

## Supporting Information

# Excellent cycling stability and superior rate capability of graphene-amorphous FePO<sub>4</sub> porous nanowire hybrid as cathode material for sodium ion batteries

Gaoliang Yang<sup>a</sup>, Bing Ding<sup>a</sup>, Jie Wang<sup>a</sup>, Ping Nie<sup>a</sup>, Hui Dou<sup>a</sup>, and Xiaogang Zhang<sup>\*a</sup>

Jiangsu Key Laboratory of Materials and Technology for Energy Conversion, College of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing, 210016, P. R. China. E-mail: azhangxg@nuaa.edu.cn

## Experimental section

### *Material synthesis*

#### *Preparation of graphene-amorphous FePO<sub>4</sub> porous nanowire hybrid.*

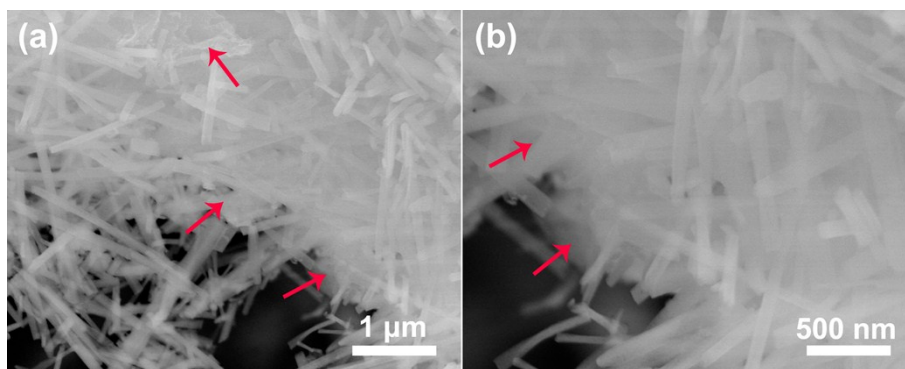
Graphene-amorphous FePO<sub>4</sub> porous nanowire hybrid were synthesized by a hydrothermal approach which has been reported by Cai et al. previously<sup>[S1]</sup>, followed by stirring with hydrazine hydrate under 90 °C. In a typical synthesis, GO solution was firstly synthesized by oxidizing graphite powder in a strong acidic medium, according to a modified Hummer's method. And then, (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1176 g), H<sub>3</sub>PO<sub>4</sub> (123 μL), urea (3.6 g), and SDS (0.3 g) were dissolved in the homogeneous GO suspension (60 mL, 0.25 mg mL<sup>-1</sup>). The mixture was vigorously stirred for approximately 10 min, transferred into an autoclave, and heated to 80 °C for 12 h. After naturally cooling to ambient temperature, the resulting products were collected by centrifugation, washed sequentially with distilled water and ethanol at least three times, and then dried at 100 °C for 12 h. The obtained products were then mixed with 5 mL hydrazine hydrate in a sealed bottle and stirred for 24 h under 90 °C. After cooling down naturally, the products were obtained by centrifugation and then dried at 100 °C for 12 h.

### *Materials characterization*

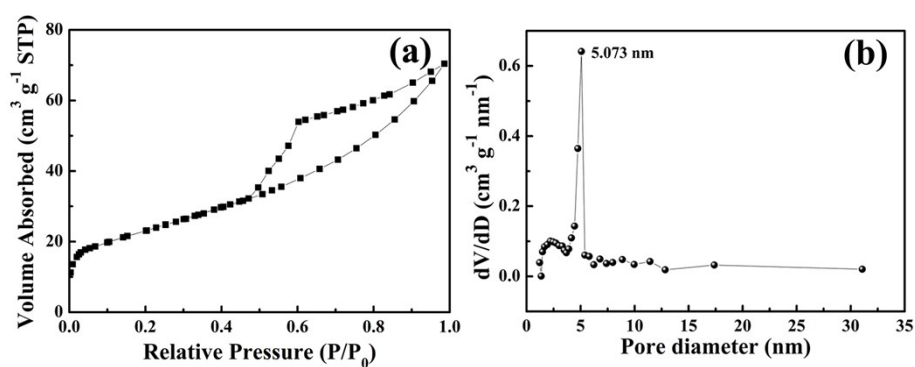
In our investigation, Hitachi S-4800 scanning electron microscopy (SEM) and JEOL JEM-2100 transmission electron microscopy (TEM) were used to observe the morphology and structure of the samples. Energy Dispersive Spectroscopy (EDS) elemental mapping attached to the TEM instrument was used to determine elementary composition. Powder X-ray diffraction (XRD) patterns were measured on a Bruker-AXS D8 DISCOVER. Copper Ka line ( $\lambda = 0.15406$  nm) was used as a radiation source. Raman spectrum measurements were carried out using a Horiba Raman spectrometer with a 514.5 nm wavelength incident laser light. The  $N_2$  adsorption/desorption tests were determined by Brunauer-Emmett-Teller (BET) measurements using an ASAP-2010 surface area analyzer. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a PerkinElmer PHI 550 spectrometer with Al Ka (1486.6 eV) as the X-ray source. thermogravimetric (TG) analysis was conducted under an air atmosphere at a heating rate of  $10$  °C  $\text{min}^{-1}$  from  $30$  to  $700$  °C on a TG-DSC instrument (NETZSCH STA 409 PC).

