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Controlled Construction of 3D Hierarchical Manganese Fluoride Nanostructures via Oleylamine-assisted Solvothermal Route with High Performance for Rechargeable Lithium Ion Batteries

Kun Rui, Zhaoyin Wen,* Jun Jin and Xiao Huang

CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.

Email: zywen@mail.sic.ac.cn

Experimental

Material preparation

Reagents: 1-Decyl-3-methylimidazolium tetrafluoroborate ($C_{10}mimBF_4$, 99%) was purchased from Shanghai Cheng Jie Chemical Co. Ltd.. Manganese(II) nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$, 98%) was purchased from Alfa Aesar. Ethanol (C_2H_5OH, AR) was purchased from Sinopharm Chemical Reagent Co. Ltd.. Oleylamine ($C_{18}H_{37}N$, 70%) used in the synthesis process was obtained from Sigma-Aldrich Co. LLC..

Synthesis process: 3D Hierarchical dendritic MnF_2 nanostructures built from a bunch of radially oriented nanorods were prepared via a facile, one-step solvothermal method using $C_{10}mimBF_4$ ionic liquid as fluorine source and $Mn(NO_3)_2 \cdot 4H_2O$ as manganese source. Commercial oleylamine was used as the surfactant and structural-directing template. In a typical procedure, take sample M-3 for example, 0.3 g $Mn(NO_3)_2 \cdot 4H_2O$ and 1 mL $C_{10}mimBF_4$ was firstly dissolved in ethanol (30 mL) under stirring at room temperature to form a clear solution. Then, 3 mL oleylamine was added dropwise to the solution followed by vigorous stirring for 1 h. The mixture was further transferred to a Teflon-lined stainless-steel autoclave, sealed and heated to 120 ºC and maintained at this temperature for 12 h. The products were washed with acetone and ethanol and centrifuged at 10000 rpm five times to remove residual ionic liquid and other impurities, followed by subsequent drying under 65 ºC for 24h. For comparison, the control samples M-X were also prepared by varying the amount of oleylamine (X) under identical solvothermal conditions.

A similar synthesis process was conducted with $BmimBF_4$ as fluorine source. The products were denoted as M-X-B.

Material characterization

X-Ray diffraction (XRD, Rigaku Ultima IV, 40 KV/30 mA, Cu- K_{α} radiation) was used to characterize the phases of the as-prepared materials. The morphology of the as-prepared materials were investigated by a field-emission scanning electron microscopy (FESEM, Magellan 400, FEI) and transmission electron microscopy (TEM, H-800, Hitachi). High-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) measurements were also performed using a JEM-2100F transmission electron microscope. Electron diffraction spectroscopy (EDS, X-Max, Oxford) was taken to examine the elemental mapping of the products.

Electrochemical measurements

The electrochemical performance of MnF_2 nanorods as anode for rechargeable lithium batteries were examined in coin type cells with lithium foil as both counter and reference electrodes. The working electrodes were prepared by mixing fluorides, acetylene black and poly(vinyldifluoride) (PVDF) dissolved in n-methyl pyrrolidinone (NMP) with a weight ratio of 60:20:20, which were then pasted onto a copper foil substrate followed by drying in vacuum at 80 ºC for 24 h. The average mass loading of the active material

MnF_2 on each electrode was about 1.5 mg (ca. 1 mg/cm^2). Glass fiber (GF/A) from Whatman was employed as the separator. The electrolyte involves 1 M $LiPF_6$ in a nonaqueous mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1. The amount of electrolyte used in a coin-type (CR2025) half-cell was controlled to be ca. 200 µL using a pipette (TopPette 200 µL, DragonLab). The cells were assembled in an Ar-filled glove box with oxygen and water contents less than 1 ppm. Galvanostatic charge-discharge measurements of fluoride anodes vs Li/Li^+ were performed at room temperature under different rates (0.1 to 10 C) in a voltage range of 0.01-3.0 V on a LANDCT2001A battery test system. Cyclic voltammogram measurements were carried out at a constant scanning rate of 0.2 mV/s in the same voltage range of 0.01-3.0 V on an electrochemical workstation (CHI700C). For *ex situ* HRTEM and FESEM at different reactive potentials, the cycled electrode sheets were required to be removed from the disassembled batteries and washed with DME.

