Supporting Information

CTAB-assisted growth of self-supported Zn_2GeO_4 nanosheets network on a conductive foam as a binder free electrode for long-life lithium ion batteries

Guoxin Gao,[a] *Yang Xiang,*[a] *Shiyao Lu,*[a] *Bitao Dong,*[a] *Sheng Chen,*[a] *Lei Shi,*[a] *Yuankun Wang,*[a] *Hu Wu,*[a] *Zhaoyang Li,*[a] *Amr Abdelkader,*[c] *Kai Xi**[b] *and Shujiang Ding**[a]

[a]Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an 710049, P. R. China. E-mail: dingsj@xjtu.edu.cn ;

[b]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB3 0FS, United Kingdom. E-mail: kx210@cam.ac.uk

[c]National Graphene Institute (NGI), University of Manchester, Booth Street East, Manchester, M13 9QS, United Kingdom

Experimental sections

Material synthesis: All the chemicals are analytical grade, supplied by Sigma-Aldrich and used directly without further purification. In a typical synthesis of self-supported ZGO NSs@NF, 1 mmol $ZnCl_2$, 0.5 mmol GeO_2 and 1 mmol cetyltrimethyl ammonium bromide (CTAB) were added into a mixing solution containing 30 mL H_2O and 10 mL ethylene glycol (EG). After magnetic stirring for 1 h, the mixed suspension was transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL. A piece of pre-treated nickel foam (2 mm × 5 mm) was placed into the autoclave. The autoclave was then heated in an electric oven at 160 ^oC for 180 min. After cooling to room temperature naturally, the nickel foam covered by the ultrathin Zn_2GeO_4 nanosheets was rinsed several times with water and absolute ethanol. Finally the black product was dried at 80 ^oC under vacuum overnight. For comparison, pristine ZGO flakes, pristine ZGO nanorods (ZGO NRs) and ZGO NRs@NF were also synthesized, without adding nickel foam for ZGO flakes, without adding CTAB and nickel foam for ZGO NRs, and without using CTAB for ZGO NRs@NF, respectively.

Materials characterization: The XRD patterns were obtained on a Bruker D8 Advanced X-Ray Diffractometer with Ni filtered Cu Kα radiation ($\lambda = 1.5406$ Å) at a voltage of 40 kV and a current of 40 mA. FESEM images of the powder deposited onto a silicon slice were observed on a JEOL JSM-6700F microscope operating at 5 kV with an EDX (JEOL JED-2300) spectrometer at an accelerating voltage of 15 kV. Correspondingly, TEM images were detected on JEOL JEM-2010 and JEOL JEM-2100F microscopes by exfoliating the ultrathin ZGO NSs from the nickel foam substrate using strong ultrasonication and directly dripping them on a copper grid

Electrochemical measurements: The electrochemical properties were evaluated by assembling CR2032 type coin cells in an Ar-filled dry glove box (Innovative Technology Inc.). The moisture and the oxygen concentrations were both below 1.0 ppm. The as-prepared ZGO NSs@NF and ZGO NRs@NF were used directly as the binder-free working electrodes with a loading density of 1.5-2.1 mg cm^{-2}, and that were verified by a high-precision balance from *METTLER TOLEDO*. However, the working electrode of pristine ZGO flakes was fabricated by mixing the pristine ZGO flaks powder, carbon black (Supper-P-Li) and polymer binder (polyvinylidene fluoride, PVDF) at a mass ratio of 7:2:1 using N-methyl-2-pyrrolidone (NMP) as a solvent. After stirring at room temperature for about 24 h, the slurry was uniformly pasted onto a copper foil as current collector and then dried in a vacuum oven at 120 ^{o}C overnight. For comparison, the mass loading of pure ZGO flakes on this working electrode was also controlled carefully at 1.5-2.1 mg cm^{-2}. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate and diethyl carbonate (1:1 by weight). Lithium discs were used as both the counter electrode and the reference electrode. For the preparation of full-cell, commercial $LiFePO_4$ was used to fabricate cathodes just like the pristine ZGO flakes, and the ZGO NSs@NF was directly used as anode. But beforehand, the ZGO NSs@NF was pre-lithiation though discharging to 0.05V in ZGO NSs@NF/Li half-cell.

