Supporting Information

Hierarchical Mn_3O_4/Graphene Microflowers Fabricated via Selective Dissolution Strategy for Alkali-Metal-Ion Storage

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Experimental Section

Material Synthesis

The synthesis of MnV_2O_6*/graphene precursors*

In a typical synthesis, 3 ml of H_2O_2 (30%, Sinopharm) and 0.135 g of V_2O_5 (AR, Sinopharm) were mixed to form a V_2O_5 sol under stirring. Graphene dispersion solution (2 g L^{-1}, XianFeng Nano Inc. Nanjing, China), formed a turbid solution. Then, 0.186 g of $Mn(CH_3COO)_2$ powder (Sinopharm) was dissolved in 20 mL of the graphene oxide dispersion under magnetic stirring. Subsequently, the $Mn(CH_3COO)_2$ solution was added dropwise into the V_2O_5 solution under stirring, and the mixed solution was stirred for 20 minutes. The suspension was then transferred to a 50 mL Teflon-lined stainless steel autoclave. The autoclave was heated at 200 °C for 56 hours and then naturally cooled to room temperature. The MnV_2O_6 nanorod bundle/graphene composites were obtained by centrifugation, washed three times with water and once with ethanol, and dried under vacuum at 70 °C for 12 hrs to obtain a precursor. In addition, the MnV_2O_6 nanorod bundles were obtained at same procedure by replacing graphene dispersion solution to deionized water.

The synthesis of nanosheet-assembled hierarchical Mn_3O_4/graphene microflowers

The MnV_2O_6 nanorod bundle/graphene composites were added into 0.2 M NaOH solution with a ratio of 4 mg mL^{-1}, and the reaction proceeded under ultrasonic (40 kHz) for 3 hrs. Then, the nanosheet-assembled hierarchical Mn_3O_4/graphene microflowers were obtained by centrifugation, washed three times with water and once with ethanol, and dried under vacuum at 70 °C for 12 hours. Mn_3O_4 microflowers were obtained from MnV_2O_6 nanorod bundles in the same manner.

Materials Characterizations

XRD measurements were performed to investigate the crystallographic structure using a D8 Advance X-ray diffractometer with a nonmonochromated Cu Kα X-ray source. The field emission scanning electron microscopy (FESEM) images were collected with a JEOL-7100F microscope. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images and energy dispersive spectrometry (EDS) elemental mappings were recorded by using a JEM-2100F STEM/EDS microscope. Nitrogen isothermal adsorption desorption curves were measured using a Tristar II 3020 instrument at 77 K. Raman spectra were obtained using a Renishaw INVIA micro-Raman spectroscopy system. XPS measurements were obtained using a VG MultiLab 2000 instrument. The TG analysis was conducted on a NETZSCH-STA449c/3/G thermoanalyzer under an air atmosphere from 30 to 600 °C with a heating rate of 10 °C min^{-1}.

Electrochemical Measurement

The working electrode was prepared by mixing as-synthesized active materials, acetylene black and carboxymethyl cellulose (CMC) in a weight ratio of 7:2:1. The uniformly mixed slurry was applied to a Cu (for LIBs) or Al foils (for NIBs and KIBs) and dried in a vacuum oven at 70 °C for 6 hours. The mass loading of the active material is about 1-1.5 mg cm^{-2}. The CR2016 coin cells were assembled in a glove box filled with pure argon ($H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm). For LIBs, the lithium foils were utilized as an anode, the electrolyte was consisted of 1 M $LiPF_6$ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) in a volume ratio of 1:1, and a polypropylene film (Celgard-2300) was used as the separator. For NIBs, the sodium foils were utilized as an anode, the electrolyte was consisted of 1 M $NaClO_4$ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) in a volume ratio of 1:1, and glass fiber membrane (GF/D What-man) was used as the separator. For KIBs, the potassium foils were utilized as an anode, the electrolyte was consisted of 0.8 M KPF_6 dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) in a volume ratio of 1:1, and glass fiber membrane (GF/D What-man) was used as the separator. Galvanostatic charge/discharge cycling behavior was investigated using a multi-channel battery test system (LAND CT2001A). Cyclic voltammetry (CV) and EIS electrochemical impedance spectroscopy were tested using a VMP3 multichannel electrochemical workstation (Bio-Logic France).