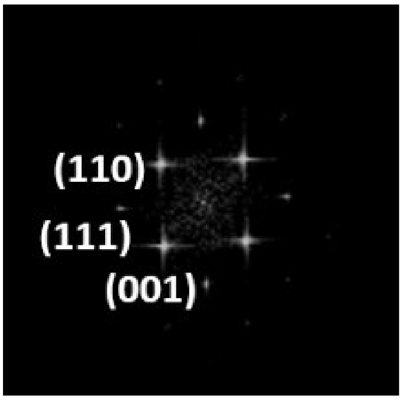

Fig. S1 FFT pattern of one individual nanorod of the as-prepared manganese-based fluoride M-3.0

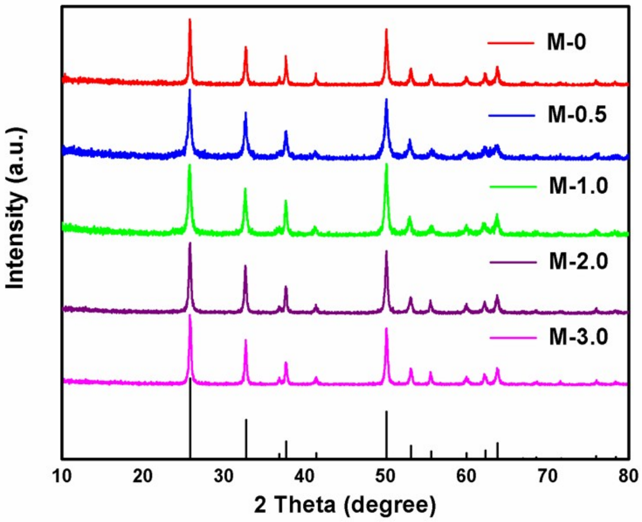

Fig. S2 XRD patterns of the as-prepared manganese-based fluoride by adjusting the amount of OAm added.

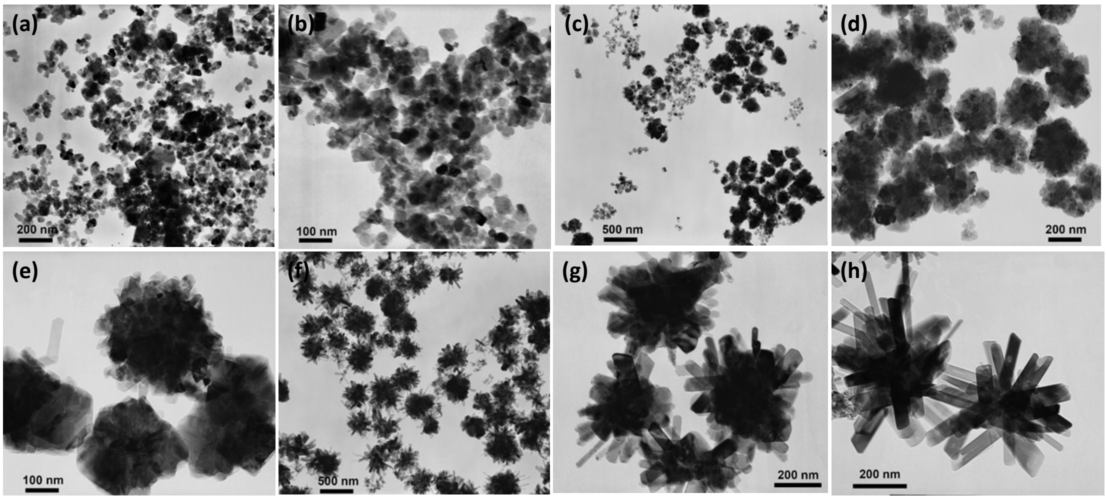

Fig. S3 TEM images of the as-prepared manganese-based fluoride by adjusting the amount of OAm added: M–0 (a–b); M–0.5 (c); M-1.0 (d-e); M-2.0 (f-g); M–3.0 (h);

