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Supporting information

Graphene activated 3D-hierarchical flower-like Li₂FeSiO₄ for high-performance lithium-ion batteries

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Experimental section

Solvothermal synthesis of 3D-hierarchical flower-like Li₂FeSiO₄ (3D-HFLFS)

To synthesize the hierarchical LFS structures (including the hierarchical bud and flower) assembled with 2D nanopetal materials, we used analytical-grade $Fe(Ac)_2 \cdot 4H_2O$, $Si(OC_2H_5)_4$ and $LiOH \cdot 2H_2O$ (molar ratio of 1:1:4) as the starting materials for the solvothermal process. The hierarchical flower-like LFS structures were obtained in a glycol/water solution with a 5/1 ratio of water and ethylene glycol at 220 °C for 7 days.

Synthesis of graphene activated 3D-hierarchical flower-like Li₂FeSiO₄ (G@3D-HFLFS)

To prepare the electrochemical activated LFS cathode material, we used a modified Hummers method (see SI for more info.). Three hundred milligrams of pristine LFS powder was added to 30 ml of a homogeneous aqueous solution containing fifteen milligrams of sucrose and fifteen milligrams of oxidized graphene. The mixture was vigorously stirred for 30 minutes, subsequently freeze-dried and mildly heated at 400 $^{\circ}$ C for 6 h under an Ar atmosphere.

Material characterization

Morphologies of the samples were investigated using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800, 10 kV) and high-resolution transmission electron microscopy (HRTEM, JEM-2100F, 200 kV). Chemical compositions of the samples were analyzed using energy-dispersive X-ray spectroscopy (EDX, Horbia EX-250, 20 kV) as well as FE-SEM and Fourier-transform infrared spectroscopy (FTIR, Nicolet Avatar 360). Crystalline structures of the samples were determined via X-ray diffraction (XRD, D / MAX-IIIA, Cu K α radiation, $\lambda = 0.15406$ nm). Specific surface area and pore size distribution were analyzed via Brunauer-Emmett-Teller

(BET) nitrogen adsorption-desorption measurements (Japan, BELSORP-Mini). Raman spectra were obtained using an RM-1000 Renishaw confocal Raman micro spectroscope with 514.5 nm laser radiation at a laser power of 0.04 mW in the range of 200-3000 cm⁻¹.⁵⁷Fe Mössbauer spectra were measured in a constant acceleration mode with a ⁵⁷Co source and electron spin resonance (ESR) measurement was carried out using a Bruker instrument at room temperature.

Electrochemical tests

The electrochemical properties were tested with 2032-type coin cells assembled in a glove box filled with pure argon. Lithium pellets were used as the anodes, a 1.0 M solution of LiPF₆ in ethylene carbonate/dimethyl carbonate (1/1) (bought from Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. China) was used as electrolyte, and the cathode electrodes were produced with 75% active material, 15% conducting agent (Vulcan XC-72, Cabot) and 10% poly(tetrafluoroethylene) binder. Galvanostatic charge/discharge measurements were performed in the potential range from 1.5 to 4.8 V vs. Li/Li⁺ with a multichannel battery testing system (LAND CT2001A) at 30 ± 5 °C. Cyclic voltammetry and alternating-current impedance (AC) Nyquist measurements were performed using an electrochemical workstation (CHI 760D).



Figure S1 Morphologies and phases of the buds. (a, b) SEM images and (c) XRD of the bud-like LFS obtained in Water/Ethylene glycol system at different temperature. The crystal structure of all the hierarchical LFS obtained in glycol/water system was identified as orthorhombic in S.G. $Pmn2_1[S1-4]$ with the similar cell parameters (a = 0.628 nm, b = 0.532 nm, and c = 0.496 nm) (**Figure S1c**).



Figure S2 SEM images of 3D-HFLFS obtained at 220 °C in glycol/water (5/1 in volume) system.



Figure S3 Nitrogen adsorption-desorption of the hierarchical bud and flower-like LFS (inset is the pore-size distribution). The determined BET specific surface areas of bud and flower are 12.3 and $35.2 \text{ m}^2 \text{ g}^{-1}$, respectively. There is a notable hysteretic effect between the adsorption and desorption isotherms, indicating the existence of slit pores. The porous structures are mainly produced from the preparation process, which is due to the exfoliation of organic micromolecule from the surface of the LFS. The corresponding pore-size distribution curves (inset of **Figure S3**) show that the pore sizes of the two samples mainly locate at ~4 nm.



Figure S4 (a) TEM and (b) HRTEM images of G@3D-HFLFS. GO sheets (inset of **Figure S4**) were synthesized from natural graphite flakes based on a modified Hummers method[S5, S6], 6 g graphite powder was placed in 150 mL cold (0 °C) concentrated H₂SO₄, and then 20 g KMnO₄ was added gradually with stirring and cooling, and the temperature of the solution was maintained below 20 °C. After stirring for 45 min, 500 mL distilled water was added slowly. The temperature was maintained at 30 °C for 45 min. Finally, 1.5 L distilled water and 100 mL of 30% H₂O₂ solution were added after the reaction. The solution was held at room temperature for 20 h and then the mixture was filtered and washed with 5% HCl aqueous solution. The GO obtained was freeze dried for 72 h. the GNS were obtained at the same heat treatment condition. According to our previous study^[S8], the specific capacity of GNS in this work is ~200 mAh g⁻¹, the capacity of 10 mAh g⁻¹ (corresponding to content of ~5 wt%) was excluded when the specific capacities of the composites were calculated.



Figure S5 Refining XRD pattern of G@3D-HFLFS using GSAS software. The XRD patterns further reveals that the phase of the G@3D-HFLFS is the different from the pristine 3D-HFLFS, indicating an orthorhombic in space group P2₁/n[S1-4] with cell parameters of a = 0.824 nm, b = 0.502 nm and c = 0.825 nm and $\beta = 99.09^{\circ}$.



