Supporting Information

Multifunctional multilayer nanospheres for ion regulation in lithium metal batteries

Yan Li [#], Manjie Xiao [#], Chunli Shen, Haoqing Ma, Lianmeng Cui, Wei Yang, Tianhao Zhao, Yan Zhao [*] and Xu Xu[*]

International School of Materials Science and Engineering, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Hubei 430070, China

* Correspondence: yan2000@whut.edu.cn; xuxu@whut.edu.cn

Keywords: solid-electrolyte interphase; multifunctional multilayer nanospheres; lithium metal batteries。

EXPERIMENTAL PROCEDURE

Fabrication of Fe_3O_4 nanospheres

The **Fe_3O_4** particles were prepared by solvothermal reaction[1]. 2.70 g $FeCl_3 \cdot 6H_2O$ and 7.20 g sodium acetate were dissolved by intense stirring in 100 mL glycol. The resulting uniform yellow solution is transferred to a Teflon-lined stainless steel high-pressure reactor, sealed, and heated at 200°C. After 8 hours of reaction, the obtained black magnetite particles were centrifuged with ethanol at differential speed for several times and dried in a vacuum of 60°C for 12 hours.

Fabrication of Fe_3O_4@AlOOH nanospheres

The **AlOOH** coating were prepared by solvothermal reaction[1]. Firstly, after stirring at 85℃ for 20 minutes, 11.3 g isopropoxyaluminum ($Al(OPr)_3$) was dissolved in 100 mL deionized water, and then HNO_3 (1.0 M) was slowly added to hydrolyse $Al(OPr)_3$. The pH of the solution was kept in the range of 3 ~ 4. The mixture was stirred at 85°C for 2 h, and then HNO_3 (9.5 mL, 1.0 M) was slowly dropped into the mixture, and stirred gently for 6 hours by reflux. AlOOH base sol was obtained after it was slowly cooled

to room temperature. The Fe_3O_4 microspheres were then dispersed in AlOOH primer sol and stirred vigorously for 1 hour, then the microspheres were sucked out with a magnet and thoroughly cleaned with ethanol. The resulting Fe_3O_4 @AlOOH microspheres will be dried in air for 30 minutes. The whole process (dispersion, extraction, drying) is repeated 10 times.

Fabrication of Fe_3O_4@$Al(OH)_3$@ZnO nanospheres

The Fe_3O_4@AlOOH (0.5 g) was placed in anhydrous ethanol (60 mL) and $Zn(NO_3)_2.6H_2O$ (1.2 g) was added to the suspension under stirring at room temperature. Stir the mixture for 1 hour, dripping in the TMAH, until the pH is between 12-13. Mix the settling mixture well and stir for 15 minutes. The precipitate with solution is placed in an automatic kettle and heated at 100°C for 5 hours. The precipitated products were centrifuged and collected, washed with ethanol, and dried in the oven at 50°C.

Fabrication of Li/Cu and Li/Li batteries

0.2g FAZ nanospheres were put in 10 ml DOL solution and fully stirred for 2 h. Then drop them on the surface of copper foil to dry naturally. At the same time, the copper foil was placed between the upper and lower magnets to ensure that the FAZ nanosphere receives uniform and parallel magnetic force. After the copper foil was completely dried, cut it into a circle with a diameter of 10 mm, assembled it into a Li/Cu battery, and electrodeposit at a current density of 1 mA/cm^2 for 5 hours. After the battery was disassembled, take off two Li/FAZ/Cu electrode pieces and assemble it into a lithium symmetrical battery for the next test.

Materials characterizations

SEM (Pharos-0092-F) is used to characterize the morphology and structure of materials at a voltage of 10 kV, and the elemental mappings were also collected on JEOL-7100F. TEM and HRTEM images were executed with a Titan G2 60-300 with EDS image corrector. Optical images are obtained by a mobile phone. XPS spectra were obtained from AXIS SUPRA with working voltage of 15 kV, current of 10 mA and step length of 0.1 eV.

Electrochemical measurements

All electrochemical characterizations are based on 2025 button cell assembled in a glovebox filled with pure argon, and operated at room temperature. A Celgard 2400 polypropylene was used as the separator. Electrolyte used to test the modified Li anode performance was 35 μL of 1.0 M LiTFSI in a liquid mixture of 1, 2-dimethoxyethane and 1, 3-dioxolane (1:1 in volume) with 1 wt% $LiNO_3$ additive. The diameter of both Li/Cu anodes and the control anodes is around 12 mm. The cycling measurements were performed with a multichannel battery testing system (Neware).

