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Supporting Information

Sulfurization of FeOOH Nanorod on a Carbon Cloth and their Conversion into Fe_2O_3/Fe_3O_4-S Core-Shell for Lithium Storage

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Experimental Section

Synthesis of Fe_2O_3-Fe_3O_4–S core-shell nanorods on a carbon cloth

The synthesis of FeOOH nanorods were first prepared according to our previous report. [1, 2] At first, 0.01 M $FeCl_3$ $6H_2O$ and 0.05 M $NaNO_3$ were add into 50 mL distilled water in a beaker and stirred severely until they all dissolved. Then some amount of concentrated hydrochloric acid was added into the solution to adjust the pH to 1. After that, 18 mL of the acidic solution was transferred to a 20 mL Teflon-lined stainless steel autoclave, together with a 2 cm × 3 cm surface area of carbon cloth cleaned by distilled water and ethanol several times. Then the Teflon-lined stainless

steel autoclave was transferred in an electric oven, which was heated and maintained at 95 ^{o}C for 6 h. Until the Teflon-lined stainless steel autoclave cooled down at room temperature, a yellowish carbon cloth was obtained. The carbon cloth was then immersed in 0.1 M thioacetamide solution for 6 h. After being washed by distilled water several times and dried at air, the carbon cloth was annealed in N_2 gas at 400 ^{o}C for 1 h at a ramping rate of 5 ^{o}C per minute, then the FFS nanorods on the carbon cloth was obtained.

Material Characterization

The morphologies of the as-prepared samples were observed by field-emission scanning electron microscope (FESEM) (FESEM, JSM-6330 F) and transmission electron microscope (TEM) (JEM2010-HR, 200kv). The structure of the samples were characterized by X-ray diffraction Spectrometry (XRD, D8 ADVANCE) with Cu Kα radiation (λ =1.5418 A), Raman spectrometer (FT-IR, Nicolet 330) and X-Ray photoelectron spectroscopy (XPS, Thermo VG) with 200 W Al Kα radiation.

Electrochemical Measurements

The electrochemical measurements were tested by using CR2032 coin type cells and lithium chips as counter and reference electrode at room temperature. The working electrode was the carbon cloth uniformly coated by the FFS core-shell nanorods. The mass loading of the active materials for the active electrode were calculated through the reading difference between the bare carbon cloth and the carbon cloth coated by the FFS core-shell nanorods in a high-precision analytical balance (Sartorius, max weight 5100 mg, d = 0.001 mg). The loading density of the active materials is 1.7-2.0 mg/cm^2. Coin cells were assembled in an argon-filled glove box [Mikrouna (China) Co., Ltd.], the separator was Celgard 2400 and the electrolyte is 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). The charge-discharge tests was carried out on a Neware battery tester (CT-3008-164, Shenzhen, China) at a voltage range of 0.01–3 V (vs. Li^+/Li). Cyclic voltammograms (CVs) (scanning rate: 0.1 mV/s) and the electrochemical impedance spectroscopy

(EIS) (frequency range: 10^{-1} Hz –10^{5} Hz) were obtained with a electrochemical working station (CHI-760d, Chenhua, Shanghai).

Capacity Contribution of the Carbon Cloth

The capacity contribution from the carbon cloth substrate is quite less compare to the total capacity of the electrode. We can calculate the capacity contribution of the carbon cloth based on the calculation below; [3]

The total mass of the electrode (0.64 cm^2) is around 9.28 mg (~2 mg FFS, 7 mg carbon cloth). The electrode has a capacity of ~3.70 mAh cm^{-2}, so the capacity for the total electrode is 398.7 mAh g^{-1}. As the carbon cloth has a capacity of ~52 mAh g^{-1}, the total contribution of carbon cloth is calculated to be around;

$$52 \text{ mAh } g^{-1} \times 7 \text{ mg } cm^{-2} = 0.36 \text{ mAh } cm^{-2}.$$

Therefore, the capacity percentage of the carbon cloth is roughly 0.36/3.7 = 9.7%. If we subtract the contribution of carbon cloth, the capacity for the FFS electrode along can be estimated

$$(3.7 - 0.36) \text{ mAh } cm^{-2} / 2 \text{ mg } cm^{-2} = 1670 \text{ mAh } g^{-1}$$

Based on our calculation, the capacity derived here (1670 mAh g^{-1}) is almost the very close to that of the experimental result according to Fig. 3b (1600 mAh g^{-1}).

