Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# Electronic Supporting Information

# $Li_2FeSiO_4$ nanorods bonded with graphene for high performance batteries

Jinlong Yang[a,b], Lin Hu[a], Jiaxin Zheng[b], Daping He[a], Leilei Tian[b], Shichun Mu[a,*] and Feng Pan[b,*]

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China ,

[b] School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen 518055, China

**Synthesis of graphene oxide nanosheets(GONS):** GONS was synthesized from natural graphite flakes using a modified Hummers' method.[1] Graphite powder (1.0 g) was pre-oxidised in a concentrated $H_2SO_4$ solution (100 mL), into which $NaNO_3$ (1.0 g) had been added and completely dissolved. $KMnO_4$ (10.0 g) was slowly added to the mixture under vigorous agitation, and the reaction flask was subsequently heated to 40 °C. The reaction was carried out for 40 h, during which the mixture became pasty and underwent a colour change gradually from dark green to reddish brown. The slurry was diluted with 150 mL of deionized water to terminate the reaction. The colour of the mixture immediately turned to bright yellow following treatment with 10 mL of 30 wt% $H_2O_2$ to reduce the insoluble manganese species to $Mn^{2+}$ ions. The suspension stood overnight to allow the precipitate to settle out and then was centrifuged to decant the supernatant. After the precipitate was repeatedly rinsed with deionized water to remove metal ions, the formation of a viscous brown dispersion was eventually observed. Then, the graphite oxide dispersion was concentrated and lyophilised to yield fluffy powders. Finally, homogeneous and stable GONS colloids were obtained by ultrasonic exfoliation of a diluted graphite oxide hydrogel with a known concentration. The mixture was bath-sonicated for 10 min and then centrifuged for 5 min. The supernatant, which contained almost exclusively thin layer of GONS, was collected.

