Electronic Supplementary Information:

Sponge-Like $NaFe_2PO_4(SO_4)_2$@rGO as High-Performance Cathode Material for Sodium-ion Batteries

Shao-Fang Li[a], Xian-Kun Hou[a], Zhen-Yi Gu[b], Yun-Feng Meng[a], Chen-De Zhao[a], Hong-Xia Zhang[a], Xing-Long Wu[a,b,*]

[a] National & Local United Engineering Laboratory for Power Batteries, Faculty of Chemistry, Northeast Normal University, Changchun 130024, Jilin China

[b] MOE Key Laboratory for UV Light-Emitting Materials and Technology, Northeast Normal University, Changchun, 130024, Jilin, China

[*]Corresponding author. E-mail address: xinglong@nenu.edu.cn.

Experimental Section:

Preparation Details. The NFPS@rGO material were successfully synthesized by a simple sol-gel self-propagating combustion and carbon-coating freeze-drying process. Firstly, 0.02 mol citric acid dissolved in 6 ml deionized water. Then adding the following component in sequence: 0.02 mol $Fe(NO_3)_3$, 0.01 mol $NaNO_3$, 0.01 mol $NH_4H_2PO_4$, and 0.02 mol $(NH_4)_2SO_4$, respectively. Using ammonium hydroxide to adjust pH = 4.5, the solution was magnetic stirring at 80 °C to obtain a clear and transparent green solution. After the water evaporates, a green wet gel was obtained. The wet gel was maintained at 120 °C for 6 h in a vacuum oven to form green dry gel. A small amount of ethanol absolute ignites in a crucible in a fume hoods, and a brick red loose spongy NFPS was obtained. Secondly, the product was evenly dispersed in an aqueous solution of graphene oxide (the graphene oxide was prepared by Hummers' method), the solution is sealed in a beaker and then quickly put into liquid nitrogen to freeze and dried until ice was removed. Finally, the precursor was transferred into a quartz tube filled with Ar atmosphere and annealed at 400 °C for 4 hours to obtain black NFPS@rGO. This material has excellent conductivity, thermal stability and a small amount of magnetism. However, its moisture absorption results in the material having to be stored in a glove box.

Material Characterizations. The crystalline of the materials was analyzed by X-ray diffraction (XRD) with a Rigaku Smart Lab X-ray diffractometer (Cu-Kα radiation, λ = 1.5418 Å) with the scan range (2θ) of 10–80°. Raman spectra on a JY HR-800 Lab Ram confocal Raman microscope in a backscattering configuration with an excitation wavelength of 514.5 nm. The size and morphology of the prepared materials were evaluated by Scanning electron microscope (SEM, HITACHI-SU8000) and transmission electron microscope (TEM, JEOL-2100F). Brunauer-Emmett-Teller (BET) specific surface area of the material was determined by utilizing an ASiQwin using the standard N_2 absorption

and desorption isotherm measurement at 77.35 K, after degassing the samples at 300 °C for 12h in vacuum. The carbon content was tested by thermogravimetric analysis (TGA) with N_2 flow from 30 to 800 °C and temperature ramp of 10 °C min^{-1}.

Electrochemical Measurements. The electrochemical measurements were measured in CR2032 coin cells with sodium metal as the counter electrode and with glass fiber (Whatman) as the separator and assembled in an Ar-filled atmosphere glove-box and the oxygen and the moisture contents were less than 0.1 ppm. Polyvinylidene Fluoride (PVDF), active material, and acetylene black were mixed in N-methyl-2-pyrrolidinone (NMP) at a weight ratio of 1:7:2 and which was slurry on aluminum foil as the working electrodes and dried at 100 °C in vacuum overnight. The loading density of the electrodes was about 1.5-2 mg cm^{-2}. 1 M $NaClO_4$ dissolved in a mixture of propylene carbonate (PC) with 5 wt % Fluoroethylene carbonate (FEC) as the electrolyte. The galvanostatic charge/discharge (GCD) tests were performed between the range of 2.0-4.4 V versus Na^+/Na at 25 ℃ and used Land CT2001A as the battery-testing systems. The CVs was performed on CHI 600E electrochemical workstation. The GITT were tested by Arbin battery tester and the voltage range is 2.0-4.4 V versus Na^+/Na at the current density of 25 mA g^{-1}. The duration time for each testing and applied galvanostatic current were 6 hours and 10 minutes, respectively. The electrochemical impedance spectroscopy (EIS) tests were implemented by using a PMC2000 (Princeton Applied Rearch) with the frequency ranging from 100 kHz to 0.1 Hz with an amplitude voltage of 10 mV.