Computational details

The computations were performed using the Vienna ab-initio simulation package (VASP) in the framework of density functional theory (DFT). The projector augmented wave (PAW) pseudopotential was adopted to describe the ion-electron interactions and the generalized gradient approximation (GGA) exchange-correlation function was described by Perdew−Burke−Ernzerhof (PBE). Particularly, we used the DFT-D3 functional to include the physical van der Waals (vdW) interaction in the simulation. In these calculations, a SCF convergence criterion of 1.0×10^{-5} Ev/atom, a force tolerance of -0.02 eV/Å and a kinetic energy cutoff of 400 eV were set up. Meanwhile, the first Brillouin zone integrations were sampled by 1×1×2 Gamma k-point meshes for geometric optimizations and static calculations to investigate the anchoring interactions between the F^- and the three kinds of substrates, respectively. The corresponding adsorption energy was calculated as the following formula:

$$E(ad) = E(total) - [E(sub) + E(F^-)]$$

Where E (total) is the total energy of the model of a F^- adsorbed on the substrate. E (sub) is the energy of substrate. E (F^-) is the energy of F^-. Here, a negative E (ad) means attractive interaction.

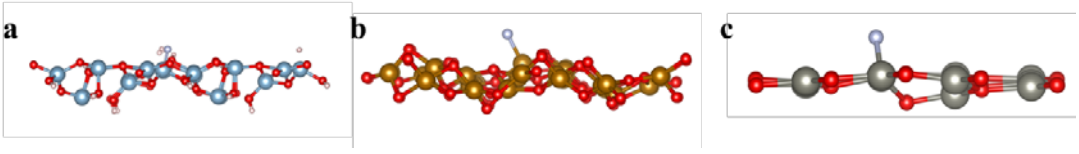


Figure S1. Adsorption model of (a) $Al(OH)_3$ and F^-, (b) Fe_3O_4 and F^-, (c) ZnO and F^- at

cross-section.

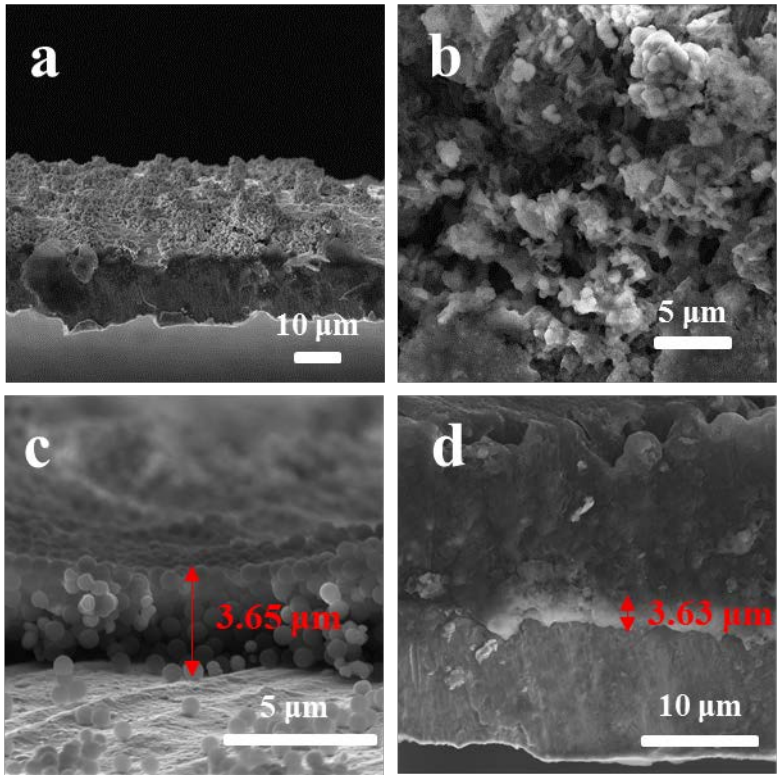


Figure S2. (a) SAZ nanospheres deposited in copper foil. (b) Lithium deposition on SAZ nanospheres. (c) FAZ nanospheres deposited in copper foil. (d) Lithium deposition on FAZ nanospheres.