Table S1. Electrode resistance obtained from the equivalent circuit fitting of EIS results.

Sample	R1(Ω)	R2(Ω)
Mn_3O_4-G	**3.45**	**25.77**
Mn_3O_4	**2.61**	**73.77**

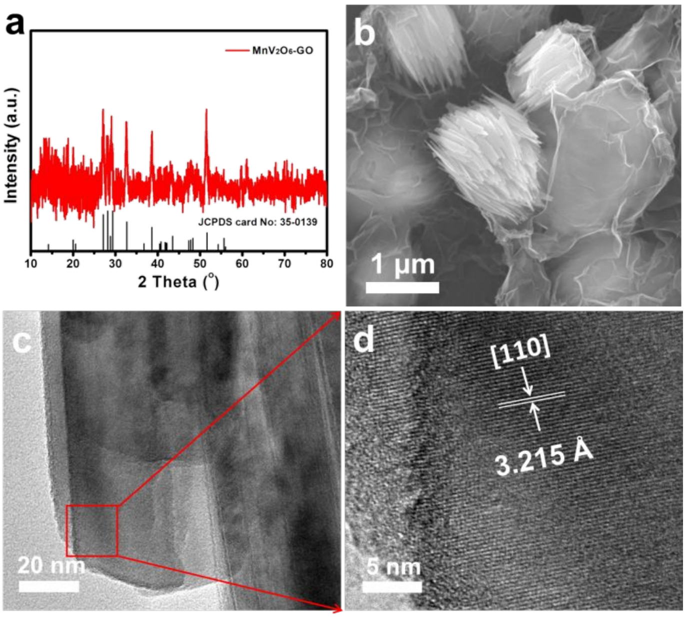

Figure S1. (a) XRD pattern, (b) SEM, (c) TEM and (d) HRTEM images of MVO-G.

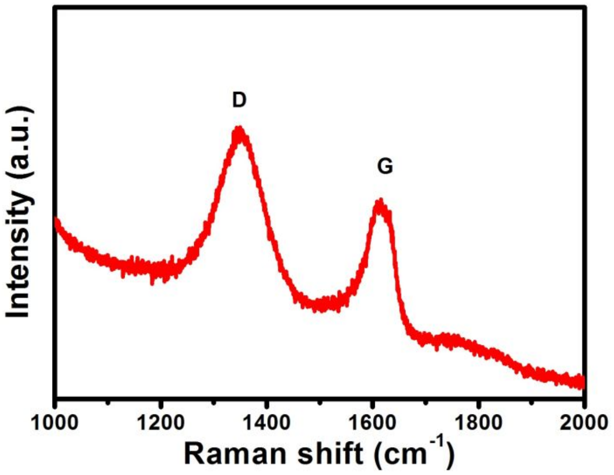

Figure S2. Raman spectrum of Mn_3O_4-G, D and G band.

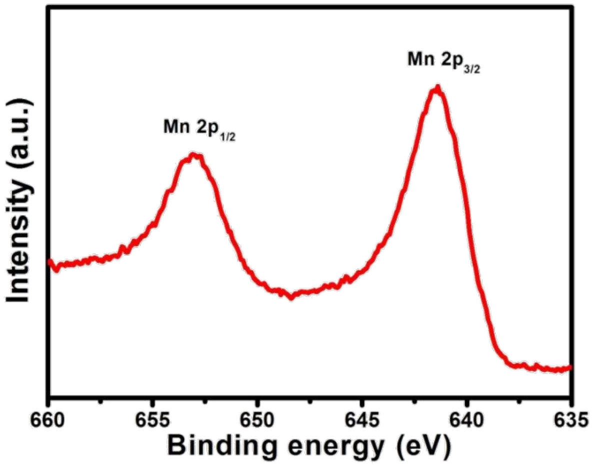

Figure S3. The Mn 2p XPS spectrum of Mn_3O_4 microflowers.

