Electronic Supplementary Information for

$MnWO_4$ Nanoparticles as Advanced Anode for Lithium-ion Batteries: F-Doped Enhanced Lithiation/Delithiation Reversibility and Li-Storage Properties

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Experimental section

Synthesis of $MnWO_4$ nano-particles

0.001 mol $MnCl_2$ was added into 15 mL water after 0.001 mol Na_2WO_4 dissolved completely. Then above solution was titrated from pH 9.0 and transfered to an autoclave, which was sealed and heated at 180 ^oC for 12 h, and the mixture was allowed to cool naturally. The dark brown precipitate was collected and rinsed thoroughly with distilled water for 3 times and ethanol and then dried at 60 ^oC in a vacuum oven for 24h. Then the bare $MnWO_4$ is obtained.

Synthesis of F-doped $MnWO_4$ nano-particles

0.05 mol% NH_4F is added into 15ml water with 1g bare $MnWO_4$ dispersed forming solution A. Then the A solution is stirred for 30 min and transfered to an autoclave which was sealed and heated at 180 ^oC for 24 h. The light brown precipitate was collected and rinsed thoroughly with distilled water for 3 times and ethanol and then dried at 60 ^oC in a vacuum oven for 24h. Then the F-doped $MnWO_4$ nano-particles are obtained.

Characterization

The morphology of the prepared simples were characterized by SEM (JEOL 6701F) and TEM (Tecnai F20) with an accelerating voltage of 200 kV. EDX-STEM-mapping was also carried out with the Tecnai F20 TEM. The phase and the crystallographic structure of the simples were characterized by powder X-ray diffraction (XRD) using a Regaku D/Max-2500 diffactometer equipped with a Cu Kα1 radiation (λ = 1.54056 Å). XPS measurement was carried out with a ESCALAB 250Xi spectrometer, with

the non-monochromatised Al Kα X-radiation (hν = 1486.6 eV) and a power of 150 W (10mA×15 kV). Galvanostatic charge/discharge measurements were carried out on an Arbin BT2000 system at different current rates between voltage limits of 0.05 to 3 V under room temperature. Cyclic voltammetry (CV) was carried out using an Autolab PG302N at a scan rate of 0.1 mV s^{-1} in the potential range of 0.05-3 V(vs. Li^+/Li), whereas EIS was performed in the frequency range of 10 mHz-100 kHz at an amplitude of 10 mV. For preparing the working electrode, a mixture of Sn-MOF, super-P (SP), and poly(vinyl difluoride) (PVDF,Aldrich) at a weight ratio of 70:10:20 was pasted on a pure Cu foil (99.6%, Goodfellow). The electrochemical performance was evaluated using Swagelok-type cells with a Li metalic anode and LBC3401A4 (Capchem) electrolyte solution. The cells were assembled in an argon-filled glove box with the concentrations of moisture and oxygen below 0.1 ppm. Both working and counter electrodes were electronically separated by a Whatman GF/D borosilicate glass-fiber sheet. All of the weight values were obtained with a high-precision electronic balance (Sartorius AG, BT 25S).To get insight view of the mechanism during electrochemical reaction, the Swagelok-type cells in which active electrode materials at different charge/discharge states were disassembled in the glovebox and the electrode active materials were washed by EC/PC (1:1 v/v) five times to remove the residual electrolyte. After evacuating the EC/PC, the electrode plates were transferred to some special designed devices for *ex situ* XRD characterizations. The electrode plates were sealed in argon to avoid exposing to air during XRD measurement; a vacuum transfer sample stage was applied for *ex situ* XRD analysis.

