Scalable Synthesis of FeS$_2$ Nanoparticles Encapsulated into N-doped Carbon Nanosheet as High-performance Sodium-ion Battery Anode

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Experimental

Method

Synthesis of ZnO/CNS: The ZnO/CNS template was prepared by solution combustion methods. In a typical process, 5.68 g of Zn(NO$_3$)$_2$ and 1.80 g of glucose was dissolve in 20 ml of deionized water in a beaker. After 10 min magnetic stirring, the beaker was placed into an oven and heated at 220°C. After several minutes，the brownness foamy product was generated. Then the product was annealed at 800°C for 1 h under N$_2$.

Synthesis of FeS$_2$/CNS: 0.2 g of obtained ZnO/CNS template was soaked into the solution of 6.48 g FeCl$_3$ and 100 ml deionized water for 6 h. The obtained powders were filtered and washed with deionized water and ethanol three times and dried at 80°C overnight. Then 0.5 g as-prepared precursor and 3 g sulfur powder were loaded into two individual boats and placed in the middle and upstream of the furnace. After annealed at 500°C for 2 h with a temperature rate of 2°C min^{-1} at N$_2$ atmosphere, FeS$_2$/CNS was obtained. For comparison, bulk FeS$_2$ was synthesis by the same method except for ZnO/CNS template was annealed at 800°C for 1 h under air. Pure CNS was obtained by removing the particles on the ZnO/CNS template with 2 M HCl.

Material characterization

The X-ray diffraction patterns were conducted on Rigaku D/max 2500 using Cu Ka radiation worked in the 2θ range of 10-90° with a scanning step of 0.12° s^{-1}. Raman and XPS measurement were performed by Renishaw RM1000 micro spectroscopic system and Thermo K-Alpha XPS spectrometer respectively. The BET specific surface areas were obtained using a Micromeritics ASAP 2020 analyzer at the boiling point of liquid nitrogen (77 K). Thermogravimetric analysis (TGA) was carried out in air (air flow: 100 ml min^{-1}) with a heating rate of 10°C min^{-1} from 30 to 800°C. The materials morphologies were measured by FESEM (Hitachi S-4800) and TEM (JEM-2010 JEOL, 200 kV).

Electrochemical measurements

The sodium storage performances of all samples were characterized by fabricating CR2032 coin-type half-cells in an Ar glove box. The anode electrode was prepared by

mixing the active material, acetylene black, and polyvinylidene fluoride (PVDF) binder with a mass ratio of 8:1:1 in N-methyl-2-pyrrolidone solvent. The obtained slurry was coated onto copper (Cu) foil and dried at 110 °C under vacuum for 12 h. Generally, the mass loading of the active material is about packing density of $\sim$0.8 g cm^{-3}. The electrolyte was a solution of 1 M $NaCF_3SO_3$ in diglyme with 5 % fluoroethylenecarbonate (FEC) additive. CV measurements were carried out by a CHI660E electrochemical workstation. LAND-BT2013A measurement system is responded for testing cycling performance and rate capacity at 25 °C.
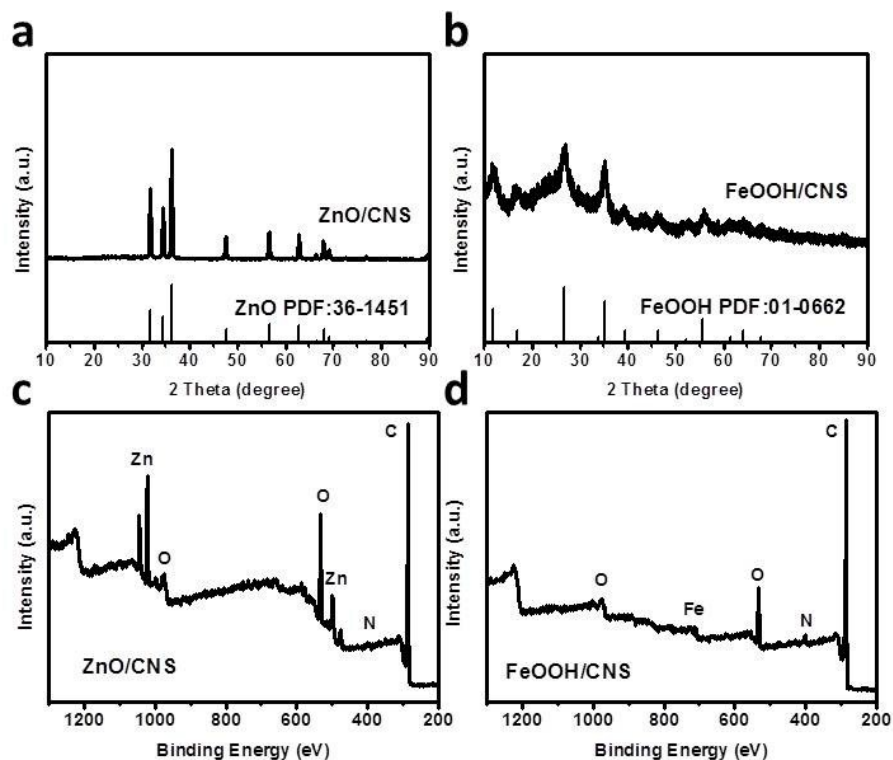
Fig. S1. XRD patterns of (a) ZnO/CNS and (b) FeOOH/CNS; survey XPS spectra of (c) ZnO/CNS and (d) FeOOH/CNS.
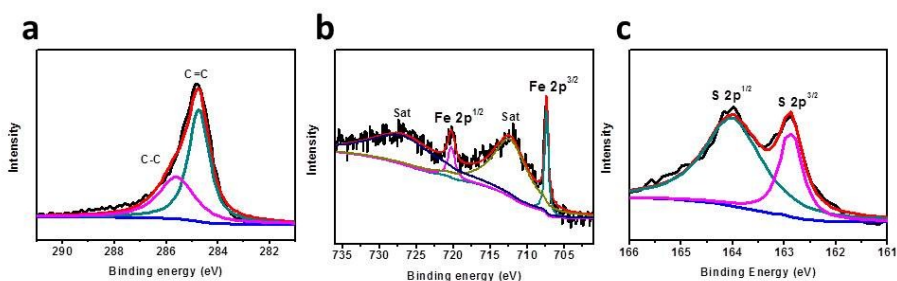

