated with 2 MoS2 ALD cycles over the 2θ range from 10° to 65° and in the narrower 2θ range from 5° to 40°. The peaks of TiO2 in anatase phase from the TNT layer and the peaks for Ti from the underlying Ti substrate are identified. Noticeably, a peak at 2θ ~ 14.3° for MoS2 is visible [26622-ICSD]. Furthermore, several peaks, marked as MoxSy, can be observed at 2θ ~ 9.3°, 2θ ~ 10.3°, 2θ ~ 12.5° and 2θ ~ 13.8° stemming from MoxSy with different stoichiometric compositions. The average grain...
The size of the MoS₂ nanosheets was calculated to be 106 Å using the Scherrer equation.

Fig. 4a shows the XPS survey spectra of MoS₂-decorated reference Ti foils (annealed to anatase prior to the ALD decoration), measured in the as-deposited state, while Fig. 4b and c show the high resolution spectra for Mo 3s and S 2p. Because of the higher intensity of the signals of Mo and S as well as lower signals from the underlying Ti substrate, the XPS spectra of Ti foils coated with 60 MoS₂ ALD cycles are additionally shown for reference. For the Ti foils decorated with 2 MoS₂ ALD cycles, Ti and O signals can be observed in the survey scan that stem from the TiO₂ of the underlying annealed Ti foil. The MoS₂ film deposited with 60 ALD cycles is too thick to observe signals from the underlying substrate. The C species detected for both decoration thicknesses can be related to the handling of the samples in air following the ALD process. For the 60 ALD MoS₂ cycles, the high resolution spectra of Mo 3d show a doublet with the Mo 3d₅/₂ peak at 229.4 eV corresponding to the Mo⁴⁺ oxidation state and the spectra of S 2p show a doublet with the S 2p₃/₂ peak at 162.2 eV corresponding to the S²⁻ oxidation state. The S
to Mo ratio determined from respective spectral areas is 1.95 confirming that the deposited ALD film was MoS2 [38]. As can be seen in the high resolution spectrum of Mo 3d for the Ti foil decorated with 2 MoS2 ALD cycles, the doublet shape is wider than that of the sample coated with 60 MoS2 ALD cycles pointing to the presence of an extra Mo state at the MoS2 and TiO2 interface. The S/Mo ratio is found to decrease to 1.75 and might stem from a built up of some Mo-O bonds between the thin TiO2 thermal oxide layer present on the annealed Ti foil and the MoS2. When larger sheets of MoS2 were grown on the Ti foil (e.g. via 60 ALD cycles), the XPS spectrum of Mo 3d exhibits only one dominant doublet state showing pure MoS2.

3.2. Application of MoS2-decorated TNTs in μLIBs

Fig. 5a shows the cyclic voltammograms (CV, the first cycle) obtained for the pristine and the MoS2-decorated (2 ALD cycles) TNT layers. Well-defined cathodic (Li+ insertion) and anodic (Li+ extraction) peaks were recorded at 1.68 and 2.2 V vs Li/Li+, respectively. These peaks correspond to the reversible reaction of Li+ with anatase TiO2 according to Eq. (1) [58,65].

\[
\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2 \quad 0 \leq x \leq 0.5
\]

(1)

Compared to the CV curve of the pristine TNT layer, the MoS2-decorated TNT layer showed broader peaks and a larger surface area under the CV curve. This effect can be attributed to three main factors. Primarily, it is the result of the multistep reaction of Li+ with MoS2. In the cathodic scan, the insertion of Li+ into MoS2 to form LixMoS2 occurred in the voltage range of 1.25–1.75 V and further lithiation at 0.3 V led to the formation of Li2S and Mo according to Eqs. (2) and (3) [30,66,67]. In the reverse anodic scan, the extraction of Li+ occurred at 1.8 V and 2.3 V corresponding to the retrieve of LixMoS2 and the oxidation of Li2S to S.