Supplementary Figures

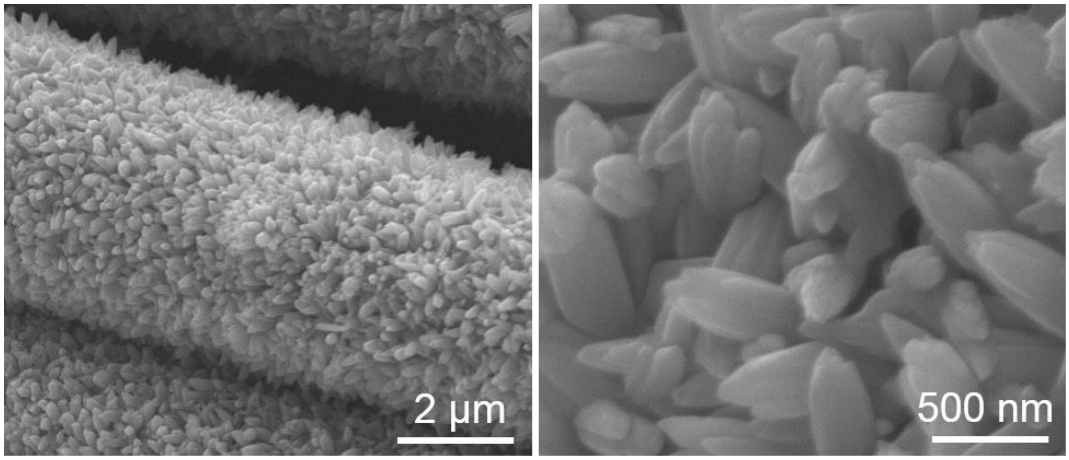

Fig. S1. SEM images of the FeOOH flower-like nanorods.

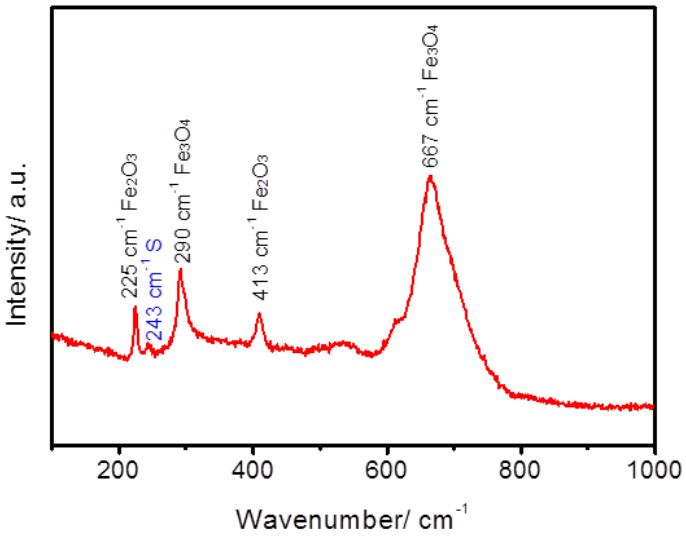

Fig. S2. Enlarge Raman Spectra of the FFS electrode showing the peak of S at 243 cm-1, and corresponds with other related report. [4]