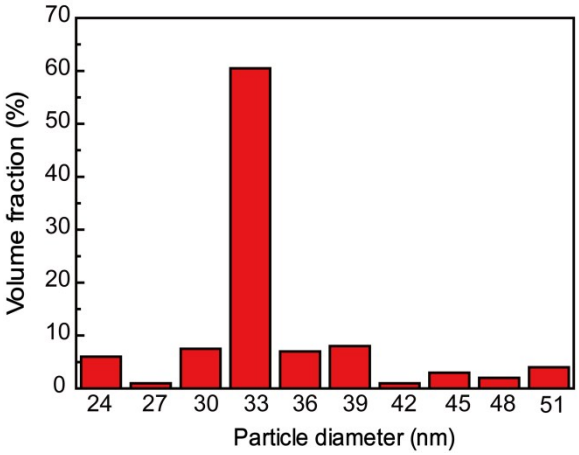

Figure S1. The transverse dimension of the as-prepared F-doped nano-$MnWO_4$

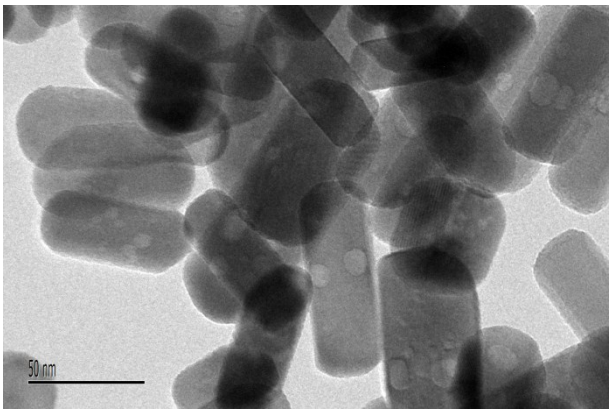

Figure S2. The TEM of the undoped $MnWO_4$

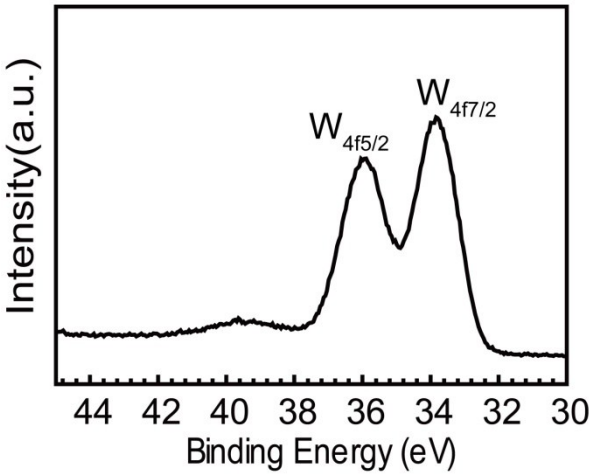

Figure S3. The high-resolution XPS spectrum of the element W in the F-doped nano-$MnWO_4$

XPS tests show the elemental valence of W in the F-doped nano-$MnWO_4$. The tungsten spectrum reveals a $W4f_{5/2}$ 36.2 eV and $W4f_{7/2}$ doublet, where the latter peak is at 34.5 eV. This is a special value for the tungsten compounds in which the tungsten oxidation state is lower than 6+ (standard example being WO_3 with $W4f_{5/2}$ 37.9eV and $W4f_{7/2}$ 35.7 eV) and higher than 4+ (standard example being WS_2 with $W4f_{5/2}$ 35.0eV and $W4f_{7/2}$ 33.2 eV). The observed binding energies of $W4f_{5/2}$ and $W4f_{7/2}$ indicate that the W^{6+} is partially reduced by F-dopping.

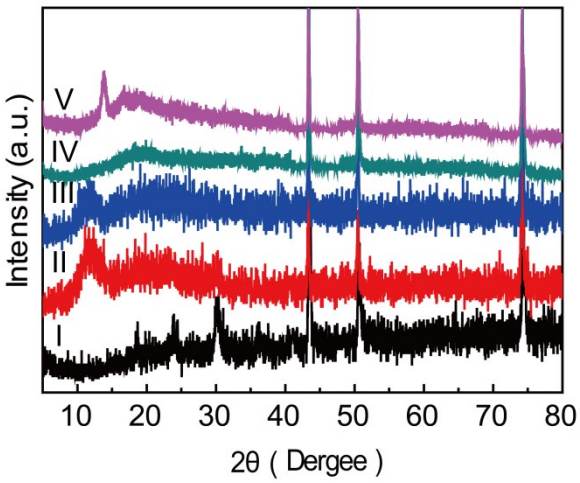

Figure S4.The ex situ XRD patterns of the F-doped nano-$MnWO_4$ electrode with different charged-discharged states at the 5th cycle. I the as-prepared electrode; II the electrode discharged to 0.6V; III the electrode discharged to 0.05V; IV the electrode charged to 0.6V;V the electrode charged to 3V

