SUPPORTING INFORMATION

Layered Titanium Disilicide Stabilized by Oxide Coating for Highly Reversible Lithium Insertion and Extraction

Sa Zhou, Zachary I. Simpson, Xiaogang Yang, and Dunwei Wang

Department of Chemistry, Merkert Chemistry Center, Boston College, 2609 Beacon St., Chestnut Hill, Massachusetts 02467

1. Comparison of cycling performances of $TiSi_2$ with and without SiO_2 overlayer.

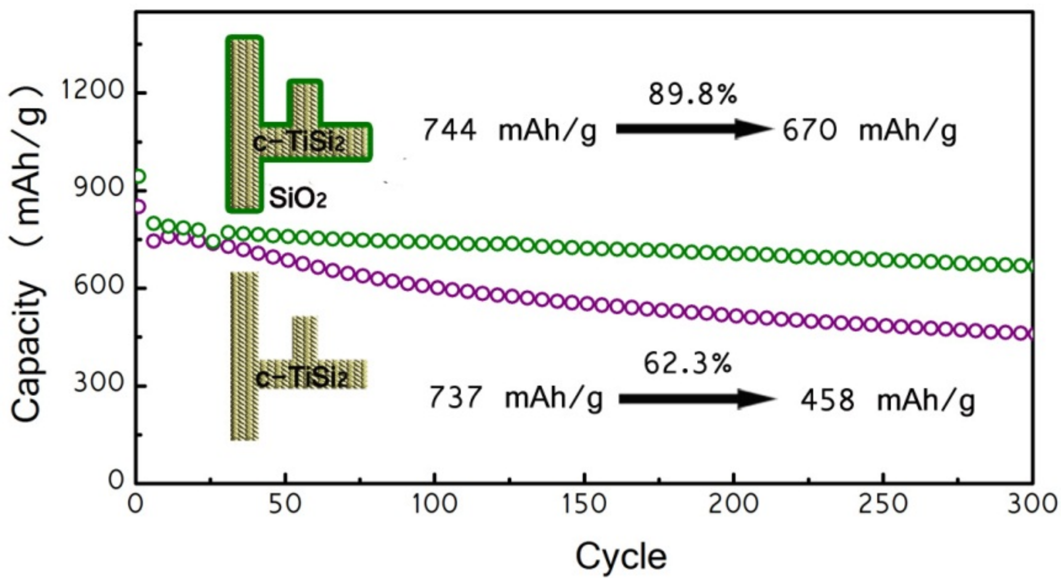

Figure S1. Cycling performance of $TiSi_2$ nanonets with (green) and without (purple) SiO_2. From the 26th to 300th cycles, SiO_2-coated nets maintained 89.8% of their capacity, while those without oxide only retained 62.3%. The result indicates the importance of the oxide overlayer for long cycling stability.