Cyclic voltammetry (CV) measurements were carried out on a CHI 660D electrochemistry workstation between 0.01 and 3 V (*vs.* Li/Li^{+}) at a scan rate of 0.5 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was also performed on the electrochemistry workstation by applying an alternating current (AC) voltage with 1 mV amplitude in a frequency range from 0.01 Hz to 100 kHz at open circuit potential. The galvanostatic charge-discharge characterization was evaluated on a NEWARE battery tester within a voltage window of 0.01-3 V (*vs*. Li^{+}/Li) at room temperature.

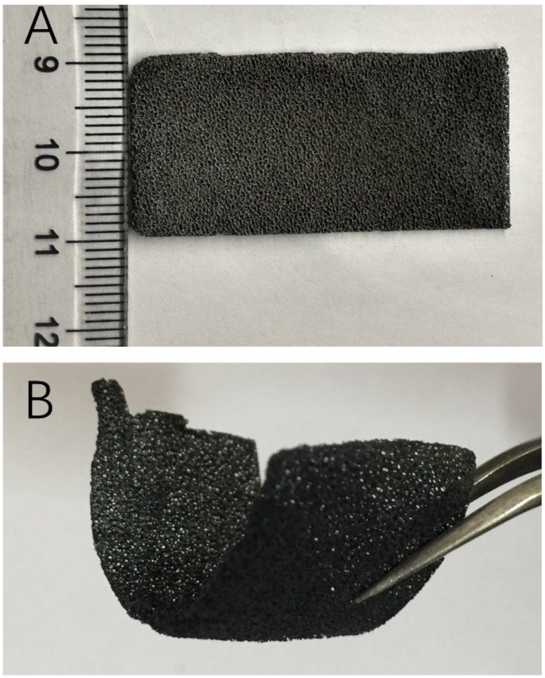


Figure S1. Digital image shows the flexibility of the ZGO NSs@NF.