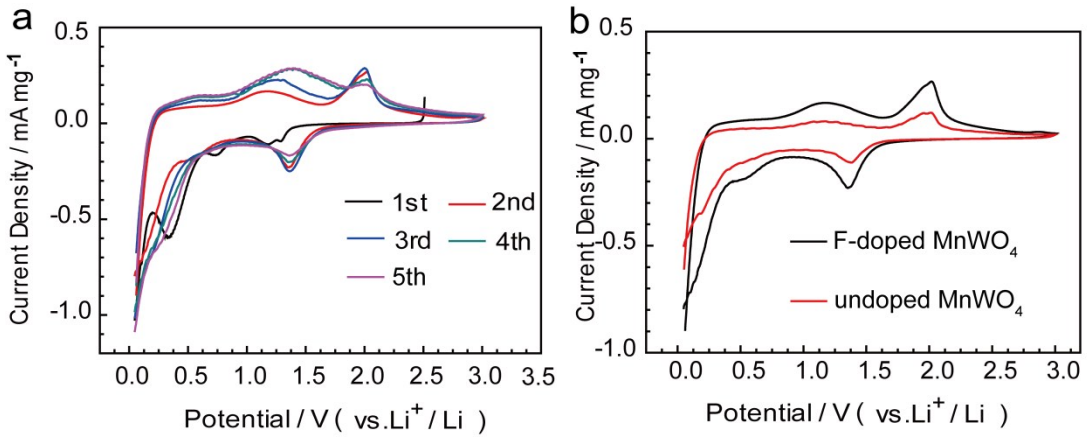

Figure S5 (a) The Cyclic voltammograms (CVs) of the F-doped nano-$MnWO_4$ electrode in Li ion battery at a scan rate of 0.1 mV S^{-1} in the voltage range of 0.01–3.0 V versus Li/Li^+ (b) the cyclic voltammetry (CV) curves in the second cycle of the $MnWO_4$ electrode

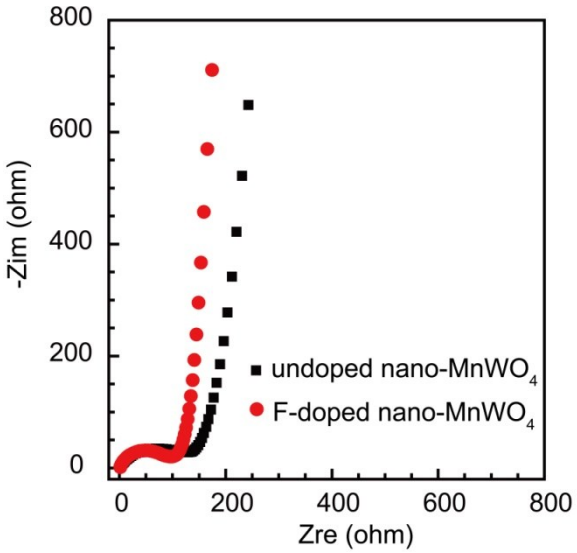

Figure S6. The typical Nyquist plots of the F-doped and undoped $MnWO_4$

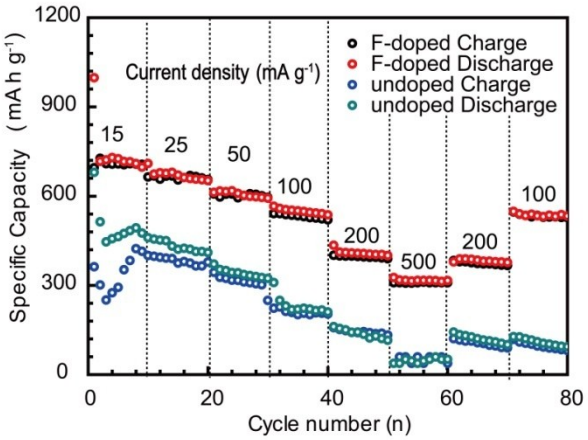

Figure S7. The rate capability of the cell using F-doped and undoped nano-$MnWO_4$ electrodes