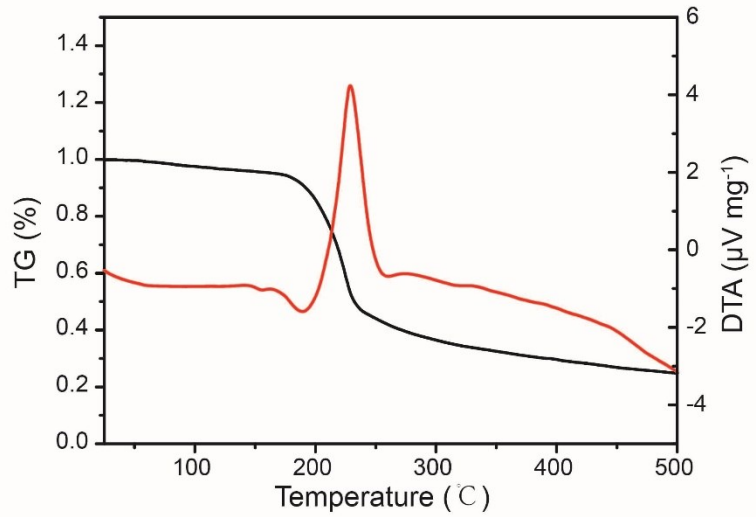

Fig S1. The DTA and TG curves of the NFPS dry gel.

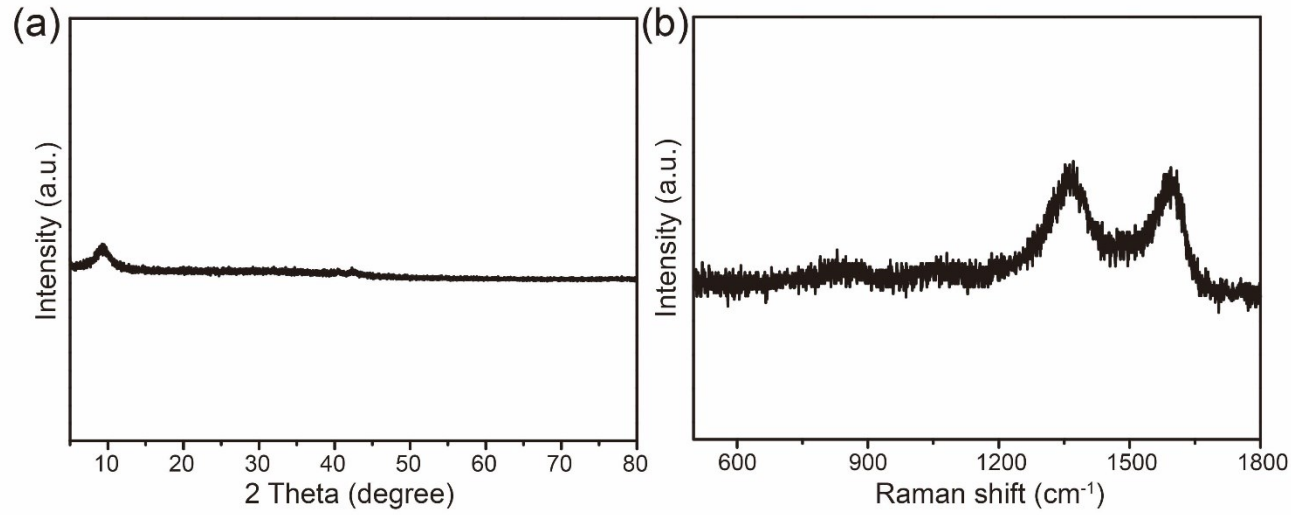

Fig S2. (a) XRD pattern and (b) Raman spectra of the rGO.