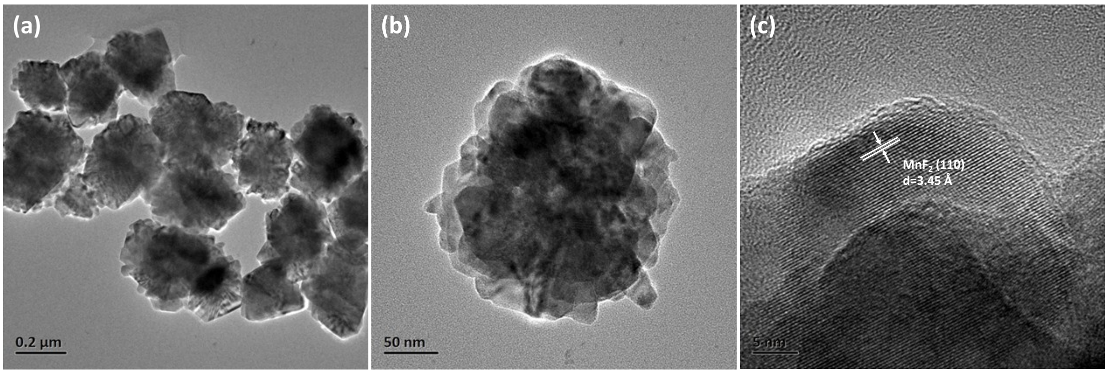

Fig. S4 (a and b) TEM and (c) HRTEM images of M-1.0.

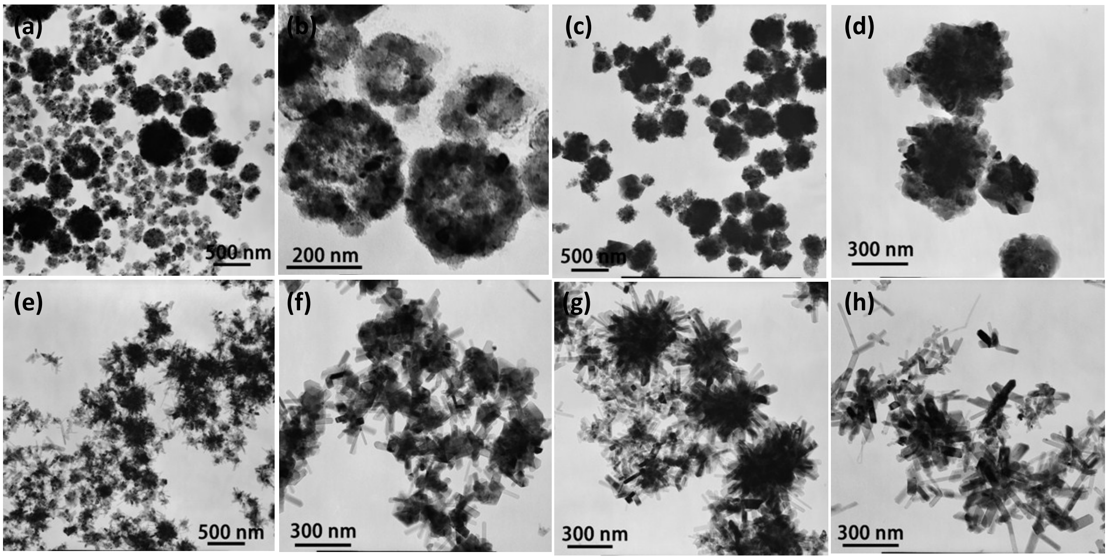

Fig. S5 TEM images of the as-prepared manganese-based fluoride with $BmimBF_4$ as fluorine source by adjusting the amount of OAm added: M–0.5-B (a-b); M-1.0-B (c-d); M-2.0-B (e-f); M–3.0-B (g-h);

