

Electronic Supplementary Information

ZnS nanoparticles embedded in porous carbon matrices as anode material for lithium ion batteries

Yun Fu, Zhian Zhang, Xing Yang, Yongqin Gan, Wei Chen*

School of Metallurgy and Environment, Central South University, Changsha Hunan 410083, China

**Corresponding author: Tel: +86 731 88830649*

E-mail address: zza75@163.com

Contents

1. Experimental Section	1
2. Materials Characterization	2
3. Electrochemical Measurements	2
4. Characterization Data	2
5. The detailed calculation of the about carbon content in ZnS/PC from the TGA profile of carbonized MOF-5	3

Experimental

Synthesis of MOF-5: 19.75 g zinc acetate dihydrate was dissolved in 500 ml N,N-Dimethylformamide (DMF), 5.98 g terephthalic acid and 8.52 ml triethylamine were dissolved in another 500 ml DMF. The above two solutions were mixed and stirred at room temperature under magnetic stirring for 6 h. The resulting white precipitates were collected by centrifugation and washed with DMF and methylene dichloride several times and finally dried at 150 °C for 12 h under vacuum to remove the solvent molecules.

Synthesis of ZnS/PC: The as-prepared MOF-5 precursor was carbonized at 600 °C for 2 h under Ar atmosphere with a heating rate of 5 °C min⁻¹. 0.1 g carbonized MOF-5 precursor and 0.2 g thioacetamide were added to the mixed solutions consisted of 25 ml deionized water and 20 ml ethylene glycol. After sonicated for another 30 min, the mixture was heated to 180 °C in a Teflon-lined autoclave (60 mL capacity) and kept for 24 h. The precipitates were cooled down to room temperature naturally and were collected by centrifugation, washed several times with ethanol and deionized water and dried at 60 °C in a vacuum oven for 12 h.

Synthesis of pure ZnS: The as-prepared MOF-5 precursor was calcined at 600 °C for 2 h under air atmosphere with a heating rate of 5 °C min⁻¹ to remove carbon framework. 0.1 g calcined MOF-5 precursor and 0.3 g thioacetamide were added to the mixed solutions consisted of

25 ml deionized water and 20 ml ethylene glycol. After sonicated for another 30 min, the mixture was heated to 180 °C in a Teflon-lined autoclave (60 mL capacity) and kept for 24 h. The precipitates were cooled down to room temperature naturally and were collected by centrifugation, washed several times with ethanol and deionized water and dried at 60 °C in a vacuum oven for 12 h.

Materials Characterization: The crystal structures of the samples were investigated by X-ray diffraction (XRD) analysis with Cu K α radiation (Rigaku D/max Diffraction System, $\lambda = 1.5406$ Å). Thermogravimetry analysis (TGA) was measured on SDTQ600 apparatus in the temperature from room temperature to 700 °C at a heating rate of 10 °C min⁻¹ in air. N₂ adsorption/desorption measurements were performed by using a Quantachrome instrument (QuabradorbSI-3MP) at 77 K. The microstructure and morphology of the samples were observed under field emission scanning electron microscope (FESEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, FEI-T20).

Electrochemical Measurements: For preparing the working electrodes, active material (70 wt. %), carbon black (Super P, 15 wt. %), and sodium alginate (15 wt. %) were mixed with deionized water to form a uniform slurry, and then pasted on a Cu foil. The foil was dried at 80 °C under vacuum and then cut into electrodes with a diameter of 1 cm. In assembling the CR2025 coin-type cells, a Celgard 2400 was used as a separator and a lithium foil was used as the counter electrode. 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1 in volume) was employed as an electrolyte. The galvanostatic discharge-charge cycling of the assembled cells was executed using a Land CT2001A battery test system in the voltage range of 0.01~2.5 V at a scanning rate of 0.02 mV s⁻¹.

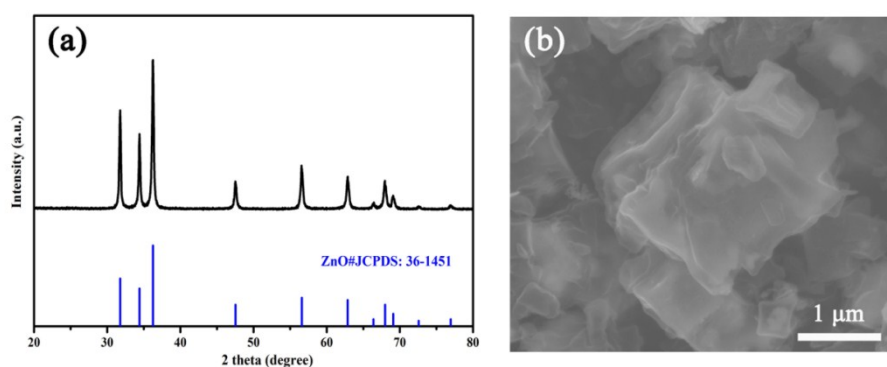


Fig. S1 (a) XRD patterns and (b) FESEM image of carbonized MOF-5 precursor

The detailed calculation of the about carbon content in ZnS/PC from the TGA profile of carbonized MOF-5: The ZnO content in carbonized MOF-5 can be calculated as $73.9 \% / 96.5 \% = 76.6 \%$. It is assumed that the total mass of carbonized MOF-5 is 100 g, the mass of carbon and ZnO would be 23.4 g and 76.6 g respectively. The corresponding mass of ZnS would be $76.6 * 97 / 81 = 91.7$ g (The molecular weight of ZnS and ZnO are 97 and 81, respectively), so the carbon content in ZnS/PC will be $23.4 / (23.4+91.7) = 20.3\%$, which is close to the value from the TGA profile of ZnS/PC.