### ***Electrochemical measurements***

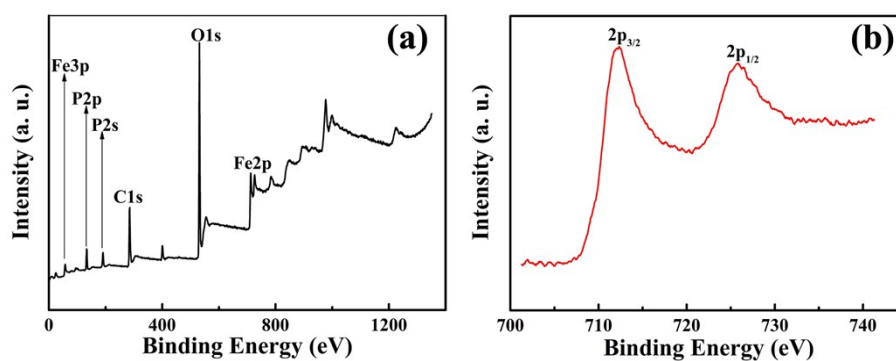
Electrochemical characterization was carried out using 2032 coin cells with Na metal as the counter electrode. The electrodes were prepared by mixing active material with acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1. The slurry was then spread onto an Al foil and dried under vacuum at  $110$  °C for 12 h. The mass loading of active material on the electrode is about  $1.5$   $\text{mg cm}^{-2}$ . Test cells were assembled in an argon-filled glove box using Na metal as the counter electrode, glass microfiber filters (GF/D, Whatman) as the separator and  $1$  M  $\text{NaClO}_4$  in a mixture of ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 by volume) as the electrolyte. Galvanostatic charge-discharge cycles were performed on a 2001A battery tester (Land Instruments). Cyclic voltammetric measurements were performed at a scan rate of  $0.1$   $\text{mV s}^{-1}$  on a CHI 750D electrochemical workstation (Chenhua Instruments Co., China). The electrochemical impedance spectroscopy was measured by using a Solatron 1260 Impedance Analyzer in the frequency range  $10^{-2}$ - $10^6$  Hz.



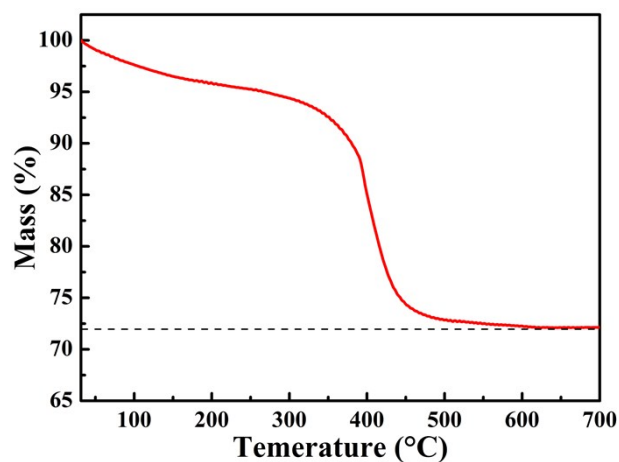
**Fig. S1** SEM images of the graphene-FePO<sub>4</sub> hybrid.