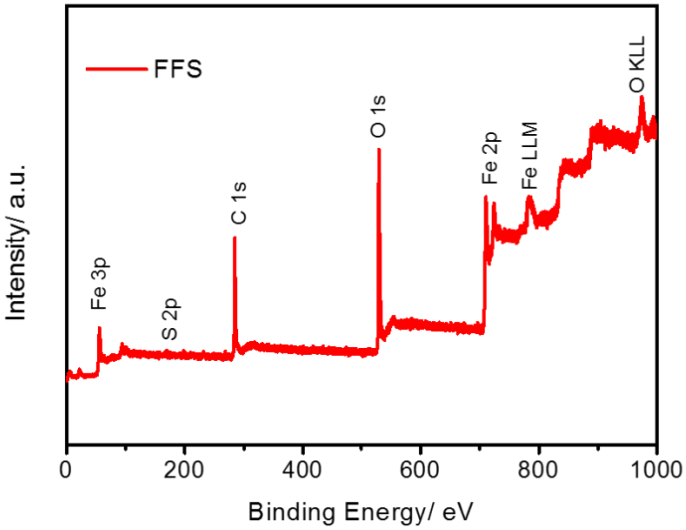

Fig. S3. XPS wide-scan spectrum of the FFS sample.

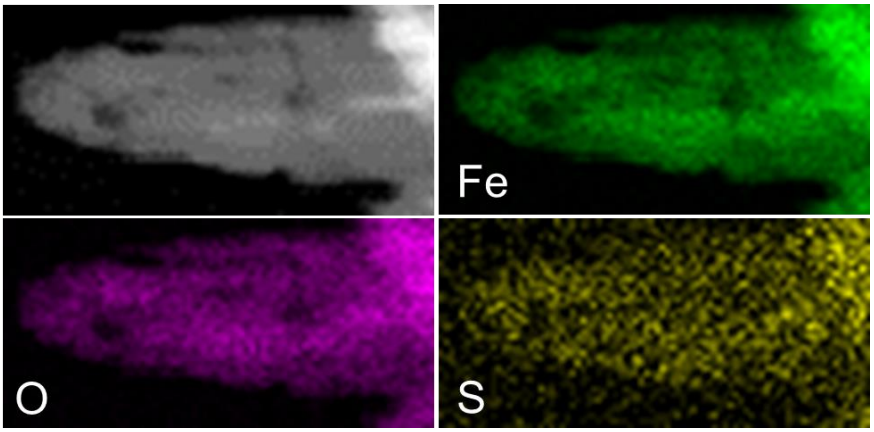

Figure S4. Elemental mapping of the same nanorod region. Fe (green), O (Pink), and S (Yellow).

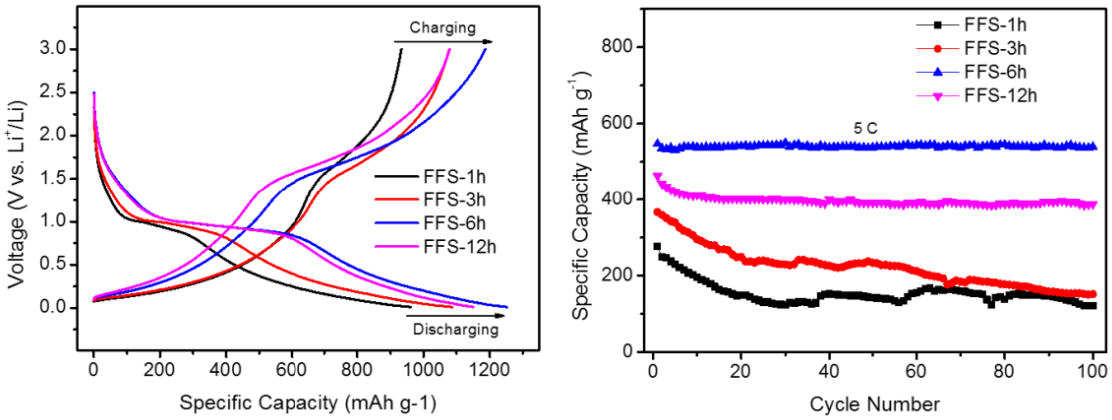

Fig. S5. Electrochemical performance of the FFS electrodes at different sulfurization duration. 5th Charge-discharge profiles (Left) and cyclic performance of the FFS electrodes at different sulfurization duration (Right).

References

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3. C. Guan, X. Wang, Q. Zhang, Z. Fan, H. Zhang and H. J. Fan, *Nano Lett.*, 2014, **14**, 4852-4858.
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