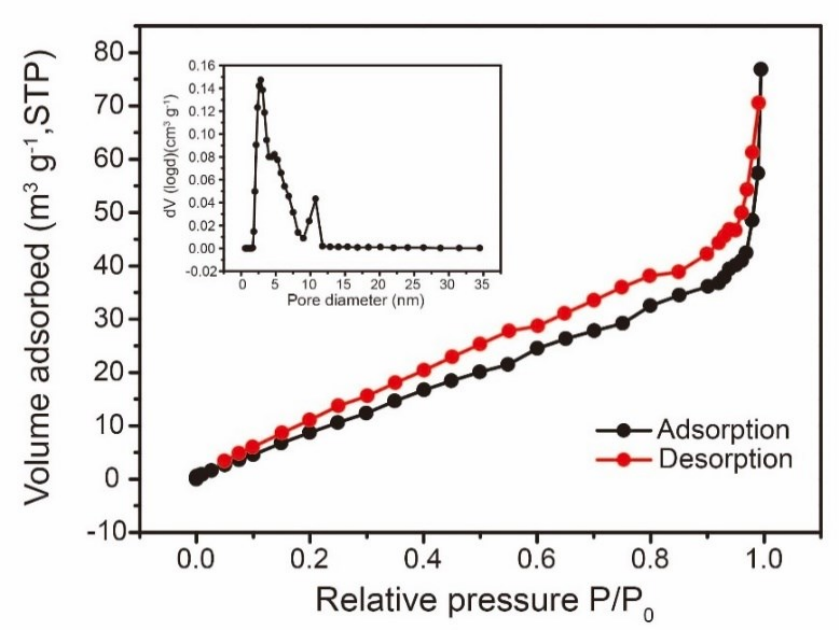

Fig S3. N_2 absorption-desorption isotherms of the NFPS@rGO sample. The inset is the corresponding pore size distribution plots.

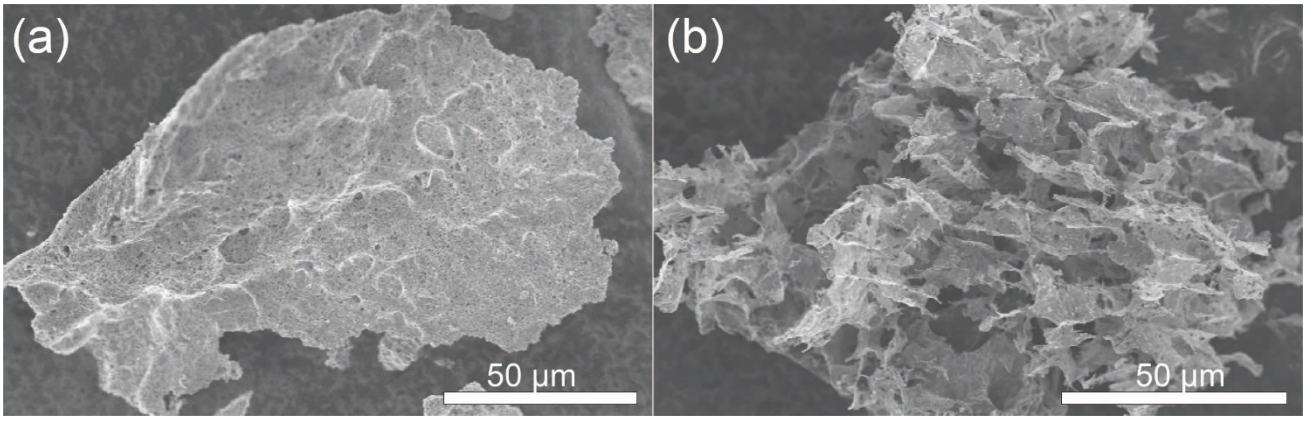

Fig S4. The SEM of (a) NFPS and (b) NFPS@rGO material.