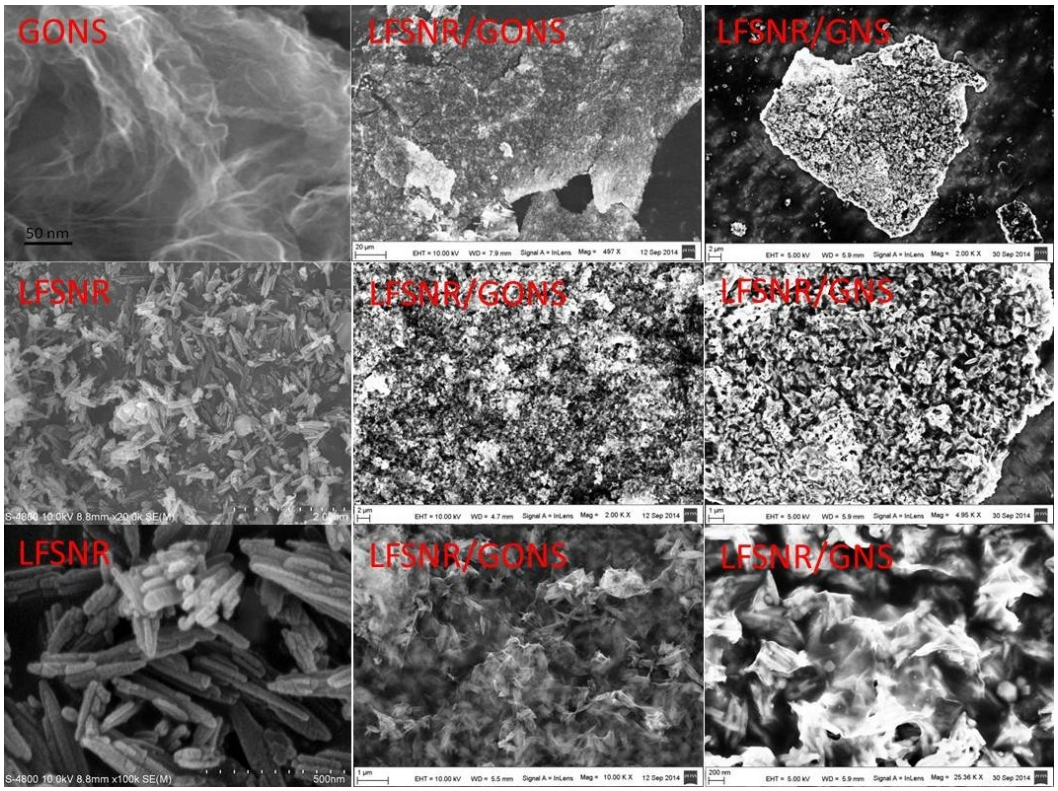


**Figure S1** SEM images of GONS, free LFSNR, LFSNR/GONS and LFSNR/GNS.

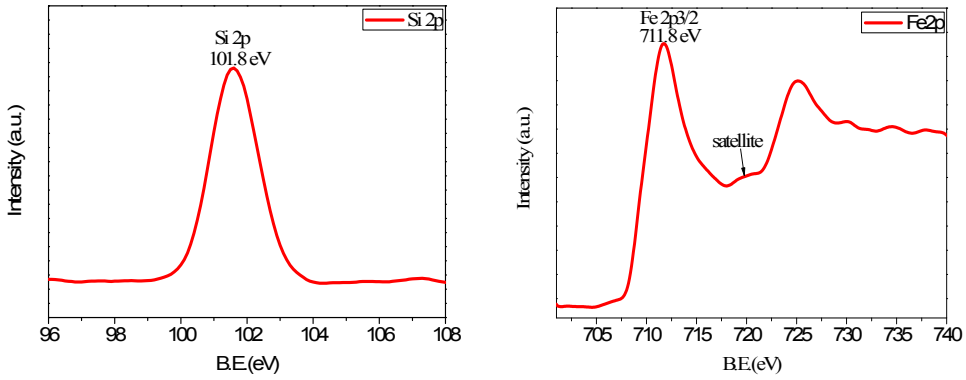


**Figure S2** Banding energies of the LFSNR@graphene hybrid at Si 2p region (left), and Fe 2p region (right).

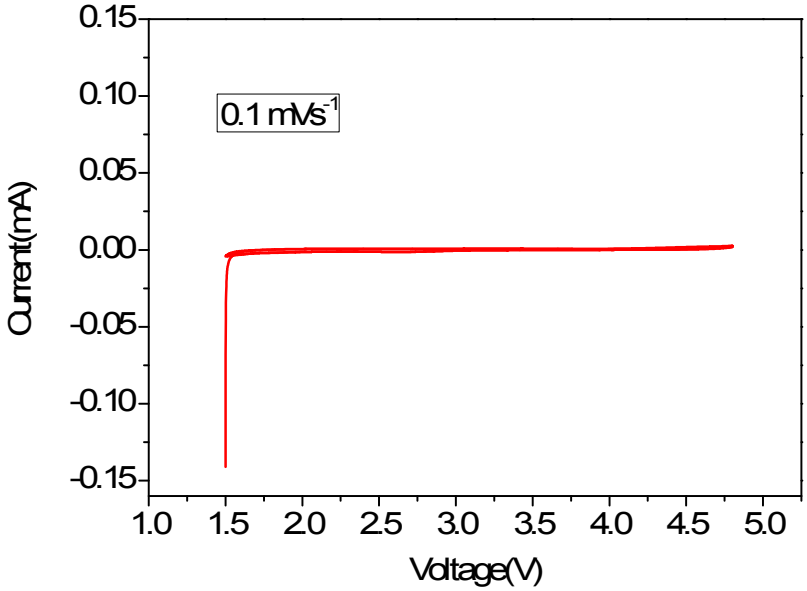


**Figure S3 CV curves for battery without cathode to reveal the stability of the using high voltage electrolyte.**

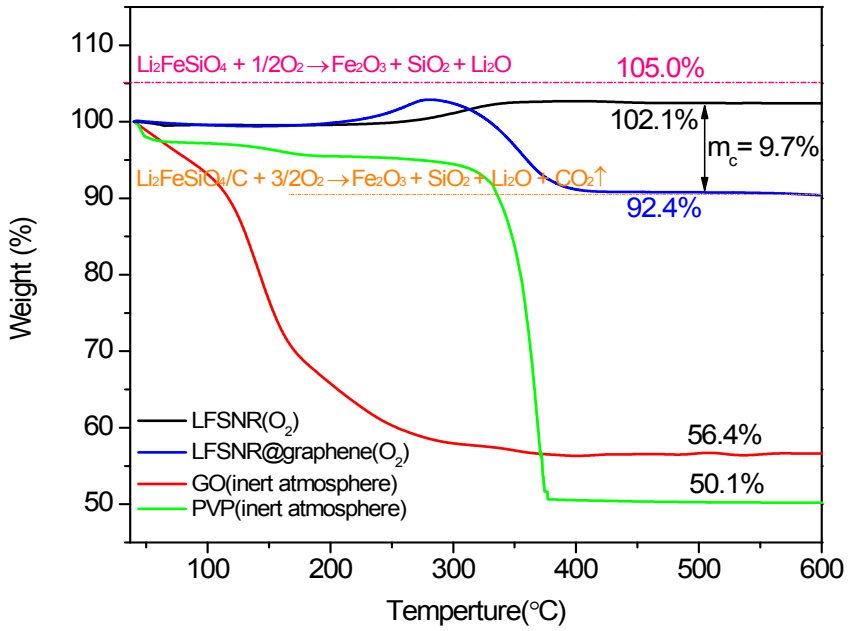


**Figure S4** TG curves of the LFSNR@graphene and LFSNR under $O_2$ flow, GO and PVP under inert atmosphere.

The oxidation of pure $Li_2FeSiO_4$ and $Li_2FeSiO_4$/C under $O_2$ flow can be carried out on the basis of the reactions (S1) and (S2):

$$Li_2FeSiO_4 + \frac{1}{2}O_2 \rightarrow Li_2O + \frac{1}{2}Fe_2O_3 + SiO_2 \quad \text{(S1)}$$

$$Li_2FeSiO_4/C + \frac{3}{2}O_2 \rightarrow Li_2O + \frac{1}{2}Fe_2O_3 + SiO_2 + CO_2\uparrow \quad \text{(S2)}$$

According to the theoretical calculation from reaction (S1), the pure $Li_2FeSiO_4$ suffered from a weight increase to 105 wt%. The content of oxidation of LFSNR under $O_2$ flow is 102.1 wt%. The difference of 2.9 wt% could be the impurities adsorbed in the surface of LFSNR. According to reaction (S2), the lose of weight are from combustion of carbon. The amount of carbon released from the LFSNR@graphene is 9.7 wt%. Acorrding to the TG curves of GO and PVP under inert atmosphere, the content of graphene in GO is 56.4 wt%, PVP-pyrolysis carbon is 50.1 wt%. In the course of the experiment, both contents of the added GO and PVP are 8.3 wt%, deducing that the content of graphene and PVP-C in LFSNR@graphene sample is ~4.7 wt% (8.3 * 56.4) and 4.15 wt% (8.3 * 50.1), respectively. The error of 0.85 wt% could be the content of $H_2O$ and other impurities in samples.