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

(2)

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

(3)

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

(4)

Secondly, the MoS2-decorated TNT layers possess an increased intrinsic electronic conductivity compared to their blank TNT counterpart. This is clearly seen from the CV curves recorded in aqueous 1 M Na2SO4 electrolyte (Fig. S1), where the dark current densities in both, the anodic and cathodic, directions clearly show higher values for the MoS2-decorated TNT layers. Since the base materials - TNT layers - are the same, this increased conductivity must stem from the MoS2 nanosheet decoration. Thirdly, the MoS2 decoration of TNTs leads to their stabilization in terms of structure and surface chemistry. Previous works on various coatings, such as Al2O3, Ag, C, and Co3O4, on TNT layers have shown similar effects [8,68–71].

Fig. 5b shows the 1st and 100th galvanostatic charge–discharge profiles obtained at 1C rate for the pristine TNT layer and the MoS2-decorated TNT layer. The insertion/extraction voltage plateaus were consistent with the redox peaks observed in the CV curves. The first discharge areal capacities for the pristine TNT layer and the MoS2-decorated TNT layer were attained 0.4 mAh cm⁻² and 0.67 mAh cm⁻², respectively. At the 100th cycle, the areal capacities were equal to 0.22 mAh cm⁻² for the pristine TNT layer and 0.44 mAh cm⁻² for the MoS2-decorated TNT layer. Clearly, a superior capacity was obtained for the MoS2-coated TNT layer compared to the pristine counterpart. This improvement can be attributed to the additional contribution of ultra-thin MoS2 nanosheets deposited onto a nanotubular support showing a very large surface area. Fig. 5c shows the cycle life performance at 1C for 100 cycles and the corresponding Coulombic efficiencies. The capacity loss observed during cycling occurs probably due to several reasons: the irreversible reaction of Li+ with trace water molecules, the Li⁺ trapping within the structural defects of TiO2, the dissolution of S, and the formation of a passive layer due to the electrolyte decomposi-

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MoS2 nanosheets, using only 2 MoS2 ALD cycles. It must be noted that 1 MoS2 ALD cycles did not lead to a capacity improvement, while higher ALD cycles led to a significant capacity increase upon galvanostatic cycling, however, with a low long-term cycle stability performance. It is, thus, a challenge for future work to optimize the MoS2 coating thickness and the stability, but the positive prospects are very high.

The Coulombic efficiency (CE) for the MoS2-decorated TNT layer at the first cycle was 96% and reached more than 98% starting from the second cycle. In comparison, the CE of the pristine TNT layer was 92% and reached 98% after fifteen cycles. The superior CE performance for the coated sample can be attributed to the enhanced electrical conductivity as the result of the MoS2 coating.

Post-cycling SEM analysis of the pristine and the MoS2-decorated TNT layers are shown in Fig. S2a and b. As one can see, the nanotubular structure is preserved on both samples after 100 cycles Li insertion/extraction at 1C rate. A thin SEI formation can be observed on the top of the TNT and a somewhat thicker SEI formation was seen in case of the MoS2-decorated TNT layer. It is known from the literature that the SEI layer built on TiO2 itself during Li insertion/extraction is very thin [73]. Therefore, a thicker SEI layer can be expected on MoS2-decorated TNT layers. Fig. S2c shows the post-cycling XRD patterns for both types of TNT layers. In accordance with the reactions discussed above, Li2MoS2 and Li2S were observed for the MoS2-decorated TNT layer. In addition, Ti[,s]O2 with different stoichiometric composition was observed for the pristine TNT layer. MoS2 was present in the lithiated form. A Ragone plot is shown in Fig. S3, comparing the performance of the electrodes used herein (pristine and MoS2-decorated TNT layers) at 1C with published microbatteries having 3D electrodes. It is clearly shown that the electrochemical performance obtained by MoS2-decorated TNTs is superior compared to the cells with other 3D electrodes.

4. Conclusions

In conclusion, for the first time the homogenous decoration of high aspect ratio TNT layers with a large density of ultra-thin MoS2 nanosheets using ALD was shown and a new precursor combination for that the electrochemical performance obtained by MoS2-decorated TNT layers are shown and a new precursor combination for ALD Al2O3-coated TiO2 nanotube layers as anodes for lithium-ion batteries, ACS Omega 2 (2017) 27–49, https://doi.org/10.1021/acs.omega.6b00463.