2. **Cycling performance of $TiSi_2$ nanonets with 1nm Al_2O_3.**

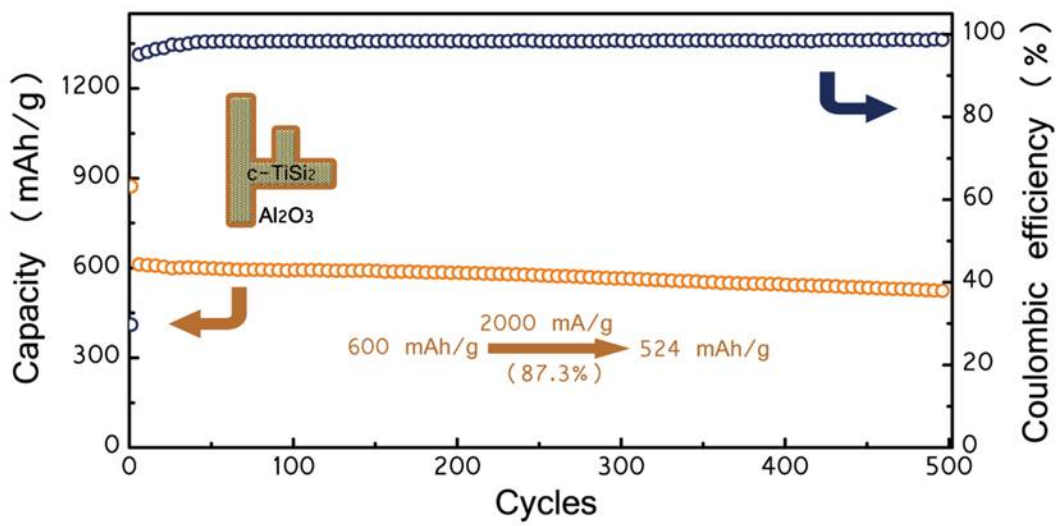

Figure S2. Cycling stability of $TiSi_2$ nanonets with a 1 nm Al_2O_3 coating. Over 500 cycles the capacity maintains 87.3% of the initial value, with a coulombic efficiency close to 99%. Compared with a SiO_2 coated anode, the capacity of Al_2O_3-coated $TiSi_2$ is slightly lower. We suggest that ALD-grown Al_2O_3 may be less permeable to Li^+ than thermally formed SiO_2.

3. **Electrochemical Impedance Spectroscopy (EIS) measurement.**

The Nyquist plot of a fully lithiated sample is shown in Figure S1, along with a fitting curve generated by the displayed equivalent electric circuit (EEC). The Nyquist plot comprises a semi-circle and an inclined line; these components contain the information pertaining to the charge transfer and Li^+ diffusion in the electrode. Two R//Q elements, R_c//Q_c and R_d//Q_d, were employed to simulate these processes, resulting a fitting error of 4.65×10^{-4} (χ^2 value between experimental and simulated data). From the fitting result, we obtained the R_c value as 101 Ω. The Q_c information is as follows: CPE = 8.158×10^{-5} Ω^{-1} s^n ; n = 0.6335.

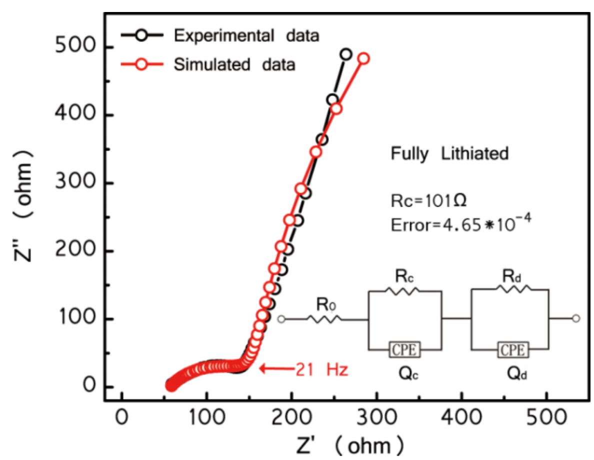

Figure S3. Nyquist plot of $TiSi_2$ with SiO_2 at 0.01 V. The experimental data are shown in black and simulated data are obtained by fitting the experimental data with the inset equivalent electric circuit (EEC).[1]