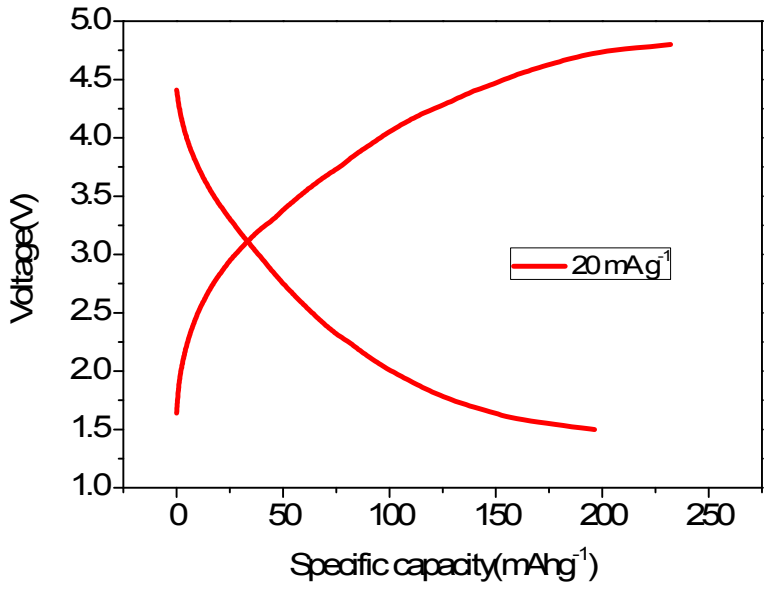


**Figure S5 Charge-discharge curve of graphene as cathode between 1.5-4.8 V.** Observing from S5 the capacity of graphene is ~200 mAh $g^{-1}$, According to its content of 4.7 wt%, 9.4 mAh $g^{-1}$ was excluded when the specific capacities were calculated.