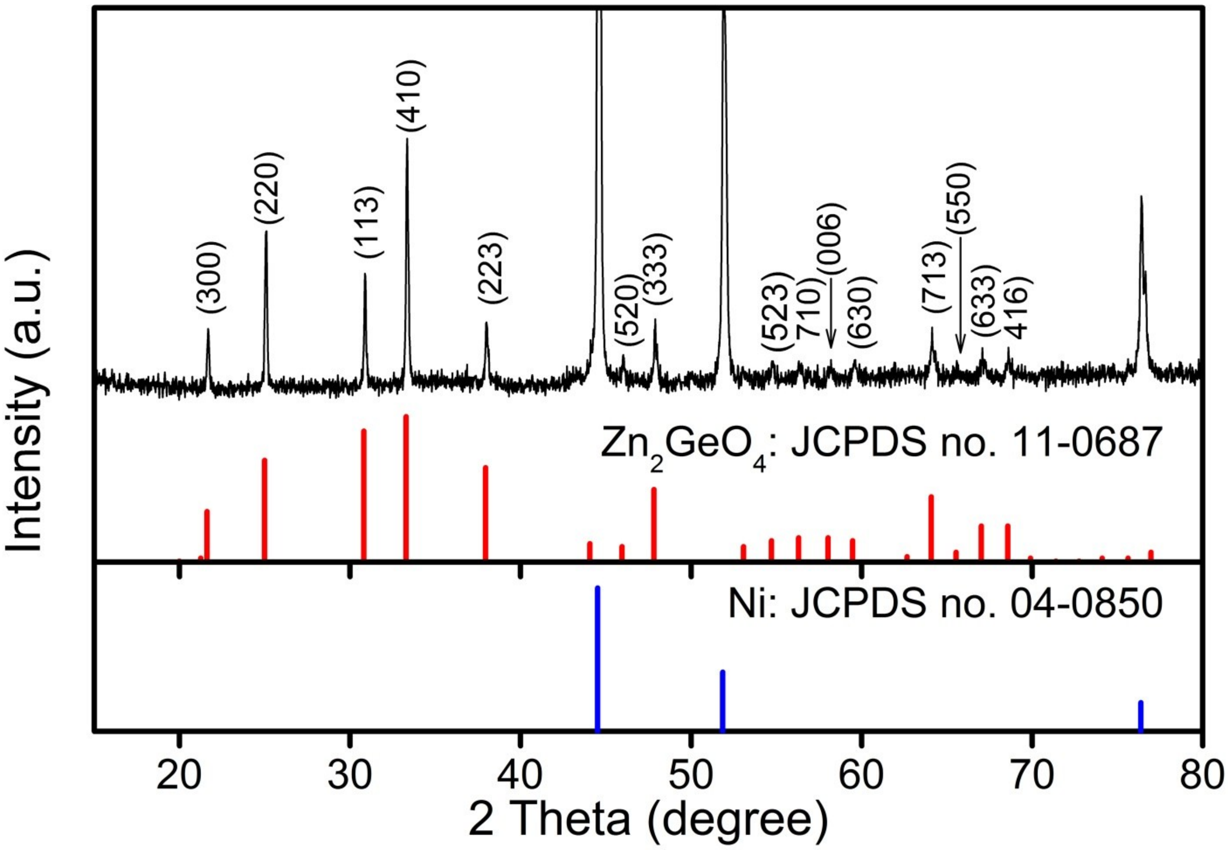
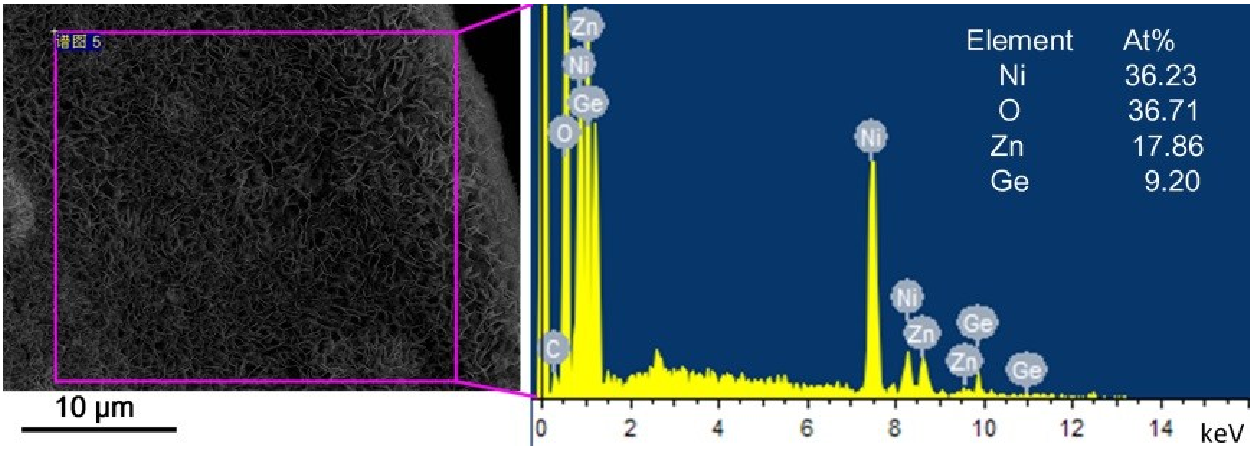


Figure S2. XRD pattern of the self-supported ZGO NSs@NF composite electrode.



Element	At%
Ni	36.23
O	36.71
Zn	17.86
Ge	9.20

Figure S3. SEM image and the corresponding EDX pattern of the ZGO NSs@NF composite, (A) shows the corresponding scanning area.

