Electronic Supplementary Information

Enhanced lithium storage capacity and cyclic performance of nanostructured TiO$_2$-MoO$_3$ hybrid electrode

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Experimental details for X-ray absorption spectroscopy

The in situ X-ray absorption spectroscopy (XAS) experiments at the Mo K-edge were performed with the X-ray absorption fine structure (XAFS) facility installed at beamlines 7C in the Pohang Accelerator Laboratory, Korea. All the samples were ground to fine powder, and then, a pouch-type cell for charge/discharge was constructed, in which the nanohybrid electrodes were made by intimately mixing 70% (by weight) active nanohybrid material, 25% Ketjenblack, and 5% poly(tetrafluoroethylene). After assembled with Li foil, a separator, and a ~ 40 μm thick TiO$_2$-MoO$_3$ electrode, the cell was vacuum sealed with an aluminium pouch. The X-ray photon flux was enough to transmit through the electrochemical cell without any chemical interaction.

The in situ XAS data were collected at room temperature in a transmission mode. All the present spectra were calibrated by measuring the spectra of Mo metal foil simultaneously with those of the samples. A Si(111) double crystal monochromator was employed to monochromatize the X-ray photon energy. A step size was 0.2 eV in the XANES region in order to accurately collect the XANES spectra. Data analysis were carried out by the standard procedure as reported previously.$^{1,2}$

References

Figure S1. N$_2$ adsorption-desorption isotherms for (a) the restacked MoO$_3$ and (b) TiO$_2$-pillared MoO$_3$.

After the intercalation of TiO$_2$ into the interlayer spaces of MoO$_3$, the specific surface area was remarkably enhanced from 10 to 210 m$^2$/g. Furthermore, the nanohybrid shows the adsorption of much large amount of nitrogen, suggesting that the pillaring reaction is very effective in enhancing the porosity of TiO$_2$-MoO$_3$. 
**Figure S2.** Charge-discharge curves of TiO$_2$ nanoparticle.

$\text{TiO}_2$ nanoparticle shows a reversible capacity of ~180 mAh/g, suggesting that TiO$_2$ nanoparticles could be used as spacers and/or pillars in electrode materials.
Figure S3. Fourier transforms of in situ Mo K-edge extended X-ray absorption fine structure (EXAFS) spectra for TiO$_2$-pillared MoO$_3$ during discharge/charge reaction.

Two FT peaks below 2 Å (non-phase-shift-corrected) can be indexed to Mo–O bonds ranged from 1.67 to 2.34 Å. The FT peaks from 3 to 4 Å are due to the Mo–Mo neighboring atoms. Before discharge (before lithium intercalation), the local structure of MoO$_3$ in hybrid material can be indexed as $\alpha$-MoO$_3$, revealing the lattice frameworks of $\alpha$-MoO$_3$ in TiO$_2$-pillared MoO$_3$ are maintained upon reassembling reaction. As the amount of the intercalated lithium ions increases, Two FT peaks below 2 Å are merged into one FT peak, showing the reduction of MoO$_3$. However, after the full charge (lithium extraction), $\alpha$-MoO$_3$ framework in TiO$_2$-pillared MoO$_3$ restores well, highlighting the reversible lithium intercalation reaction.
Figure S4. Cross-sectional TEM image for the exfoliated MoO$_3$ nanosheets.

As seen in the Figure S4, very thin layers can be attributed to the exfoliated MoO$_3$, clearly showing the nanosheet structure.
Figure S5. FE-SEM image for (a) the pristine MoO$_3$, (b) Li$_{0.4}$MoO$_3$ and (c) the exfoliated and restacked MoO$_3$.

As seen in the figure, the pristine MoO$_3$ has very clean and smooth surface, and the size of the pristine MoO$_3$ is in the range of few micrometers. After the intercalation of lithium ions, the size of crystallite is somewhat smaller, but still in the micrometer range. The edge of the Li$_{0.4}$MoO$_3$ is relatively rough due to the intercalation of lithium ions. After the exfoliation and the restacking, the overall size of crystallite becomes smaller due to the elastic deformation. The layered morphology is still maintained even after exfoliation and restacking reaction.