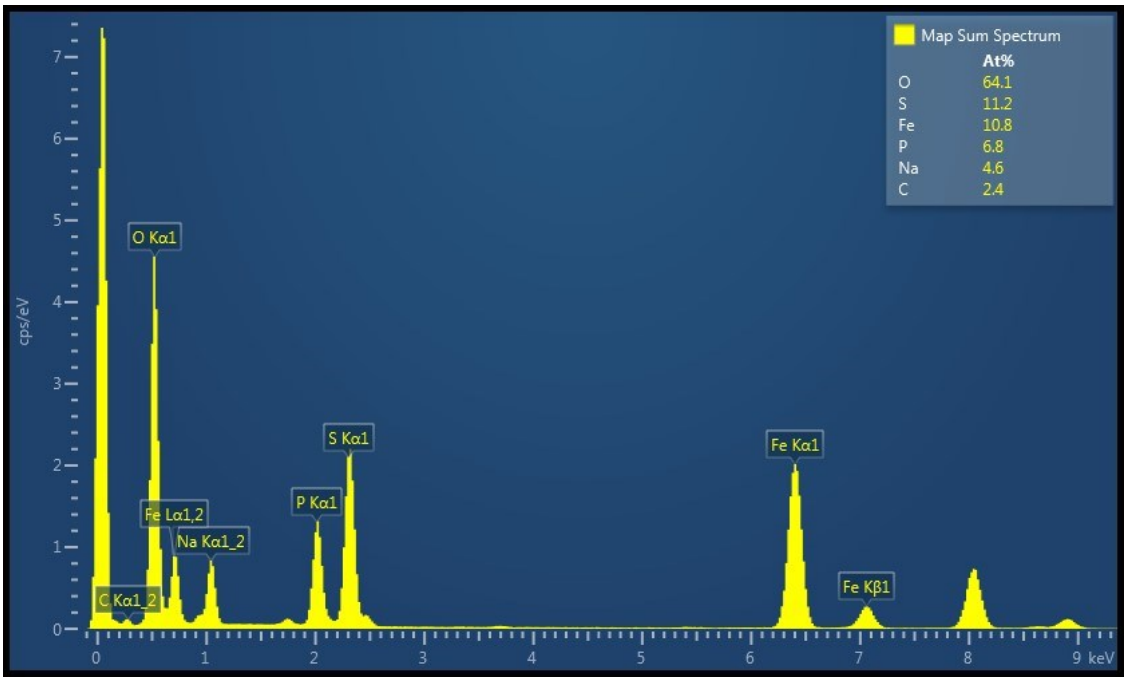

Fig S5. The EDX element content of NFPS@rGO material.

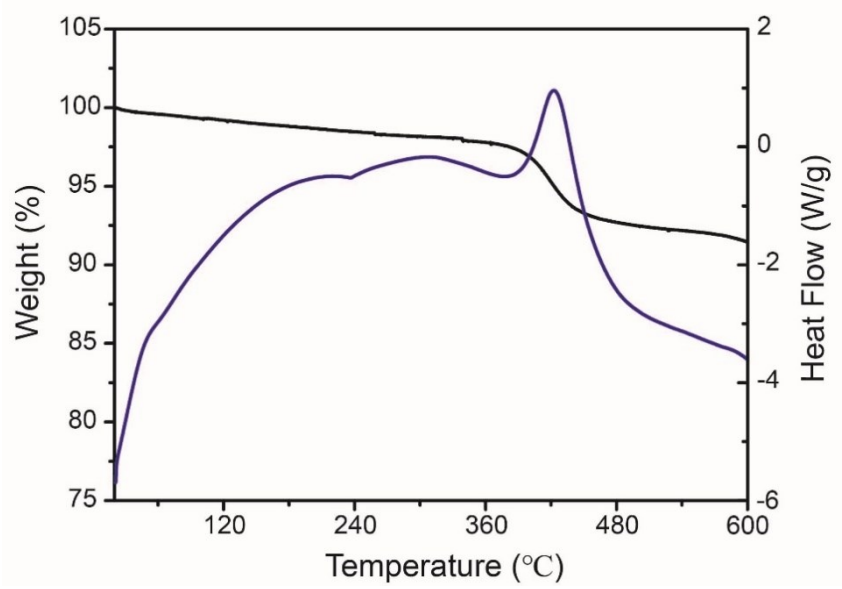

Fig S6. TGA curves of the NFPS@rGO samples.