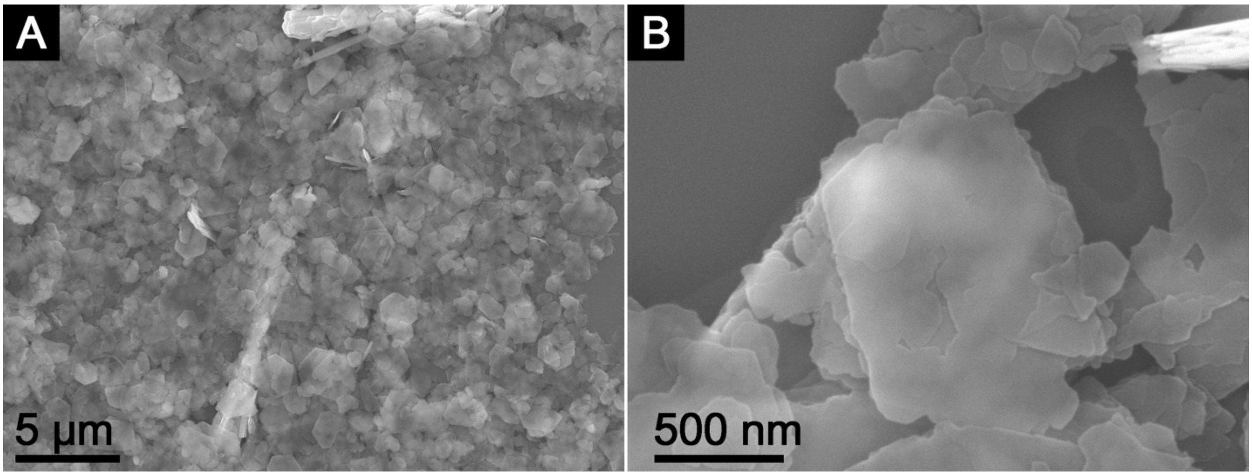


Figure S4. FESEM images of pristine ZGO flakes obtained at 160 ^{o}C for 3 h only without placing nickel foam substrate in the hydrothermal solution. The material has obvious tendency to grow in-plan and forming a 2D structure.

