Supporting Information (SI) for

The structure control of ZnS/graphene composites and their excellent properties for lithium-ion battery

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Experimental Details

Preparation of graphene oxide (GO). GO was prepared from purified natural graphite according to the Hummers method[1]. In detail, graphite powder (1.0 g), $NaNO_3$ (0.5 g) and $KMnO_4$ (3.0 g) were slowly added into concentrated H_2SO_4 (98%, 23 mL) cooled by ice bath and the mixture was vigorously stirred at 35±3°C for 30 min. On completion of the reaction, deionized water (46 mL) was added into above solution, and the temperature was kept at 98 °C for 15 min. Then the temperature was reduced to 60 °C with the addition of warm deionized water (140 mL), H_2O_2 (30%, 10 mL) was added and the reaction was further stirred for 2 h. The above mixture was filtrated to collect the solid product and washed with aqueous HCl (4 wt %) for 5 times, and then washed repeatedly with deionized water until the pH of the supernatant was neutral. Finally the material was dried in vacuum to obtain a loose brown powder.

Synthesis of ZnS/graphene composites. 10 mg of GO was dispersed in 30 mL of ethanol and sonicated for 0.5 h (Branson Sonifer S-450A, 400 W). 0.168 g of $Zn(Ac)_2$ was added into as-prepared GO dispersions while stirring for 0.5 h, followed by the addition of 0.225 g of thioacetamide. The mixture was then transferred into a 50 mL Teflon-lined stainless steel autoclave, sealed tightly, and heated at 180 °C for 6 h. After cooling naturally, precipitates were collected by centrifugation, washed with deionized water and ethanol, and dried in a vacuum oven at 60 °C for overnight. The composites were annealed in a conventional tube furnace at 350 °C for 2 h in a stream of argon flowing at 200 sccm (standard cubic centimeter per minute).

Characterization. Field emission scanning electron microscopy (FESEM, Model JSM-7600F, JEOL Ltd., Tokyo, Japan) was used to characterize the morphologies and size of the synthesized samples. The chemical composition was investigated by the energy dispersive spectroscopy (EDS). High resolution transmission electron microscopy (HRTEM) images were carried out with a JOEL JEM 2100F microscope. X-ray powder diffraction (XRD) patterns were recorded on a Bruke D8 Advance powder X-ray diffractometer with Cu Kα (λ =0.15406 nm). X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250. Thermogravimetric analysis (TGA) was measured from 30 to 800 °C at a heating rate of 10 °C/min under 80 mL/min of

flowing air with a Perkin-Elmer TGA 4000.

Electrochemical Measurements. To evaluate the electrochemical performance of ZnS/graphene composites, coin-type cells were assembled in an argon-filled glove box. For preparing the working electrodes, the active material, carbon black and carboxyl methyl cellulose (CMC) were mixed in a weight ratio of 80:10:10, and in deionized water and absolute alcohol mixture, stirred at a constant speed for 24 h in order to form a homogeneous slurry, which was spread uniformly on a copper foil. The coated copper foil was cut into round pieces with a diameter of 1 cm, dried at 60 °C in vacuum overnight. A Celgard 2400 microporous polypropylene membrane was used as a separator. The electrolyte contained a solution of 1 M LiPF6 in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1, in wt %). These cells were assembled in the glovebox (Super 1220/750, Switzerland) filled with highly pure argon gas (O_2 and H_2O levels less than 1 ppm). The cells were aged for 12 h before the measurements to ensure percolation of the electrolyte to electrodes. The cyclic voltammetry and galvanostatic cycling was performed using an Arbin BT2000 system in the voltage of 0.01-3.0 V (vs. Li^+/Li). Nyquist plots were recorded using a Zahner IM6 electrochemical work station.

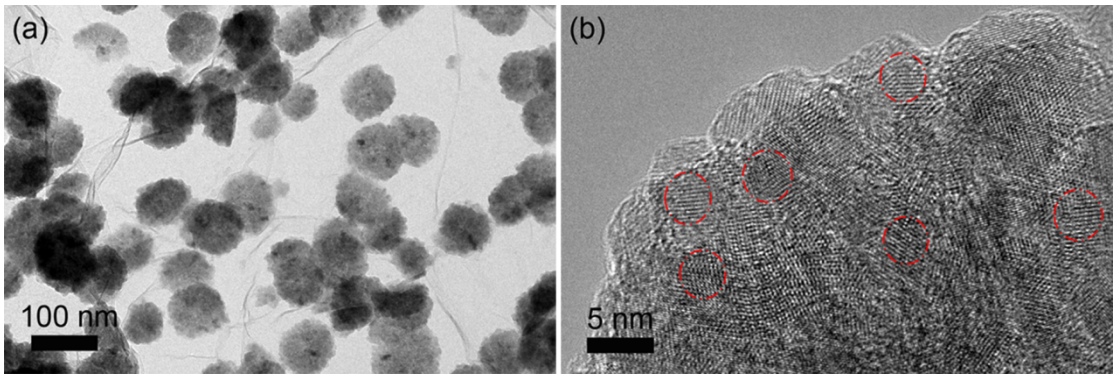

Fig. S1 (a, b) TEM and HRTEM images of ZnS/graphene composites.