Figure S6 FTIR of 3D-HFLFS and G@3D-HFLFS. The characteristic absorption peaks of Si-O-Si from Li_2SiO_3 at 1048 and 1086 cm⁻¹ are not observed in the activated LFS, confirming the absence of Li_2SiO_3 . The vibrational spectra of LFS were dominated by the fundamental vibrations of the LiO₄, FeO₄ and SiO₄ tetrahedra, where the LiO₄ vibration, SiO₄ bending and stretching modes were identified.



Figure S7 Energy dispersive spectroscopy (EDS) spectrums. (a) and (b) correspond to dots 1 and 2 in **Figure 2b**. Energy dispersive spectroscopy (EDS) spectrums in TEM show that the presence of C, Si and Fe elements are inlayer of the coated materials and only C element outside, indicating that sucrose coated on the surface of LFS plays an important role as the connection of LFS and grapheme by a large of alcoholic hydroxyl groups.



Figure S8 X-ray photoelectron spectroscopy (XPS) of G@3D-HFLFS. X-ray photoelectron spectroscopy further evaluates the valence of the various elements. The peak at 55.7 eV is attributed to Li 1s. Fe 3p peak at 53.7 eV demonstrate that only Fe^{2+} is present. The strong peaks at O 1s can be assigned to the O²⁻in [SiO₄] structure [S7].



Figure S9 (a) CV curves for battery without cathode, Galvanostatic charge/discharge of 2032-type coin cells with LiFePO₄ cathodes at 0.1C between 1.5-4.8V (b) and 2.5-4.2V(C) within 50 cycles. Discharge specific capacity of LiFePO₄ is approximate 160 mAh g⁻¹ at 0.1 C between 2.5 and 4.2 V. When the voltage window changes to 1.5-4.8 V, the curves and capacities is similar to that tested at 0.1C between 2.5 and 4.2 V. Especially, there is no voltage plateau in the high voltage range from 4.2 to 4.8 V. The above analysis results reveal that there is almost no electrolyte decomposed compound such as Li₂CO₃ or oxygen residue produced extra capacity at the voltage windows of 1.5-4.8 V.



Figure S10 Charge/discharge curves and cycle capability of the pristine 3D-HFLFS. The Charge/discharge curves and cycle capability of the pristine 3D-HFLFS without GNS activated layer was also evaluated under a current-rate of 0.1C at 30 ± 5 °C. It can be seen the capacity fast declined from initial charge/discharge capacity of 241.5/218.2 to 95.2/94.3 mAh g⁻¹. The mainly reason is due to that the pristine flower-like LFS without carbon coating layer was rapidly corroded resulting in some side reaction under the electrolyte condition.



Figure S11 The discharge/charge curves of the activated bud-like LFS at 0.1C. The initial charge/discharge capacity is 345.0/237.5 mAh g⁻¹ with a low coulombic efficiency of 68.8%. After 10 cycles the charge/discharge capacity is 328.2/245.1 mAh g⁻¹ with a low coulombic efficiency of 74.6%.



Figure S12 (a) Capacity retention ratio of G@3D-HFLFS at 0.1C within 50 cycles, (b) Discharge specific capacity for four batches of cell testing experiments from a low current rate of 0.1C to high current rate of 20 C.



Figure S13 Morphological analyses of G@3D-HFLFS electrode (a) before and (b) after cycled for 200 cycles at C-rate of 5C. Based on conversion reaction, the activated LFS structure may be amorphous after the discharge-charge cycle. The mixture (G@3D-HFLFS / XC-72/PVDF) was compressed onto a copper foil to form a thin film, and then the film was taken from the copper foil for SEM testing. As shown in SEM image, G@3D-HFLFS display high dispersity in electrodes with conductive networks for the ion and electron transport, indicating the high capacity could be released from G@3D-HFLFS. The morphology after 200 cycles is seen from SEM image, it is interesting that the nanopetal morphology in flowers has involved negligible changes, confirming the attractive morphological stability. In our case, the hierarchical micro-flower structure that was assembled with nanopetals plays a more important role in determining electrochemical properties.



Figure S14 Relationship of Iron oxidation state with isomer shift vs a metallic Fe standard [S9].

| Sample | component | IS(mms ⁻¹) | QS(mms ⁻¹) | area% |
|--------|------------------|------------------------|------------------------|-------|
| OCV | Fe ³⁺ | 0.416 (05) | 0.917(11) | 45.3 |
| | Fe ²⁺ | 0.963(05) | 2.469(11) | 54.7 |
| C-4.8V | Fe ³⁺ | 0.184(12) | 0.712(15) | 79.8 |
| | Fe ³⁺ | 0.427(19) | 0.936(38) | 20.2 |
| D-2.9V | Fe ³⁺ | 0.169(18) | 0.885(15) | 59.9 |
| | Fe ³⁺ | 0.431(15) | 0.901(61) | 40.1 |
| C-3.3V | Fe ³⁺ | 0.141(64) | 0.856(48) | 45.9 |
| | Fe ³⁺ | 0.420(12) | 0.937(84) | 52.5 |
| | Fe ²⁺ | 1.035(65) | 3.031(30) | 1.61 |

Table S1 Mössbauer parameter fitting results for G@3D-HFLFS electrodes. The cells charged/discharged to different voltages, were opened in an Ar-filled glove box after charged or discharged to different voltages, the active material removed and rinsed with dry solvent to remove residual electrolyte and binder, and dried. Ex-situ Mösbauer and EPR measurements were carried out at room temperature.



Figure S15 AC curves of of G@3D-HFLFS compared to the pristine 3D-HFLFS.

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