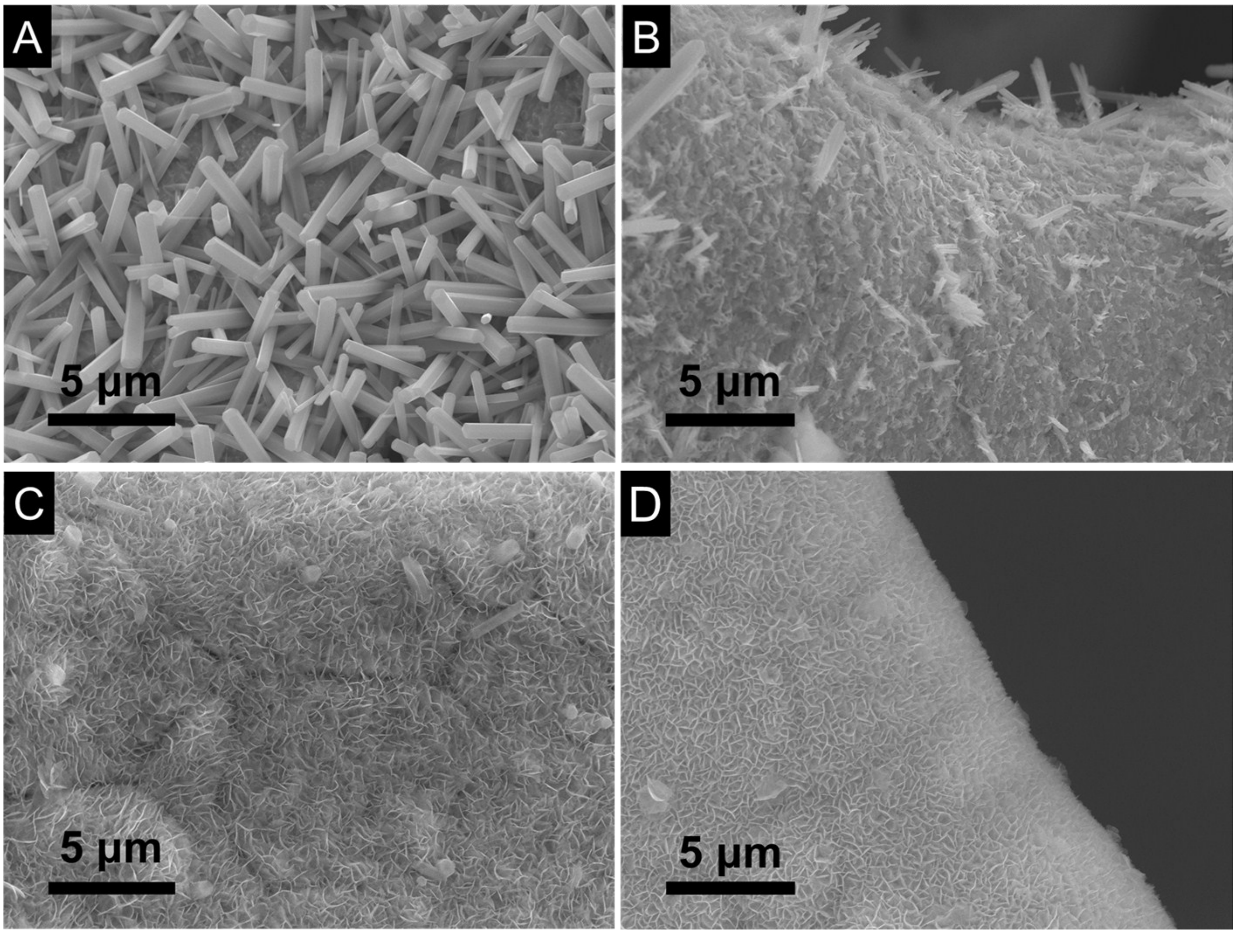


Figure S5. FESEM images of the as prepared ZGO@NF with different amounts of CTAB (A) 0 mmol; (B) 0.3 mmol; (C) 0.7 mmol; (D)2 mmol. All the samples were treated at 160 °C for 3 h.

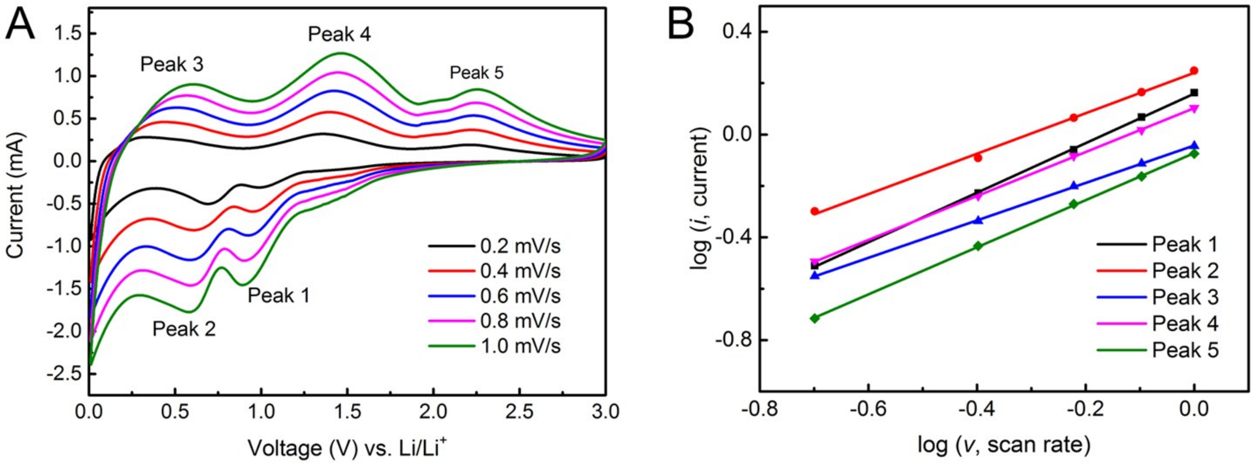


Figure S6. (A) CV curves of Li/ZGO NSs@NF half-cell at different scan rates after 100 cycles, and (B) log(*i*) versus log(*v*) plots at different redox states of the as-prepared ZGO NSs@NF