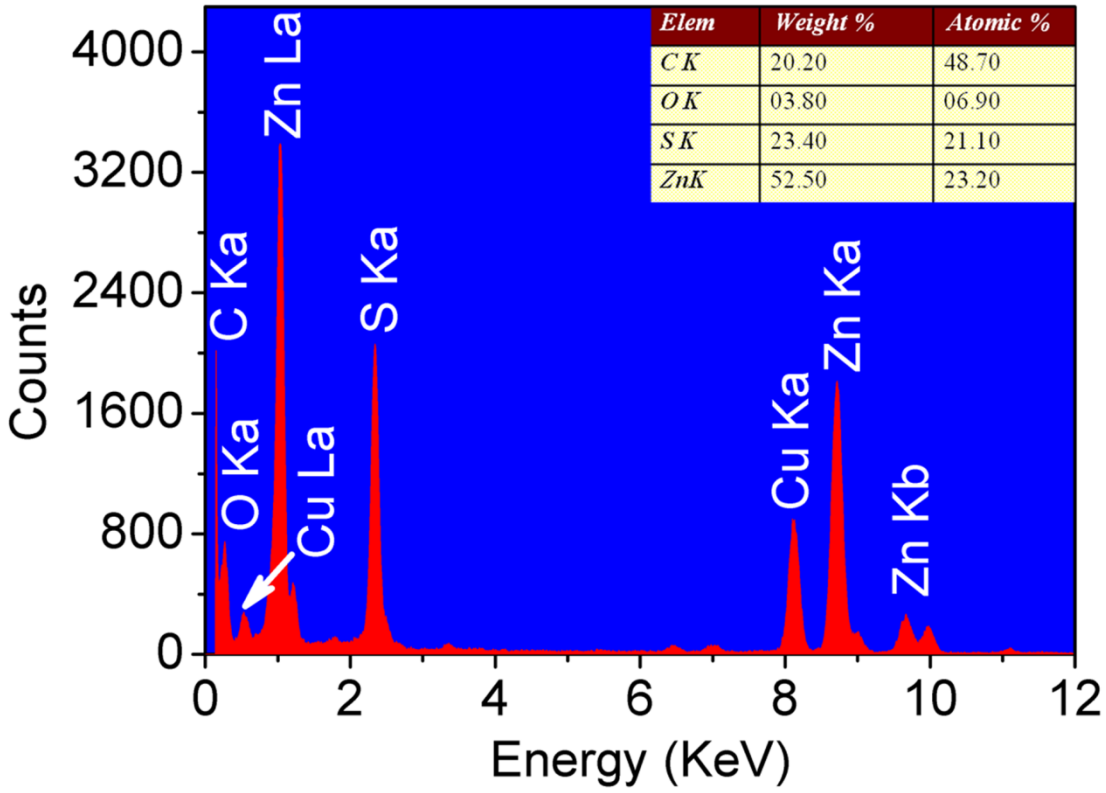

Fig. S2 The energy dispersive spectroscopy spectra of ZnS/graphene composites.

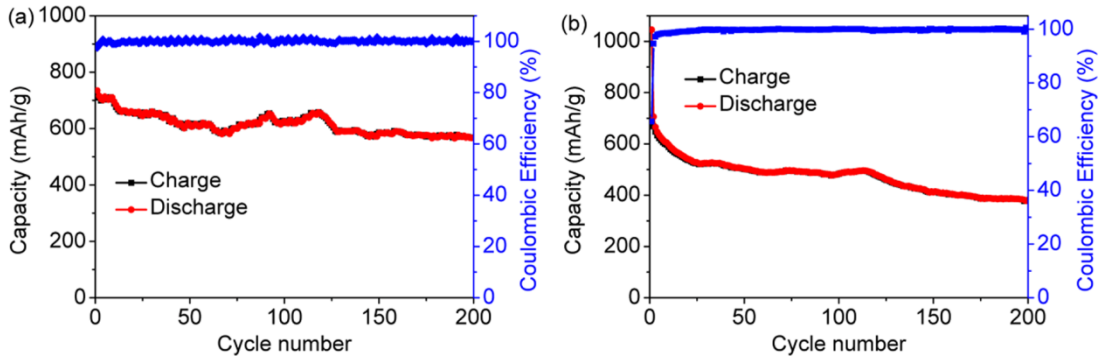

Fig. S3 Cycling performance and Coulombic efficiency of ZnS/graphene composites tested at a current density of 200 mA/g (a) and 2000 mA/g (b) in the range of 0.01-3 V (vs. Li^+/Li).