4. **Morphology of $TiSi_2$/ SiO_2 after 100 cycles.**

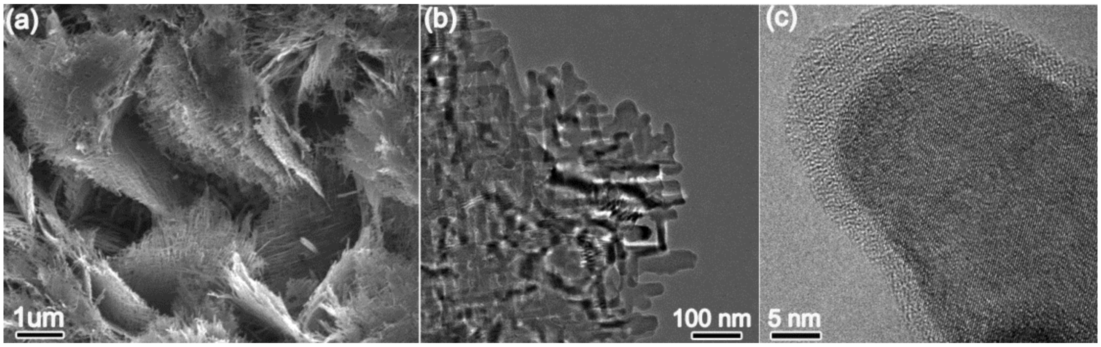

Figure S4. Electron micrographs of $TiSi_2/SiO_2$ after 100 cycles of lithiation/delithiation. (a) A SEM image displaying the densely packed nanonets on the substrate. (b) A low magnification TEM image confirming the well preserved nanonet morphology. (c) A high resolution TEM image shows the crystalline nature of the nanonets after 100 cycles.

5. **TEM of fully lithiated $TiSi_2$.**

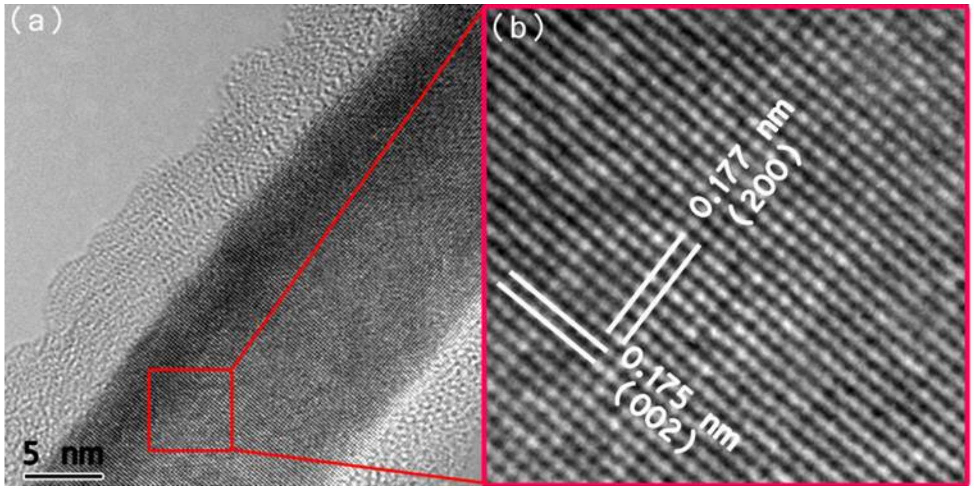

Figure S5. TEM images of fully lithiated $TiSi_2$ nanonets (0.01V). The enlarged image indicates the lattice of $TiSi_2$ along [002] and [200] directions does not exhibit obvious expansion upon full lithiation.