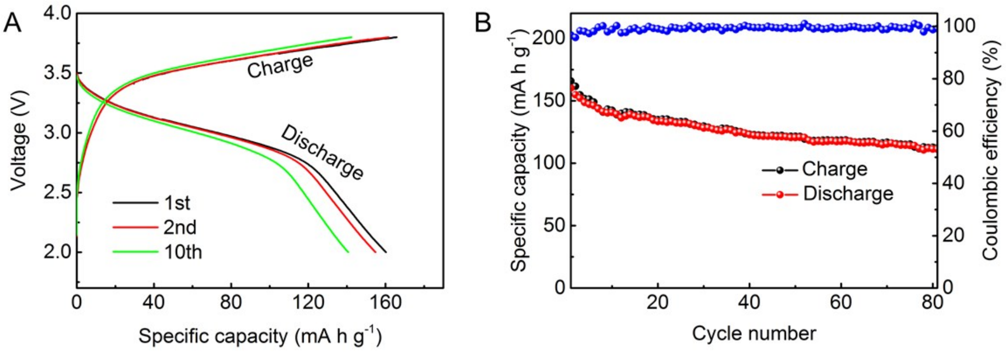


Figure S7. Performance of LiFePO4/ ZGO NSs@NF full-cell:(A) charge and discharge curves and (B) cycling performance at 0.2C(1C=170 mA h g^{-1},$LiFePO_4$)

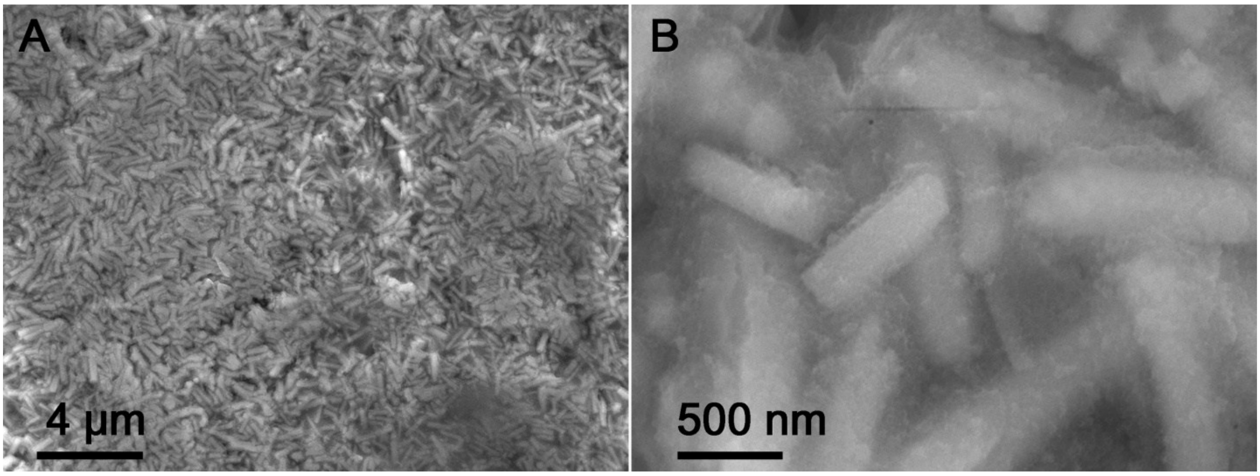


Figure S8. Post-mortem FESEM images of ZGO NRs@NF anodes after 100 cycles at 200 mA g^{-1}.

