Supporting Information

Synchronous synthesis of kirkendall effect induced hollow FeSe₂/C nanospheres as anodes for high performance sodium ion batteries

Yang Lan, Jianbin Zhou*, Kangli Xu, Yue Lu, Kailong Zhang, Linqin Zhu and Yitai Qian*

Corresponding Author: Jianbin Zhou, E-mail: zjianb@mail.ustc.edu.cn; Yitai Qian, E-mail: ytqian@ustc.edu.cn.

Department of Chemistry and Hefei National Laboratory for Physical Science at Microscale, University of Science and Technology of China, 96 JinZhai Road, 230026, Hefei, China.

Experimental section

Synthesis of Fe₃O₄ nanospheres

The Fe₃O₄ nanospheres were synthesized by using a solvothermal method. FeCl₃ was used as the iron source and trisodium citrate as the stabilizer in ethylene glycol solution. Firstly, FeCl₃ $6H_2O$ (3.25 g), trisodium citrate (1.3 g) and H₂O (1.0 ml) were dissolved in ethylene glycol (100 ml) after vigorously stirring for 1.5 h. Sodium acetate (6.0 g) was then added into the mixed solution with constantly stirring. After that, the obtained yellow solution was transfered into a Teflon-lined autoclave. Then the autoclave was heated at 200 °C for 10 h. After naturally cooled down to room temperature, the Fe₃O₄ nanospheres were eventually obtained after washing three times with deionized water and ethanol.

Synthesis of Fe₃O₄@RF nanospheres

The obtained Fe₃O₄ (0.15 g) nanospheres, cetyltrimethylammonium bromide (0.46 g) and H₂O (14.08 ml) were mixed uniformly and then transferred into a flask. After being stirred for 1 h, resorcinol (0.7 g), absolute ethanol (56.4 ml) and NH₄OH (0.2 ml) were added sequentially. The mixed suspension was stirred at 35 °C for 0.5 h and then formalin (0.1 ml) was finally added. After continually stirring for 6.0 h and polymerization followed by ageing overnight, the Fe₃O₄@RF nanospheres can be collected after washing with deionized water and alcohol several times.

Synthesis of hollow FeSe₂/C nanospheres and FeSe₂ solid nanospheres

The Fe₃O₄@RF nanospheres and selenium powders with a certain ratio were ballmilled to get a homogeneous mixture. Then, the mixture was carefully sealed in a quartz tube under vacuum. After heating at 650 °C for 20 h (2 °C min⁻¹), the tube was left to cool naturally. The final product hollow FeSe₂/C nanospheres was obtained. And the bare FeSe₂ solid nanospheres was prepared by Fe₃O₄ nanoparticles reacted with selenium powders directly.

Material characterization

X-ray diffraction (XRD) of these samples was conducted on a Philips X' Pert Super diffractometer with Cu K α radiation (λ =1.54178 Å). The thermos-gravimetric analysis (TGA) of samples was carried out on a TGA Q5000IR system under the air atmosphere. Microstructure and morphology characterization was collected on scanning electron microscopy (SEM, JEOL-JSM-6700F) and transmission electron microscopy (TEM, JEOL). Energy dispersive spectroscopy (EDS) was used to characterize the structure and the elemental distribution of the sample (JEM-ARM 200F TEM). X-ray photoelectron spectroscopy (XPS) was collected on an ESCALAB 250 spectrometer (Perkin-Elmer) and a monochromatic Al K α (1486.6 eV) was applied as the X-ray source.

Electrochemical measurement

The mixture of the as-prepared active materials, super P and carboxymethyl cellulose binder with a mass ratio of 7:2:1 was ball milled in water solvent homogeneously and then carefully pasted on the copper foils. And then, the foils were dried at 80 °C for 720 min in a vacuum oven and punched into wafer-shaped electrodes. The mass loading of active materials was about 2.0-3.0 mg cm⁻² in each electrode. The 2016 coin cells were assembled in a pure argon filled glove box (H₂O, $O_2 < 0.1$ ppm) with Na foil as the counter electrode, microporous polypropylene film as the separator, respectively. The electrolyte was 1 M NaClO₄ (Aldrich) dissolved in a mixture of ethylene carbonate/dimethyl carbonate (v/v=1:1), in which 5 wt% fluoroethylene carbonate was added. Galvanostatic discharge/charge measurements with different current densities were conducted by using a LAND-CT2001A systems within the range of 0.001 V to 3.0 V versus Na⁺/Na. Cyclic voltammetry (CV) was tested in an electrochemical workstation (AUT302N, Metrohm, Switzerland) with a scanning rate of 0.1 mV s⁻¹. It should be noted that the calculated specific capacity is based on the FeSe₂ active materials.



Fig. S1 The XRD patterns of Fe₃O₄ and Fe₃O₄@RF nanospheres.



Fig. S2 XPS spectra of the FeSe₂/C nanospheres.



Fig. S3 C 1S signal of the FeSe₂/C nanospheres.



Fig. S4 (a) The mixed elemental mapping image of the hollow FeSe₂/C nanospheres; (b) The magnified TEM image of the hollow FeSe₂/C nanospheres.



Fig. S5 TEM image of bare FeSe₂ nanospheres.



Fig. S6 The SEM (a) and TEM (b) images of the FeSe₂/C nanospheres after cycling for 20 cycles at 0.5 A g^{-1} under fully charged state.



Fig. S7 Nyquist plots of the bare FeSe₂ and FeSe₂/C nanospheres before cycling.