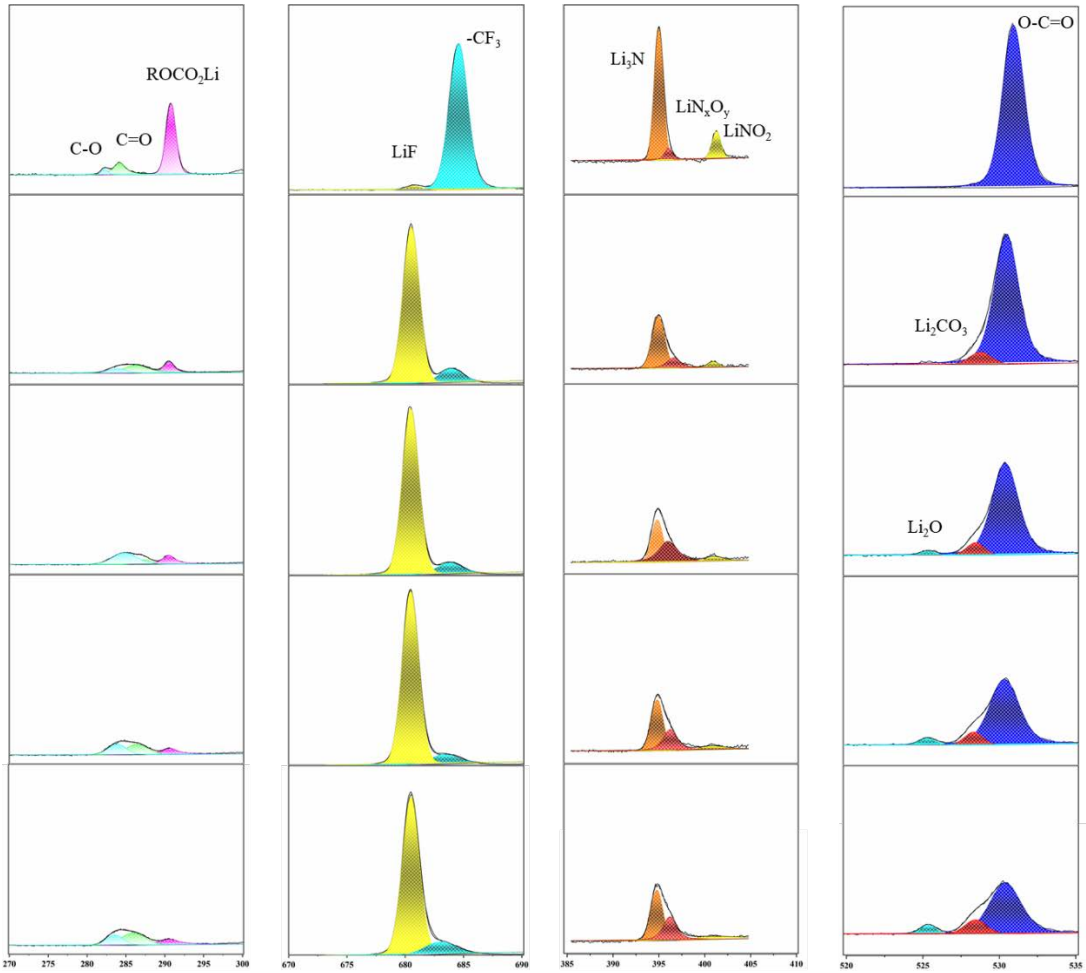


Figure S3. In-situ XPS etching tests for C, F, N and O elements at 0, 50, 100, 150 and 200 sec on lithium metal deposited on blank copper foil.

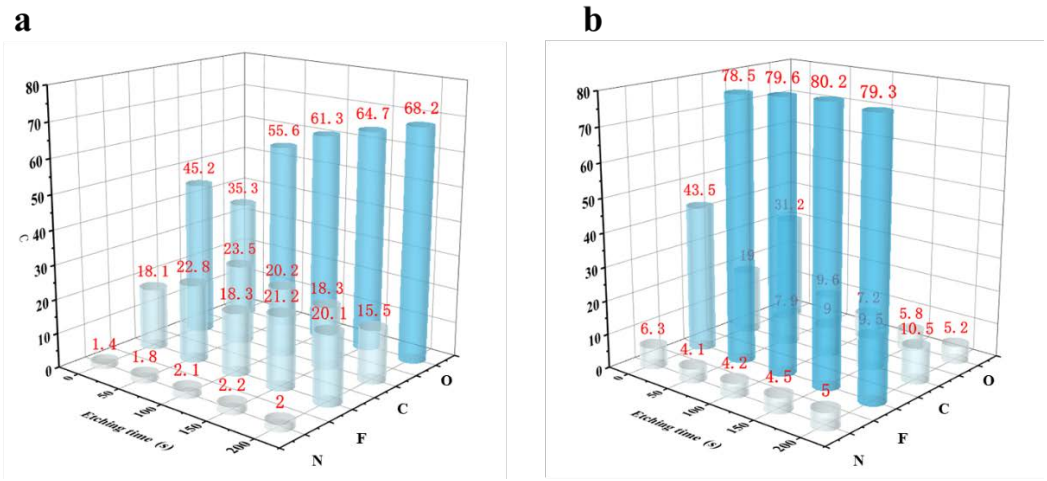


Figure S4. In-situ XPS etching tests for C, F, N and O elements at 0, 50, 100, 150 and 200 sec. The histogram of the element ratio for N, F, C and O elements at 0, 50, 100, 150 and 200 sec on (a) blank copper foil (b) FAZ nanospheres.