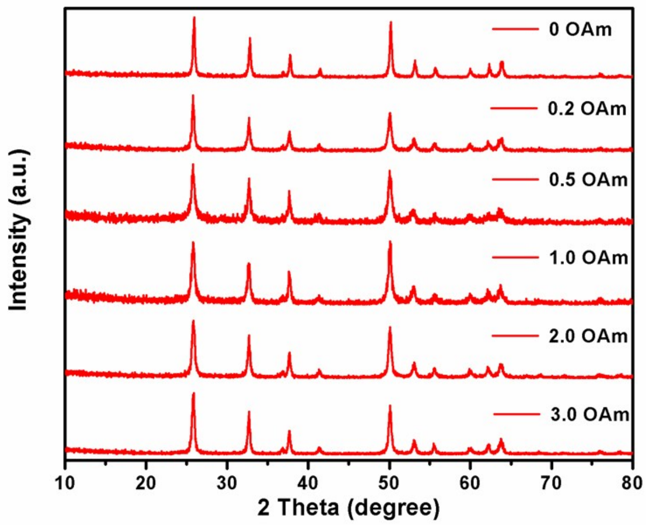

Fig. S6 XRD patterns of the as-prepared manganese-based fluoride by adjusting the amount of OAm added with $BmimBF_4$ as fluorine source.

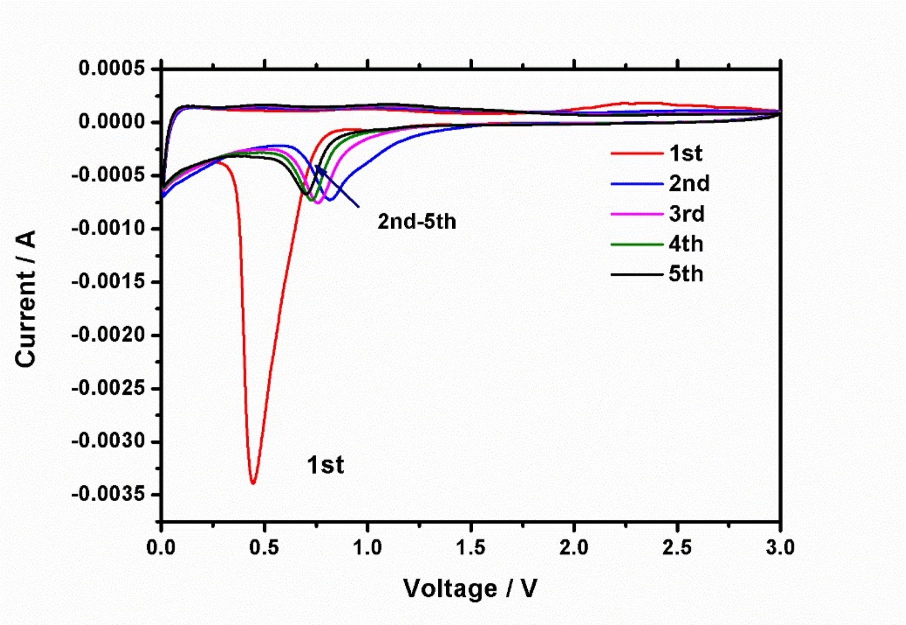

Fig. S7 Cyclic voltammograms of the first five cycles for the M-3.0 anode between 0.01 V and 3.0 V at a scan rate of 0.2 mV s^{-1}