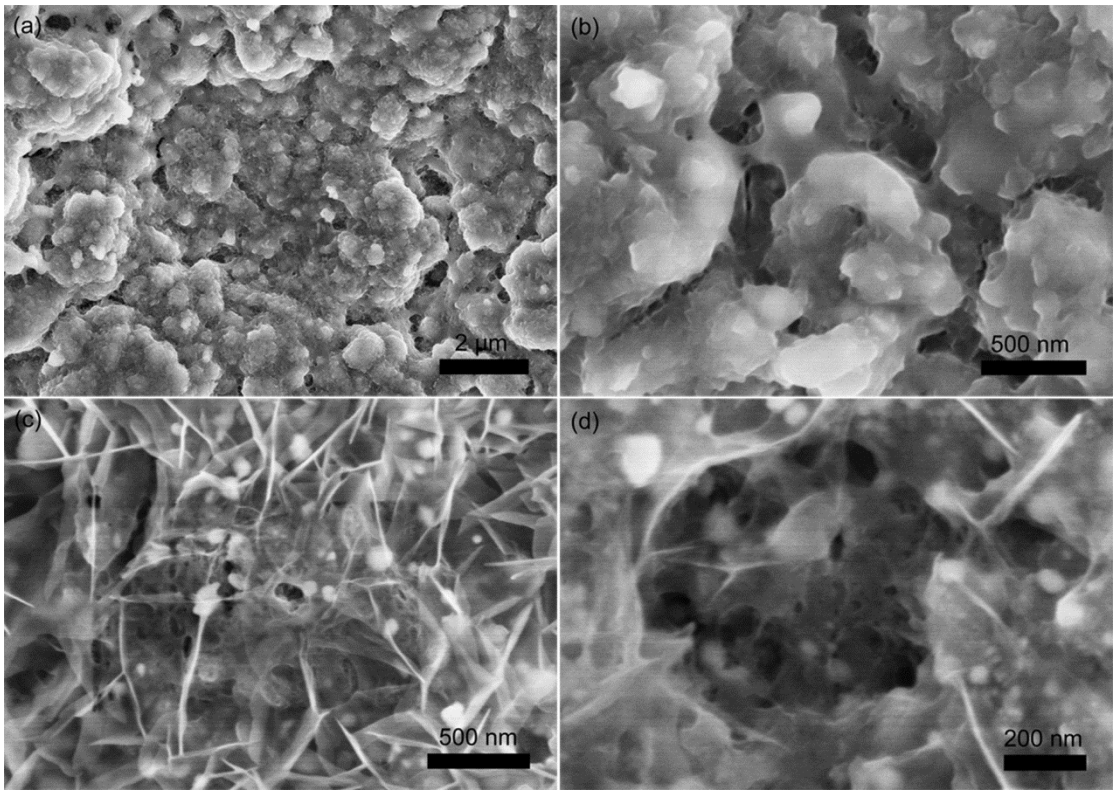

Fig. S4 SEM images of ZnS/graphene composites (a, b) and bare ZnS (c, d) after 200 cycles.

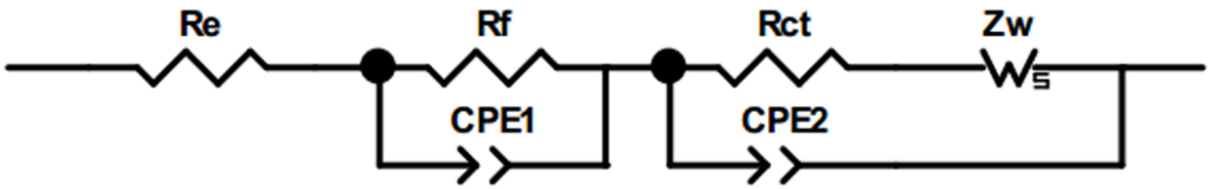

Fig. S5 Equivalent circuit model of the studied system.

electrode	R_e (Ω)	R_f (Ω)	Q_1 (μF)	R_{ct} (Ω)	Q_2 (μF)
ZnS	3.23	795.9	83.97	11.255	205.49
ZnS/graphene	4.66	170	783.25	5.368	188.95

Table S1. Impedance Parameters Derived Using Equivalent Circuit Model for ZnS and ZnS/graphene composites Electrodes after 200 cycles.

REFERENCES

1. B. Li, H. Cao, J. Shao, G. Li, M. Qu and G. Yin, *Inorganic Chemistry*, 2011, 50, 1628-1632.