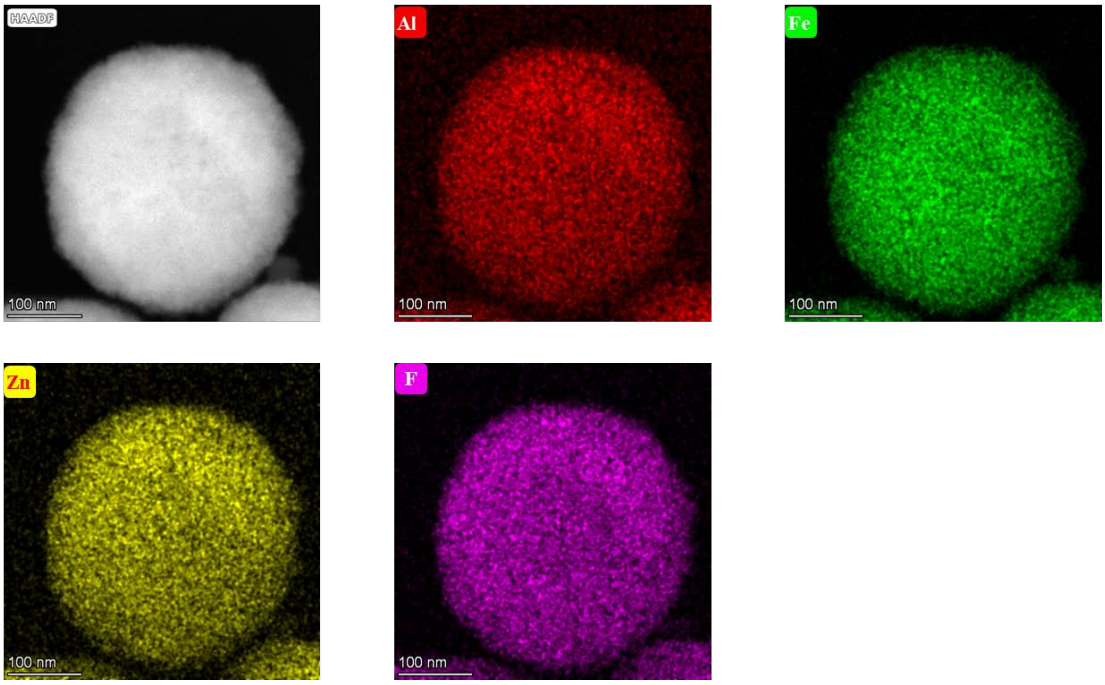


Figure S5. The TEM and element mapping images of FAZ nanospheres after lithium deposition.

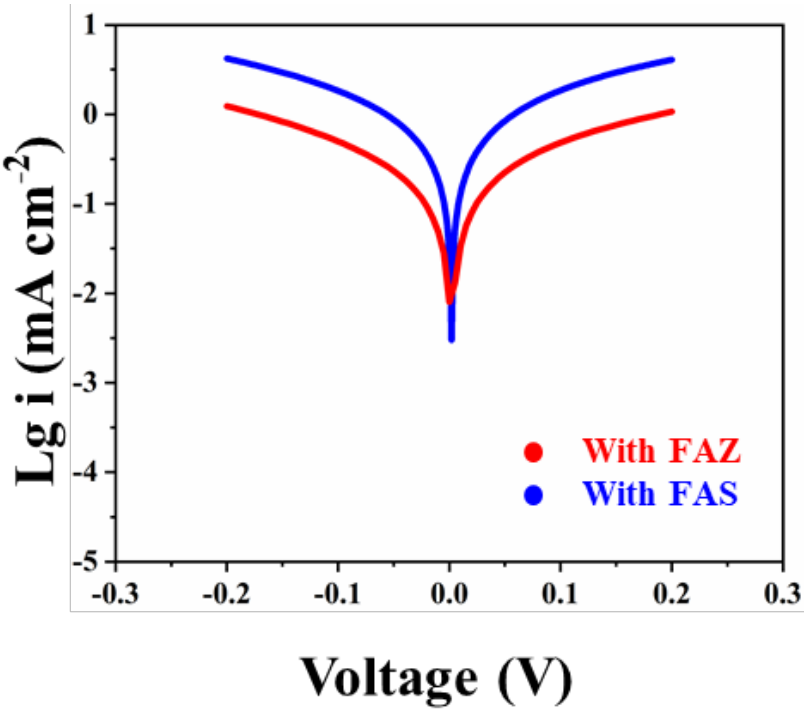


Figure S6. Tafel plots obtained from cyclic voltammetry test in Li||Li battery.