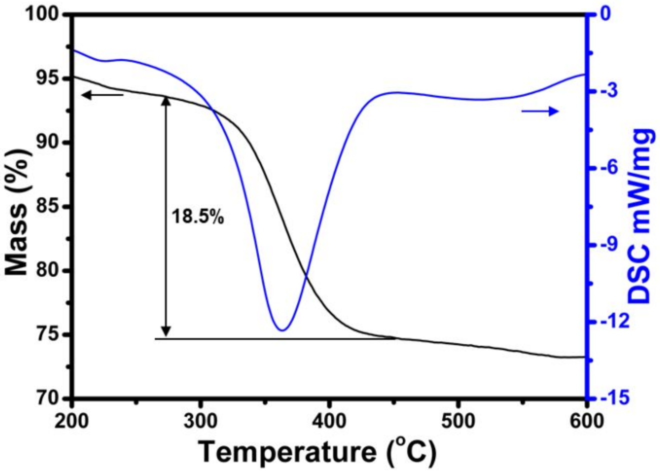

Figure S4. The TG and DSC curves of Mn_3O_4-G

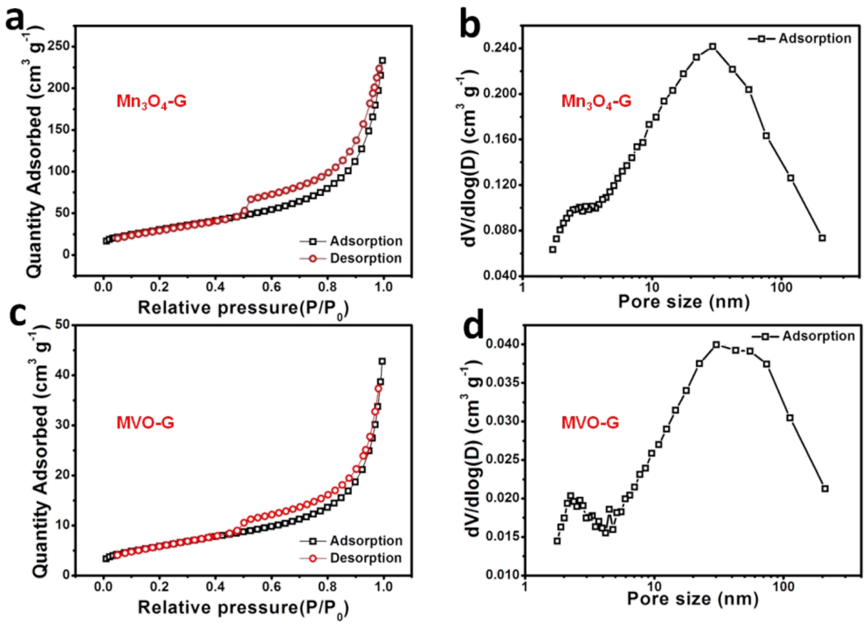

Figure S5. (a, c) Nitrogen adsorption−desorption isotherms and (b, d) corresponding pore size distribution of Mn_3O_4-G (a, b) and MVO-G (c, d), respectively.

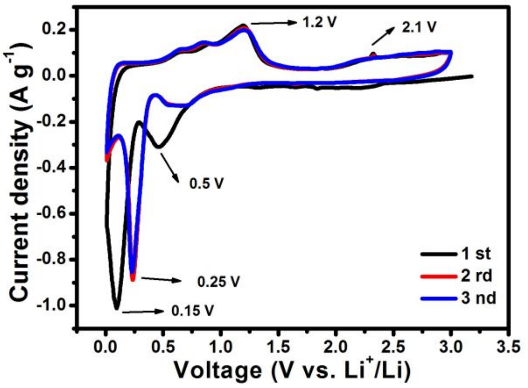

Figure S6. CV curves of Mn_3O_4 at 0.1 mV s^{-1}.

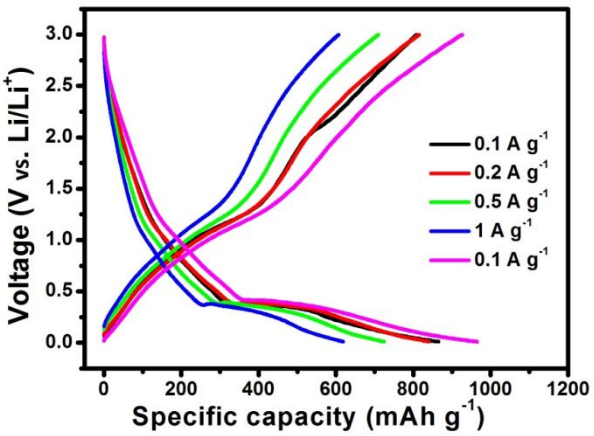

Figure S7. The charge/discharge curves of Mn_3O_4-G at different current density.