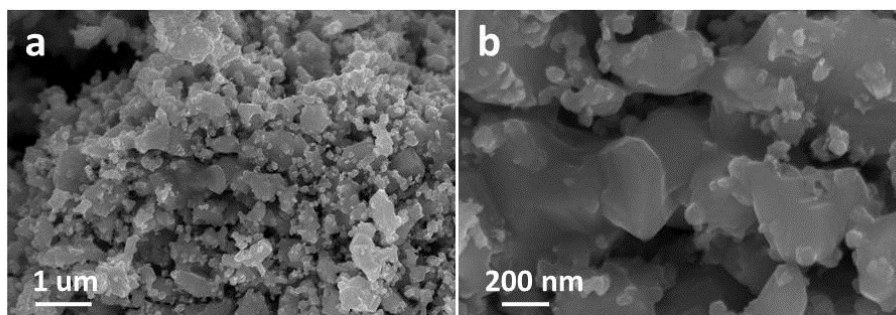**Fig. S2**. (a)-(c) High resolution XPS spectra of C 1s, Fe 2p and S 2p in FeS_2/CNS, respectively.

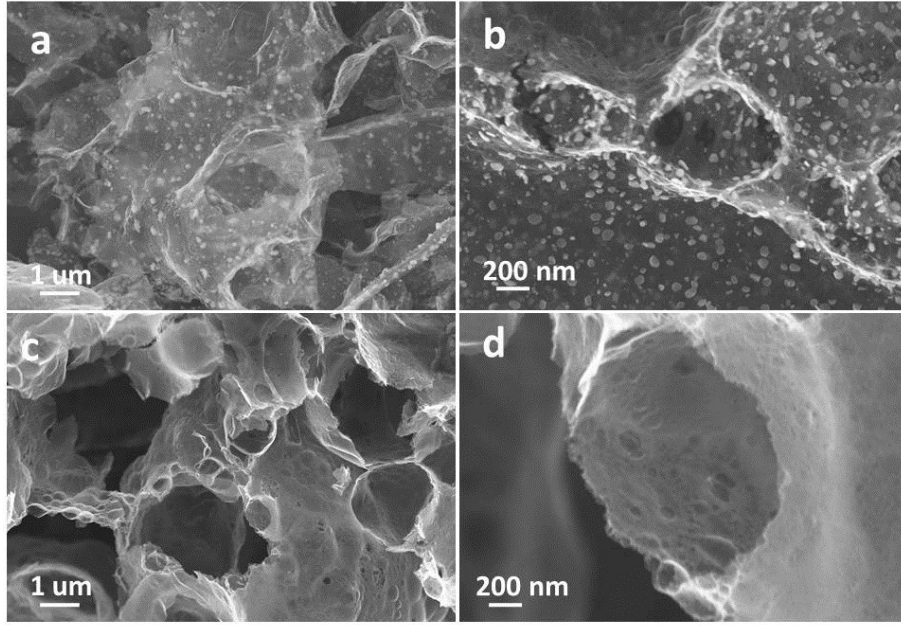**Fig. S3.** (a)-(b) SEM images of bulk FeS_2, showing dense agglomerates.