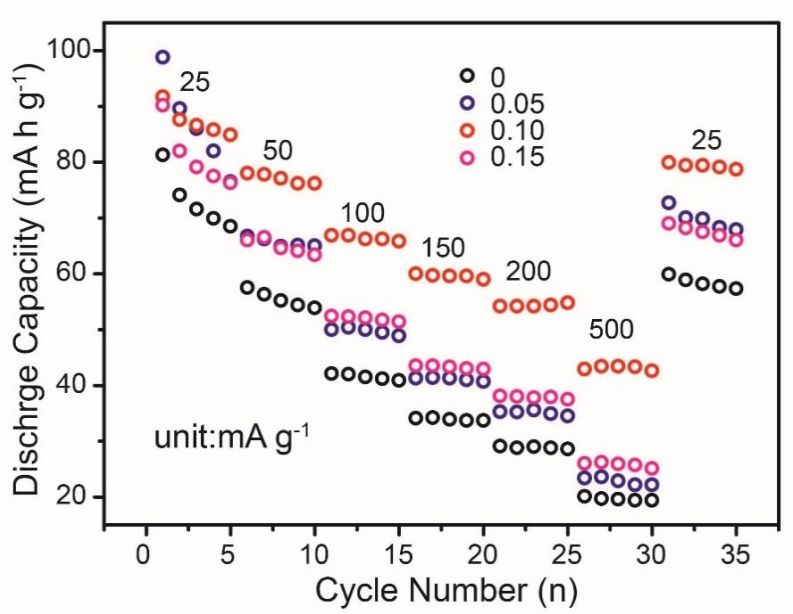

Fig S7. Rate performance of NFPS and NFPS@rGO at different current densities with various carbon contents.

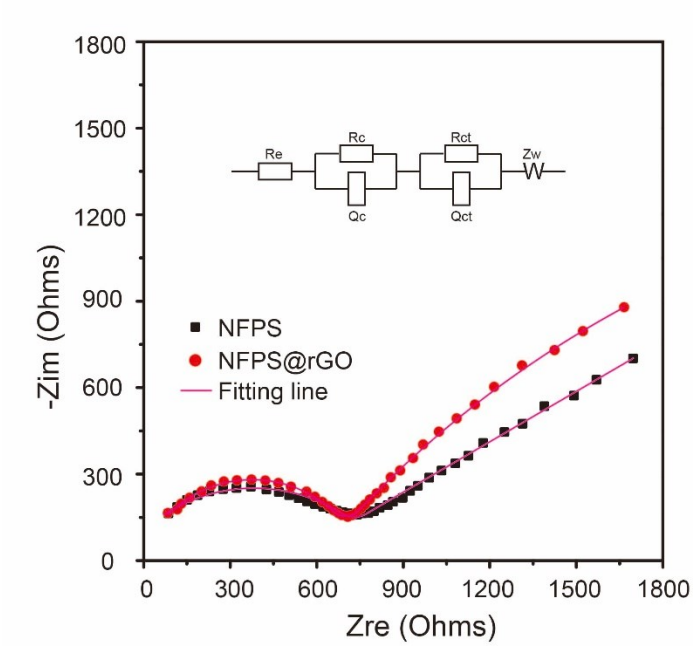

Fig S8. Nyquist plots of electrochemical impedance spectra (EIS) of NFPS and NFPS@rGO.