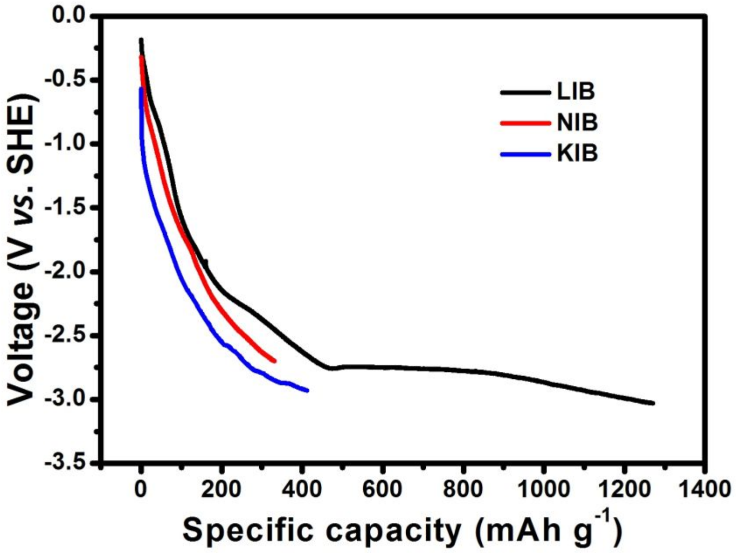

Figure S8. The first discharge curves of Mn_3O_4-G in LIB, NIB and KIB, respectively.

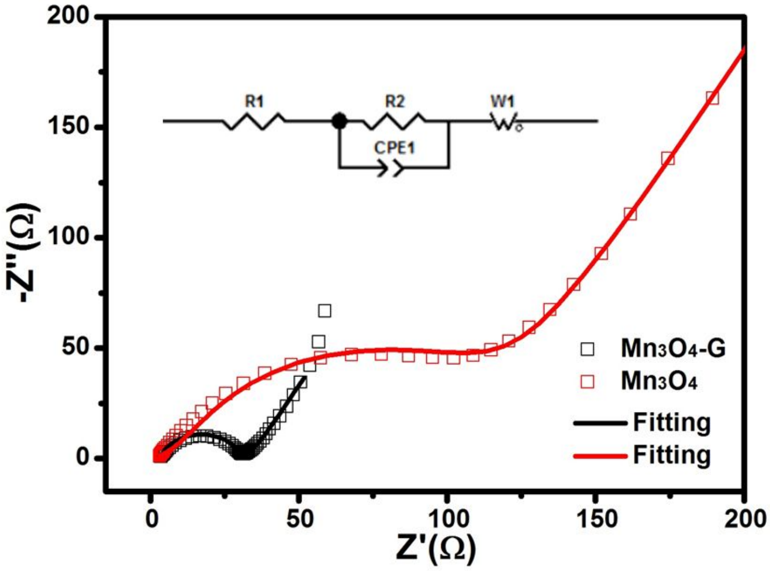

Figure S9. Nyquist plots of Mn_3O_4-G and Mn_3O_4, inset is the equivalent circuit.

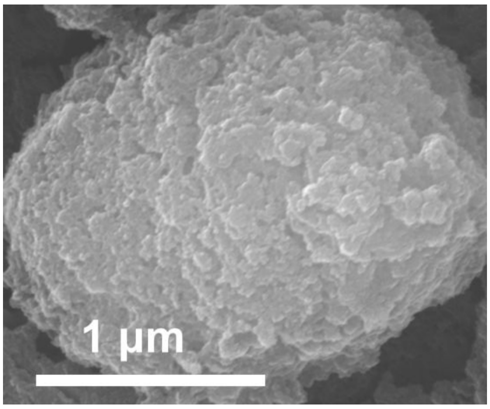

Figure S10. The SEM images of the Mn_3O_4-G after 100 cycles.