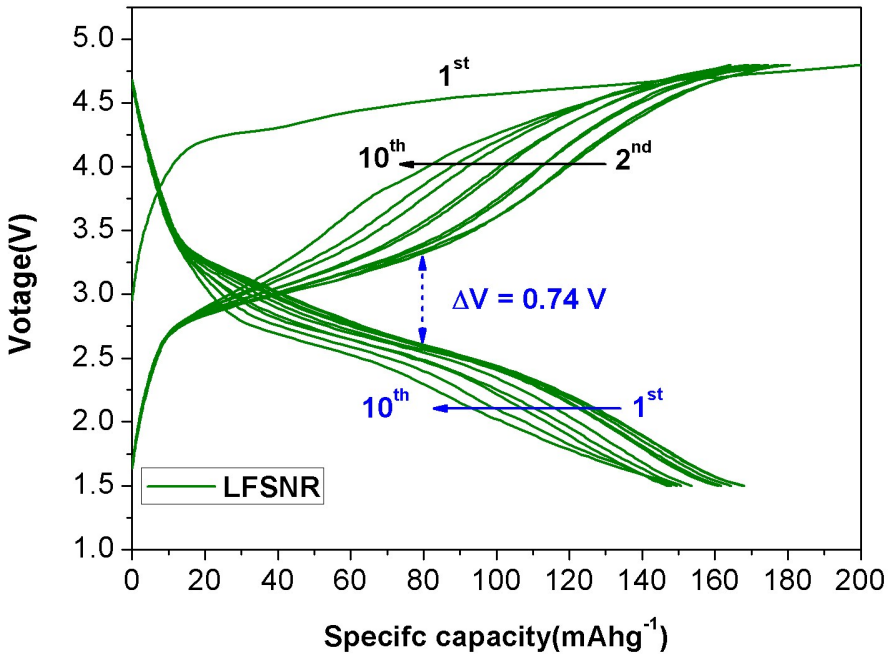


**Figure S6** Typical charge-discharge curves of LFSNR at 20 mA $g^{-1}$ between 1.5-4.8 V for 10 cycles.

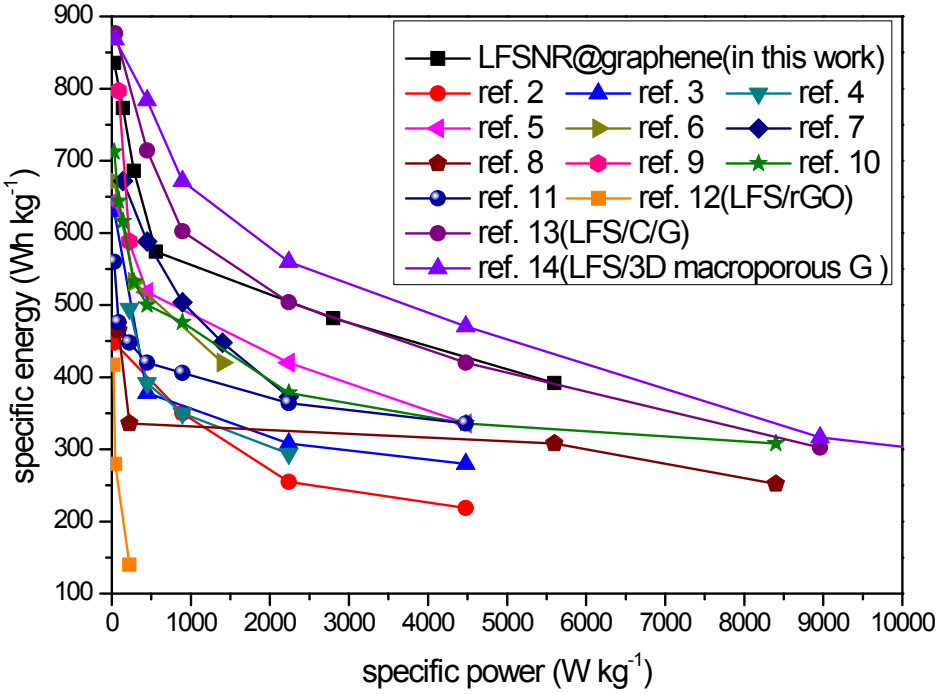


**Figure S7** Ragone plots of LFSNR@graphene hybrid in this work with other relevant data recently reported in the literature.

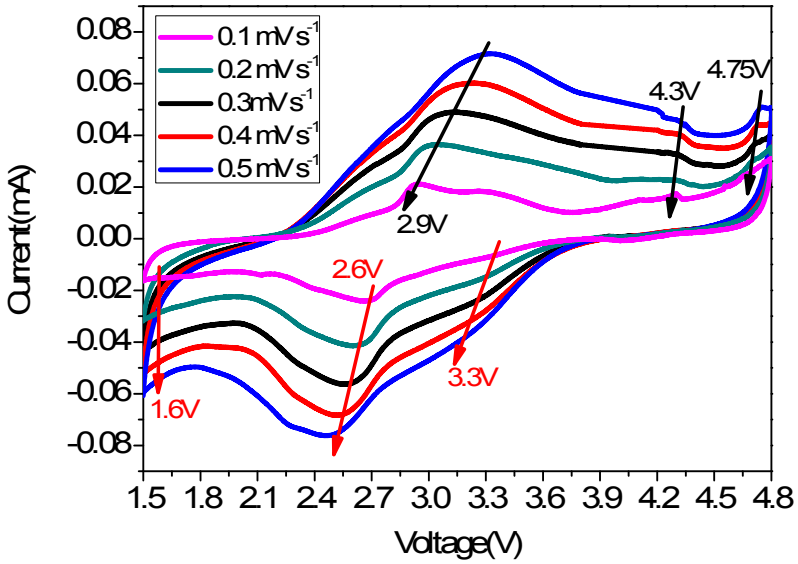


**Figure S8** Different rate CV curves for LFSNR@graphene hybrid.

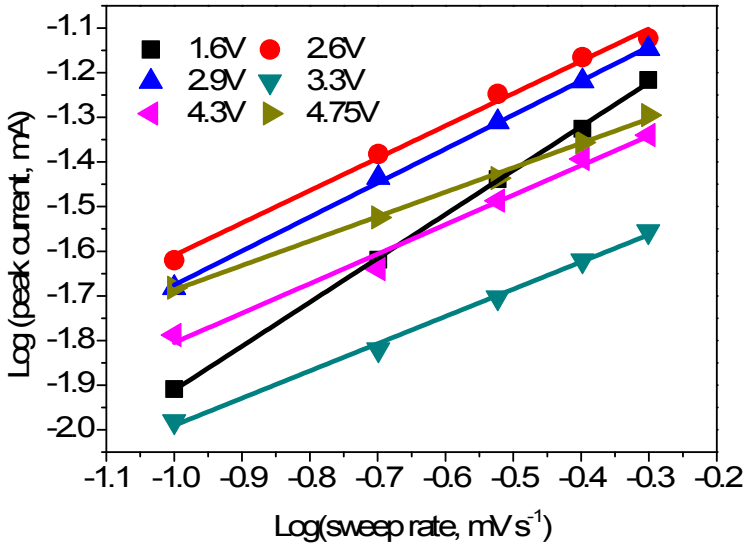


**Figure S9** Slope of the peak current versus the potential scan rate in a logarithm scale at different anodic and cathodic peaks position.