Fig. S4. SEM images at different magnifications of (a)-(b) ZnO/CNS and (c)-(d) CNS.

Base on the fact that FeS_2 is fully converted into Fe_2O_3 at 800°C in air, it can be calculated that the weight content of carbon and FeS_2 in FeS_2/CNS composite is around 8.5% and 91.5%, respectively. The detailed calculation process is presented as follow:

$$wt(FeS_2) = \frac{wt(residue) \; x \; 2 \; M(FeS_2)}{M(Fe_2O_3)} = \frac{wt(residue) \; x \; 240}{160} = wt(residue) \; x \; \frac{3}{2}$$

$$wt(C) = 100\% - wt(FeS_2)$$

Thus, the FeS_2 content of two FeS_2/CNS composite showed in Fig. S5 is 91.5% and 68.6%, respectively. It is feasible to control the content of FeS_2 in the composite by controlling the amount of glucose during solution combustion process. With higher content of FeS_2, the composite performs higher specific capacity and poorer cycle stability.
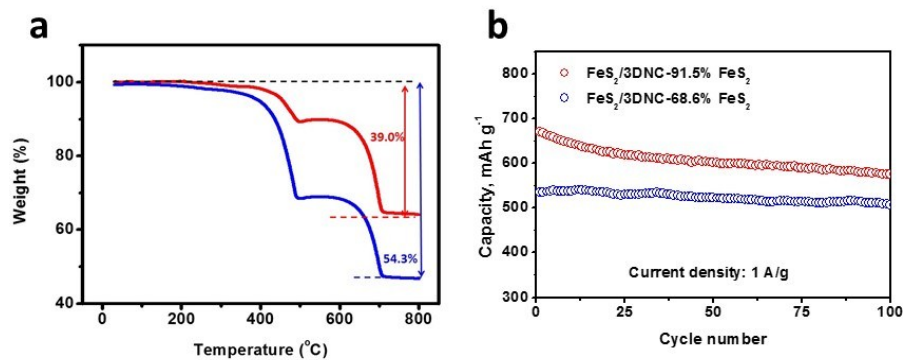
Fig.   S5. (a) TG curves and (b) cycling performance of the FeS$_2$/CNS with different FeS$_2$ content.
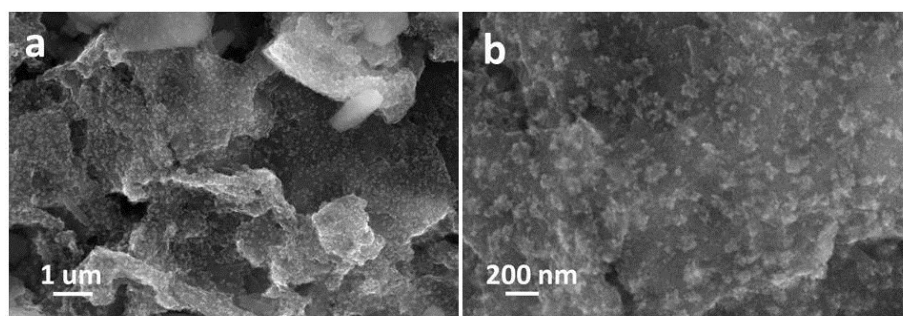

Fig.   S6. (a)-(b) SEM images of FeS$_2$/CNS electrode after 50 cycles at 1 A g^{-1}.

The specific surface area of FeS$_2$/CNS, CNS and FeS$_2$ are 576.6, 2446.3, 5.33 m^2 g^{-1}, respectively. It is proved that the composited construction of FeS$_2$ and CNS greatly improves the specific surface area of FeS$_2$.
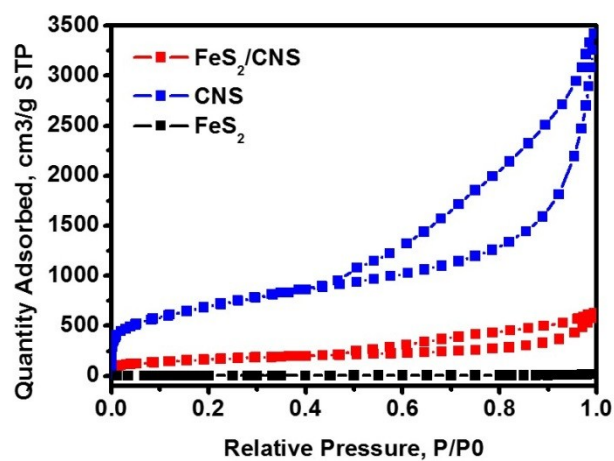

Fig.   S7. Nitrogen adsorption-desorption isotherms of FeS$_2$/CNS, FeS$_2$ and CNS.