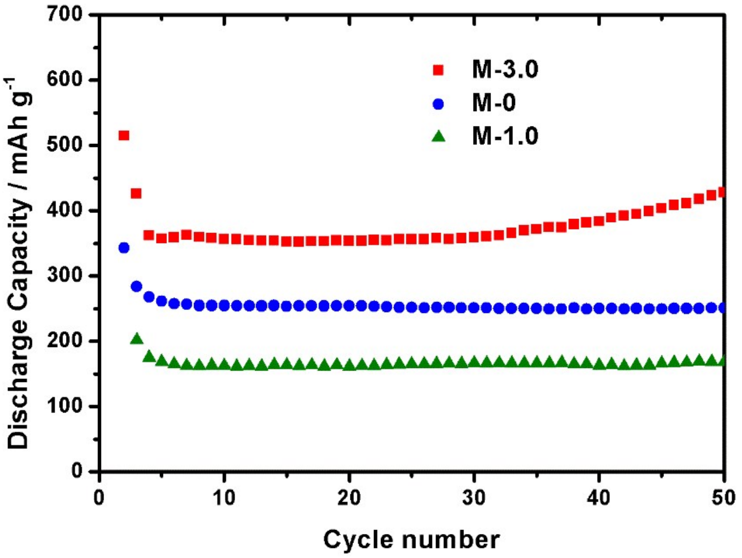

Fig. S8 Cycle performance plots at 1C for M-3.0, M-1.0 and M-0 anodes

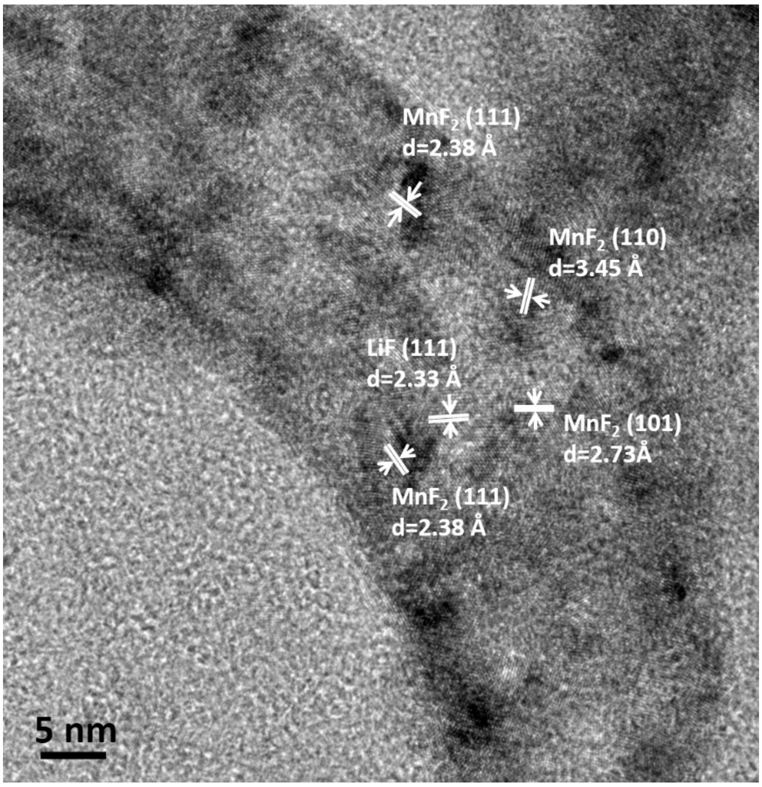

Fig. S9 Representative HRTEM image of the MnF_2 anode at the first recharged state.

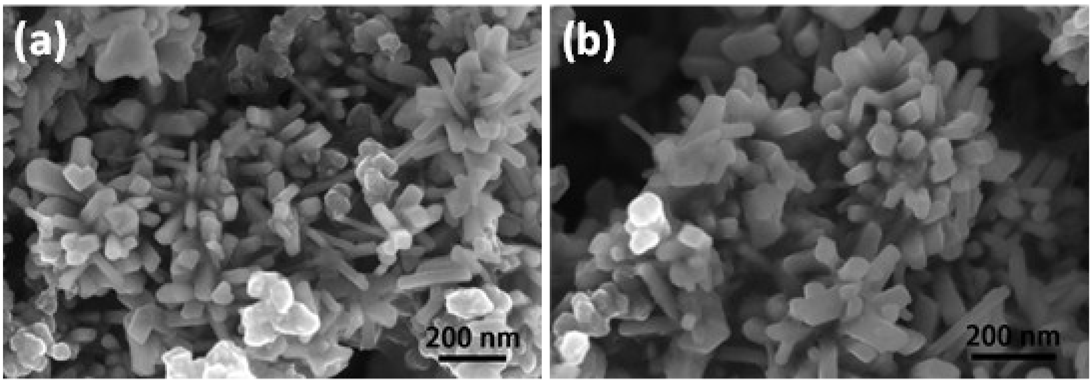

Fig. S10 *Ex situ FESEM* images for MnF_2 anode after long cycle performance.