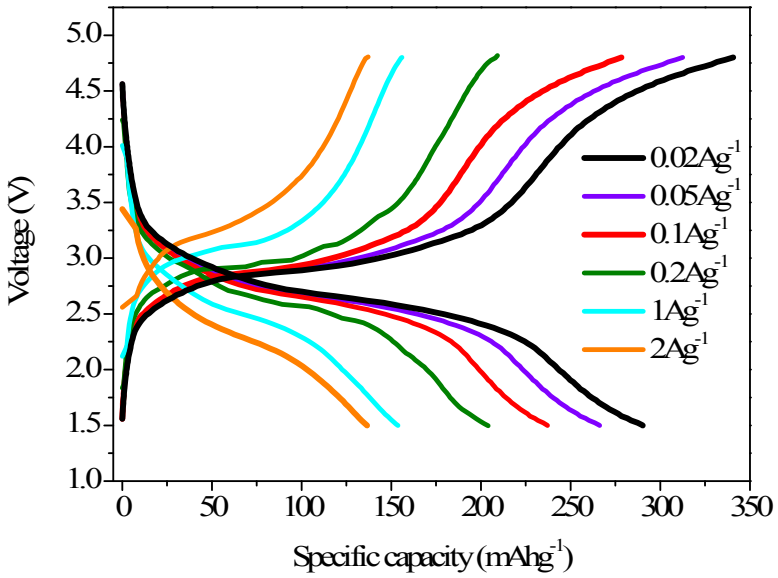


**Figure S10** charge-discharge curves at different current rate for LFSNR@graphene hybrid.

(1) a) L. J. Cote, F. Kim, J. Huang, *J. Am. Chem. Soc.* 2009, 131, 1043; b) D. P. He, K. C. Cheng, H. G. Li, T. Peng, F. Xu, S. C. Mu, M. Pan, *Langmuir* 2012, 28, 3979; c) D. He, Y. Jiang, H. Lv, M. Pan, S. Mu, *Appl. Catal. B: Environ.* 2013, 132, 379.

(2) Z. L. Gong, Y. X. Li, G. N. He, J. Li, Y. Yang, *Electrochem. Sol-Stat. Lett.* 2008, 11, A60.

(3) D. Lv, W. Wen, X. Huang, J. Bai, J. Mi, S. Wu, Y. Yang, *J. Mater. Chem.* 2011, 21, 9506.

(4) Z. Zheng, Y. Wang, A. Zhang, T. Zhang, F. Cheng, Z. Tao, J. Chen, *J. Power Sources* 2012, 198, 229.

(5) X. Wu, X. Jiang, Q. Huo, Y. Zhang, *Electrochim. Acta* 2012, 80, 50.

(6) J. Bai, Z. Gong, D. Lv, Y. Li, H. Zou, Y. Yang, *J. Mater. Chem.* 2012, 22, 12128.

(7) Y. Zhao, J. Li, N. Wang, C. Wu, Y. Ding, L. Guan, *J. Mater. Chem.* 2012, 22, 18797.

(8) X. Wu, X. Wang, Y. Zhang, *ACS appl. Mater. Inter.* 2013, 5, 2510.

(9) H. Gao, Z. Hu, K. Zhang, F. Cheng, J. Chen, *Chem. Commun.* 2013, 49, 3040.

(10) Z. Chen, S. Qiu, Y. Cao, J. Qian, X. Ai, K. Xie, H. Yang, *J. Mater. Chem. A* 2013, 1, 4988.

(11) D. Li, R. Xie, M. Tian, S. Ma, L. Guo, X. Fan, L. Hao, J. Mater. Chem. A 2014, 2, 4375.

(12) D. Bhuvaneswari, N. Kalaiselvi, Dalton Trans. 2014, 43,18097.

(13) H. Zhu, X. Wu, L.Zan, Y. Zhang, Electrochim. Acta, 2014, 117, 34.

(14) H. Zhu, X. Wu, L.Zan, Y. Zhang, ACS Appl. Mater. Interfaces 2014, 6, 11724.