6. **SEM images of as-grown and lithiated $TiSi_2/SiO_2$ nanonets.**

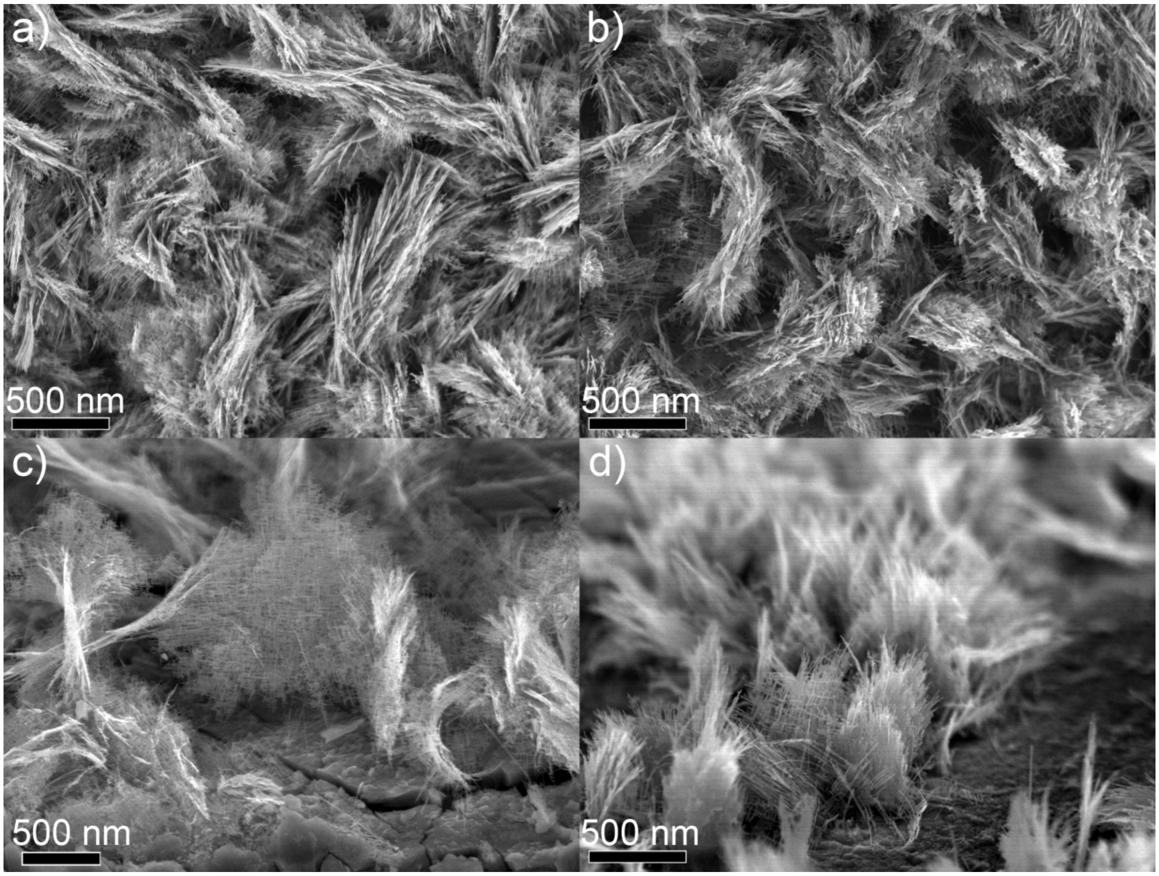

Figure S6. SEM images from the top (a,b) and side (c,d) of $TiSi_2/SiO_2$ nanonets before lithiation (a,c) and after complete lithiation (b,d). The lithiated nets were cycled twice and then fully lithiated within a potential window of 1.0 – 0.10 V.

