Reviewer 1

We thank the reviewer for the consistent comments. The quality of the paper has been improved and we hope that now, it can be accepted.

Summary and general comment:

TiO2 nanotube layers (TNTs) decorated with Al2O3/MoS2/Al2O3 is investigated as an anode. The anode materials give a stable discharge capacity of 414 μAh cm-2 after 200 cycles at a fast 3C rate. Please either provide the electrochemical and cell performances done by real Li-ion Microbatteries or remove the misleading term "Li-ion Microbatteries" for the manuscript. A few comments below are listed for the authors as a reference.

Additional Comments:

1. Please provide the corresponding EDX spectra that is collected together when the STEM-EDX elemental maps are analyzed.
   Response
   The text has been corrected accordingly.

   P3, line 133: Figure 1 shows a high angle annular dark field (HAADF) STEM image of the edge of TNT decorated with 9 cycles Al_2O_3 – 15 cycles MoS_2 – 9 cycles Al_2O_3 and the corresponding EDX maps (see Figure S1a for the EDX spectrum).
   P8, line 264: 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).

   Supplementary Materials, Figure S1 shows the EDX spectrum of $Al_2O_3/MoS_2/Al_2O_3$-TNTs before and after 100 cycles at 1C. The presence of Mo, Al, S, Ti, and O peaks confirms the $Al_2O_3/MoS_2/Al_2O_3$ surface coating and the underlying self-supporting TNTs. The additional C and Cu peaks are attributed to the membrane and the TEM sample grid. Fe, Co, and Zr peaks are from the TEM column and Si is ascribed to the SDD EDX detectors.

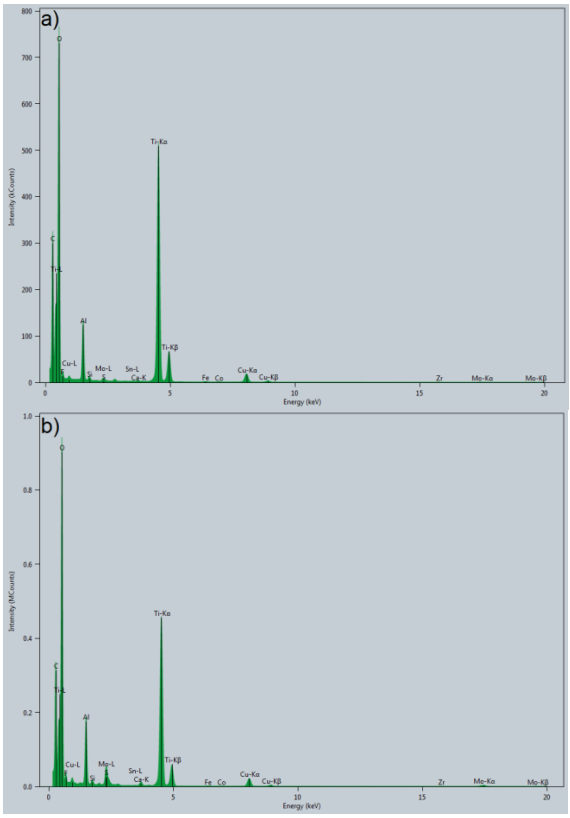


Figure S1. EDX spectrum of $Al_2O_3/MoS_2/Al_2O_3$-TNTs (a) before and (b) after 100 galvanostatic cycles.

2. In the high resolution XPS spectra, it is suggested to add the integration area of the signal peak.
Response:
The XPS discussion and Figure 2 has been modified accordingly.

P 4, line 150: The C species detected on both TNT layers are related to adventitious carbon. Figure 2b shows the corresponding Mo 3d high resolution (HR) spectra 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_2O_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_2O_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), 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 MoS2 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-} (sulphate) [46], possibly due to the interaction of sulphur with the water used in Al_2O_3 synthesis.

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41. Ganta, D.; Sinha, S.; Haasch, R.T. 2-D material molybdenum disulfide analyzed by XPS. *Surf. Sci. Spectra* **2014**, *21*, 19-27.
42. Benoist, L.; Gonbeau, D.; Pfister-Guillouzo, G.; Schmidt, E.; Meunier, G.; Levasseur, A. XPS analysis of lithium intercalation in thin films of molybdenum oxysulphides. *Surf Interface Anal* **1994**, *22*, 206-210.
43. Hopfengärtner, G.; Borgmann, D.; Rademacher, I.; Wedler, G.; Hums, E.; Spitznagel, G. XPS studies of oxidic model catalysts: Internal standards and oxidation numbers. *J Electron Spectros Relat Phenomena* **1993**, *63*, 91-116.
44. Patterson, T.A.; Carver, J.C.; Leyden, D.E.; Hercules, D.M. A surface study of cobalt-molybdena-alumina catalysts using x-ray photoelectron spectroscopy. *J. Phys. Chem.* **1976**, *80*, 1700-1708, doi:10.1021/j100556a011.
45. Alstrup, I.; Chorkendorff, I.; Candia, R.; Clausen, B.S.; Topsøe, H. A combined X-Ray photoelectron and Mössbauer emission spectroscopy study of the state of cobalt in sulfided, supported, and unsupported Co Mo catalysts. *J. Catal.* **1982**, *77*, 397-409.
46. Moulder, J.F.; Stickle, W.F.; Sobol, P.E.; Bomben, K.D. *Handbook of X-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data*; Physical Electronics: MN, 1995.