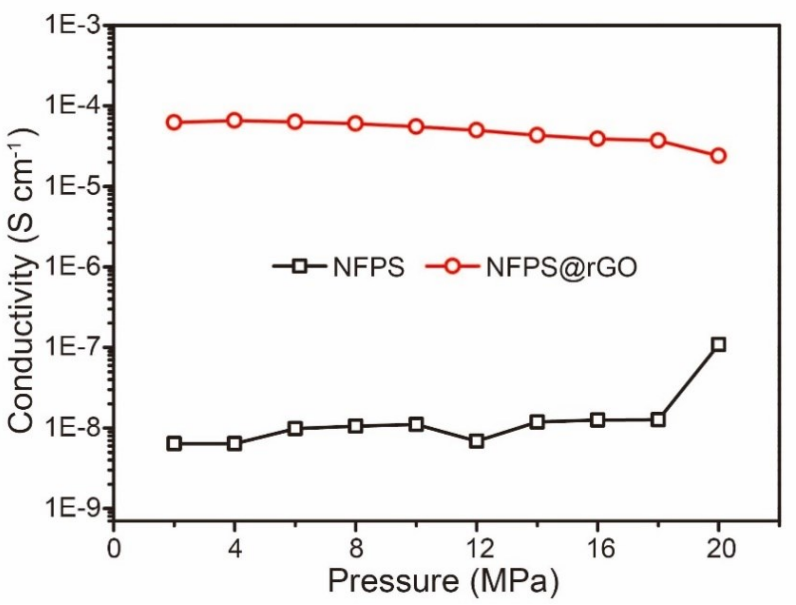

Fig S9. The electronic conductivity of NFPS and NFPS@rGO.

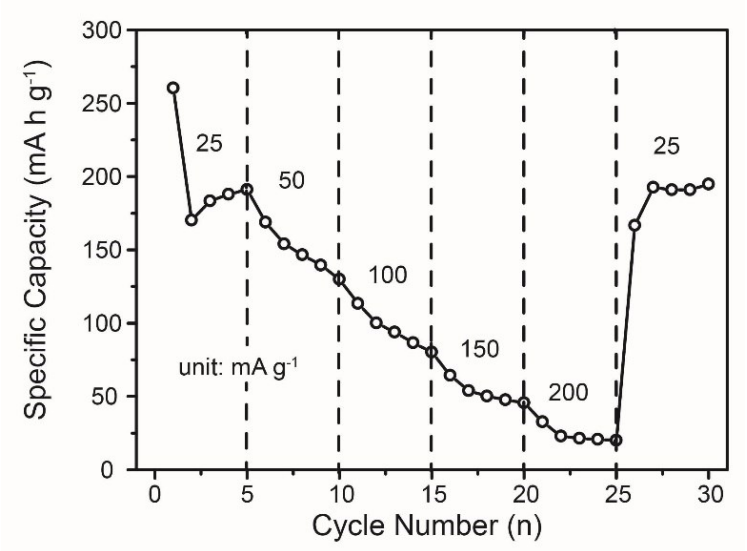

Fig S10. Rate performance of carbon cloth at different current densities.

Table S1. The CV linear fitting results of NFPS and NFPS@rGO.

CV	NFPS	NFPS@rGO
A(cm^2)	1.13	
C(mol cm^{-3})	0.00939	0.01056
$Slope_{ch}$	0.0009762	0.00464
$Slope_{dis}$	-0.00163	-0.00473
D_{ch}(cm^2 s^{-1})	1.17×10^{-13}	2.09×10^{-12}
D_{dis}(cm^2 s^{-1})	3.26×10^{-13}	2.17×10^{-12}
D_{ave}(cm^2 s^{-1})	2.215×10^{-13}	2.13×10^{-12}

Table S2. The GITT linear fitting results of NFPS and NFPS@rGO.

GITT	NFPS	NFPS@rGO
τ(s)	600	
S (cm^2)	1.13	
m_B (mg)	0.72	0.61
$\rho=M_B/V_M$ (g cm^{-3})	3.233	3.174
D_{ch}(cm^2 s^{-1})	1.03×10^{-12}	1.61×10^{-12}
D_{dis}(cm^2 s^{-1})	2.53×10^{-12}	8.46×10^{-12}
D_{range}(cm^2 s^{-1})	$1.03\sim2.53\times10^{-12}$	$1.61\sim8.46\times10^{-12}$