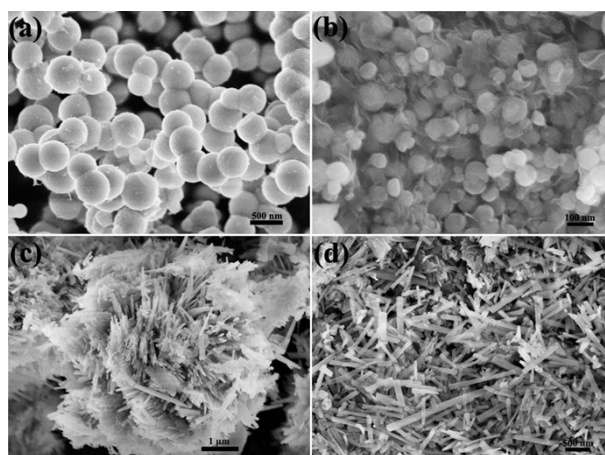
**Fig. S2** (a) N<sub>2</sub> adsorption-desorption isotherms, and (b) the corresponding pore size distribution of graphene-FePO<sub>4</sub> hybrid.



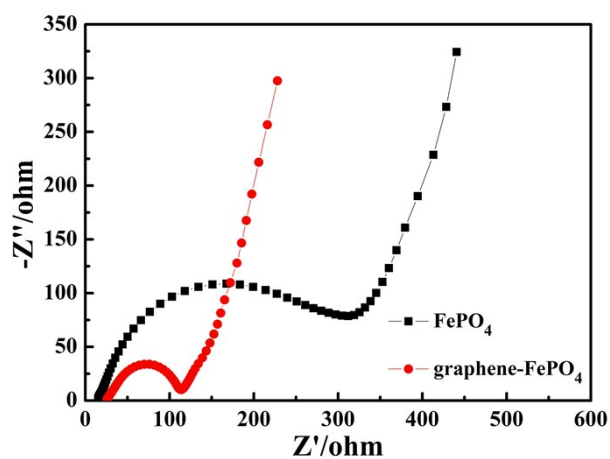
**Fig. S3** (a) Survey XPS spectrum; (b) spectrum in the region of the Fe2p peak of graphene-FePO<sub>4</sub> hybrid.



**Fig. S4** TG curve of the graphene-FePO<sub>4</sub> hybrid under air.



**Fig. S5** SEM images of (a) FePO<sub>4</sub> nanospheres without graphene; (b) FePO<sub>4</sub> nanospheres with graphene (c) FePO<sub>4</sub> nanorods after reacting with hydrazine hydrate under 90 °C for 12 h (without graphene); (d) FePO<sub>4</sub> nanorods after reacting with hydrazine hydrate under 90 °C for 24 h (without graphene).



**Fig. S6** EIS spectra of the FePO<sub>4</sub> and graphene-FePO<sub>4</sub> hybrid.

**Table S1** Comparison of electrochemical performances between graphene-FePO<sub>4</sub> nanowires and other previously reported results.

Electrode material	Capacity (mAh g <sup>-1</sup> )	Current density	Cycles	Maximum current density	References
graphene-FePO <sub>4</sub> nanowires	124.2	0.5 C	300	20 C	This work
FePO <sub>4</sub> /SWNTs composite	66	50 mA g <sup>-1</sup>	300	100 mA g <sup>-1</sup>	[S2]
FePO <sub>4</sub> /C nanocomposite	151	20 mA g <sup>-1</sup>	160	1000 mA g <sup>-1</sup>	[S3]
FePO <sub>4</sub> /rGO composite	130.5	0.1 C	70	1 C	[S4]
FePO <sub>4</sub> @MCNT composite	155.2	0.1 C	70	1 C	[S5]
Bio-FePO <sub>4</sub> -CNT	129	0.1 C	200	10 C	[S6]

**References:**

- [S1] Y. Yin, Y. Hu, P. Wu, H. Zhang and C. Cai, *Chem. Commun.*, 2012, 48, 2137-2139.
- [S2] Y. Liu, Y. Xu, X. Han, C. Pellegrinelli, Y. Zhu, H. Zhu, J. Wan, A. C. Chung, O. Vaaland, C. Wang and L. Hu, *Nano Lett.*, 2012, **12**, 5664-5668.
- [S3] Y. Fang, L. Xiao, J. Qian, X. Ai, H. Yang and Y. Cao, *Nano Lett.*, 2014, **14**, 3539-3543.
- [S4] Y. Liu, S. Xu, S. Zhang, J. Zhang, J. Fan and Y. Zhou, *J. Mater. Chem. A*, 2015, **3**, 5501-5508.
- [S5] S. Xu, S. Zhang, J. Zhang, T. Tan and Y. Liu, *J. Mater. Chem. A*, 2014, **2**, 7221.
- [S6] M. Moradi, Z. Li, J. Qi, W. Xing, K. Xiang, Y. M. Chiang and A. M. Belcher, *Nano Lett.*, 2015, **15**, 2917-2921.