7. **Oxide coating thickness uniformity.**

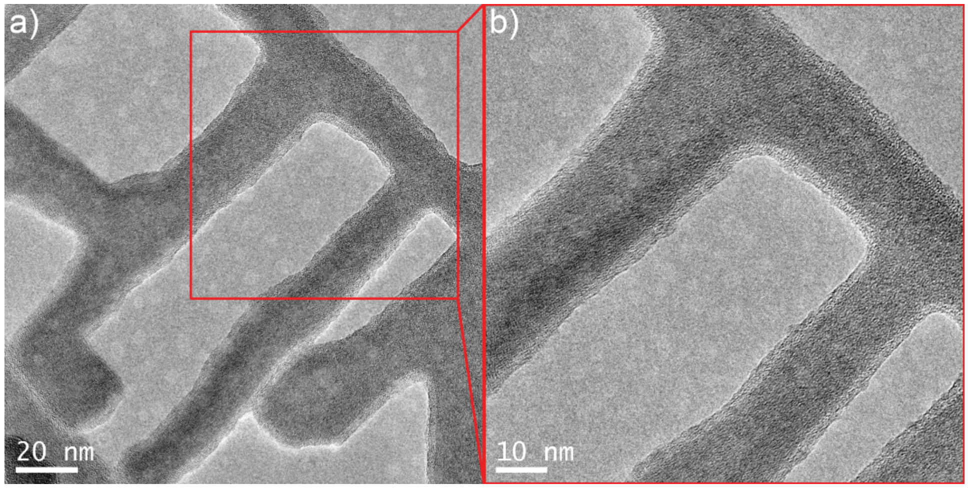

Figure S7. a) TEM image of a section of a $TiSi_2$ nanonet demonstrating the uniformity of the SiO_2 coating b) a higher magnification image of the same section for more detail is presented here. Because the coating was not formed due to a post-growth deposition, but rather formed by the oxidation of the nanostructure, the uniformity of the coating is good.

8. **Method for the determination of the quantity of nanonets on a sample.**

To measure the amount of active material deposited on a sample, a small piece of the substrate containing the active material was weighed 9 times using a Sartorius CPA2P microbalance. The average mass was calculated; after obtaining the average mass, the active material was removed. After removing the active material, the bare substrate was weighed 9 times, and the mass was averaged. The mass of the bare substrate was subtracted from that of the substrate and active material. The area of the sample was also measured using a pair of digital callipers. With the area and mass, the areal density was calculated. The average areal density of the samples was approximately 100 μg cm^{-2}, and the average active material mass was 20 μg.

9. **High-resolution TEM image of the $TiSi_2/SiO_2$ interface.**

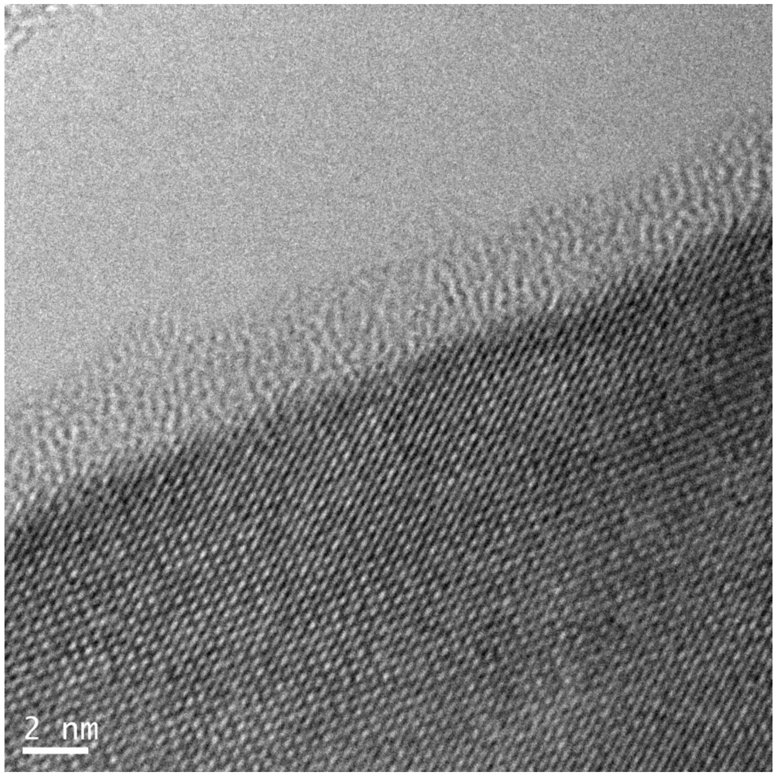

Figure S8. A high-resolution TEM image depicting the interface between the $TiSi_2$ nanonet and the SiO_2 coating.

References

1. Ruffo, R.; Hong, S. S.; Chan, C. K.; Huggins, R. A.; Cui, Y., Impedance Analysis of Silicon Nanowire Lithium Ion Battery Anodes, *J. Phys. Chem. C* **2009,** *113*, 11390-11398.