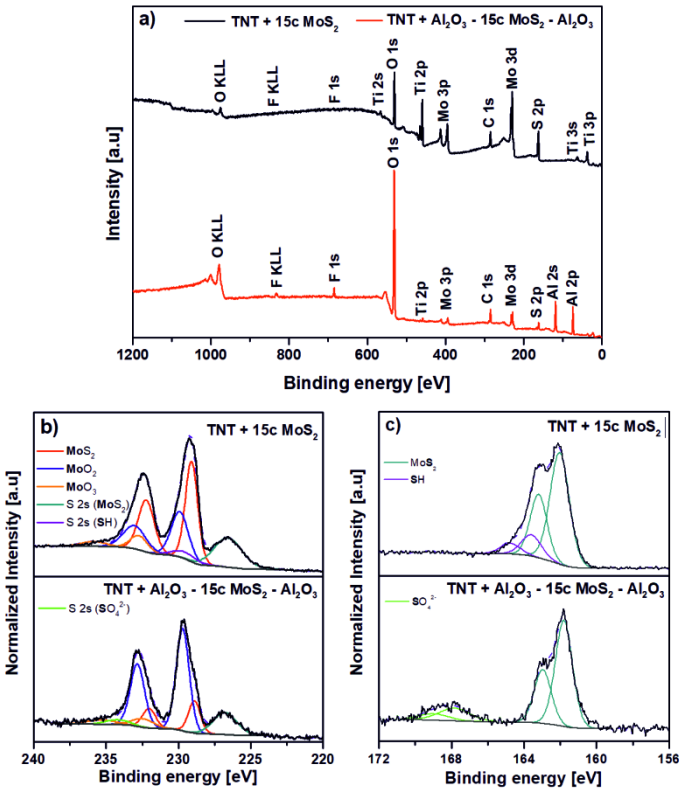


Figure 2. (**a**) XPS survey spectra, (**b**) Mo 3d high resolution spectra and (**c**) S 2p high resolution spectra for TNT layers decorated with 15 cycles MoS_2 and with 9 cycles Al_2O_3 – 15 cycles MoS_2 – 9 cycles Al_2O_3.

3. Why the coulombic efficiency is low and unstable? Please propose any improvements to address this drawback.
   Response:
   The reviewer is right; the first coulombic efficiency values were low for as-prepared and coated TNTs samples. However, as shown in our paper significant electrochemical improvement was obtained for the TNTs samples protected by Al2O3 coating sandwiching the MoS2 nanosheets with cycling.

   A stable and high CE (99%) obtained for the Al2O3/MoS2/Al2O3-TNTs cycled at 1C only after 3 cycles. In comparison, TNT and MoS2-TNT takes them 15 cycles and 85 cycles to reach 98%, respectively.

4. Why TNT and MoS2-TNT show increasing Coulombic efficiency? Why Al2O3/MoS2/Al2O3-TNTs show a decreasing Coulombic efficiency?
   Response:
   Please, refer response 3.

5. The anode performance is conducted by a half cell. Please provide the dimensions of the lithium foil. For an anode, using a thickness, or a heavy lithium, would give an estimated performance.
   Response:
   The text has been modified.
   P3, line 112: The half-cells consist of as-prepared TNTs, MoS_2-TNTs, or $Al_2O_3/MoS_2/Al_2O_3$-TNTs as the working electrode and Li foil (1mm in thickness and 9 mm in diameter) as the reference electrode.

6. What is the amount of liquid electrolyte used?
   Response
   The text has been modified.
   P3, line 114: The two electrodes were separated by a Whatman glass microfiber soaked in organic liquid electrolyte solution (0.35 mL) composed of 1M $LiPF_6$ dissolved in a 1:1 vol.% mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) .

7. The electrochemical and cell performances are analyzed by a two-electrode swagelok cell. Please provide the electrochemical and cell performances done by real Li-ion Microbatteries or remove the misleading term “Li-ion Microbatteries” for the manuscript.
   Response:
   The term is consistent as our materials (thicknesses = 20 µm) were investigated as a potential negative electrode for Li-ion microbatteries.

8. Please provide the specific capacity based on mAh/g of anode material.
   Response:

Areal capacity is used to characterize the electrochemical performance because the gravimetric capacity is not consistent regarding the extremely low amount of active materials and the desired application.