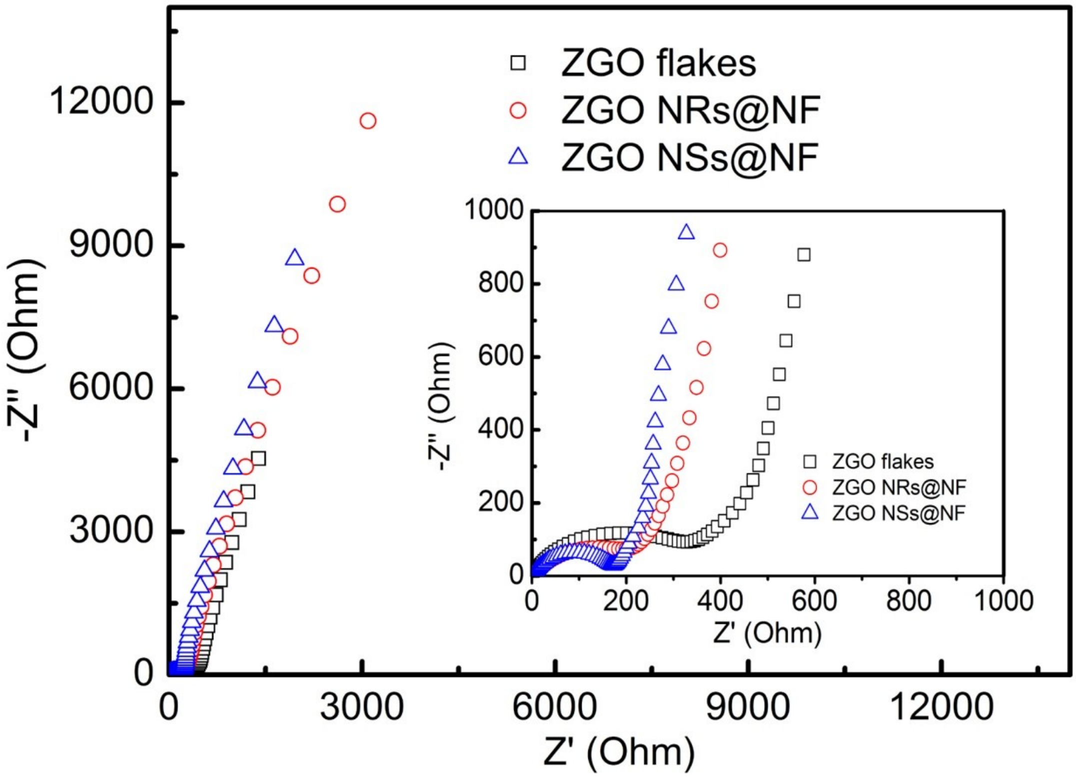


Figure S9. Nyquist plots of the ZGO NSs@NF, the hybrid ZGO NRs@NF and the pristine ZGO flakes electrodes measured with the amplitude of 5.0 mV over the frequency range of 100 kHz and 0.01 Hz by applying a sine wave.

Table S1. Electrochemical comparison between our ZGO NSs@NF and other reported ZGO materials.

Morphology	Initial discharge capacity[mA h g^{-1}]	Cycle number	Final capacity[mA h g^{-1}]	Current density[mA g^{-1}]	
ZGO NSs@NF	1564	500	794	200	This work
ZGO NRs	1820-995	100	616	400	1
ZGO NRs mixed N-doped graphene	1463	100	1044	100	2
ZGO NRs mixed graphene	1508	50	768	200	3
ZGO NRs mixed gaphene oxide	873	100	1155	200	4
ZGO Film on Ni foam and carbon	1414	50	933	200	5
ZGO Hollow nanoparticles	1479	60	1175	200	6
ZGO NRs	1587	60	975	200	6
ZGO NPs@g-C_3N_4	1068	140	1370	200	7
ZGO@CNT microsphere	1211	300	762	1500	8
Porous ZGO nanofibers	1695.8	130	1242	200	9
ZGO Nanowires	2161	100	1220	144	10
ZGO NRs@TiO_2	410	150	330	200	11
Zgo Nanofibers	1705.6	50	1084.1	200	12
ZGO NRs(coated by carbon and Ag particles)	1440	50	561	200	13
fascicular ZGO structure	1461	160	1034	500	14
ZGO@graphene	1158.7	600	702	300	15

Reference

1. J. K. Feng, M. O. Lai and L. Lu, *Electrochem. Commun.*, 2011, **13**, 287-289.
2. F. Zou, X. L. Hu, Y. M. Sun, W. Luo, F. F. Xia, L. Qie, Y. Jiang and Y. H. Huang, *Chem. Eur. J.*, 2013, **19**, 6027-6033.
3. R. Wang, S. P. Wu, Y. C. Lv and Z. Q. Lin, *Langmuir*, 2014, **30**, 8215-8220.
4. F. Zou, X. Hu, L. Qie, Y. Jiang, X. Xiong, Y. Qiao and Y. Huang, *Nanoscale*, 2014, **6**, 924-930.
5. W. M. Chen, S. Maloney and W. Y. Wang, *Electrochim. Acta*, 2015, **176**, 96-102.
6. Y. Feng, X. D. Li, Z. P. Shao and H. T. Wang, *J. Mater. Chem. A*, 2015, **3**, 15274-15279.
7. X. D. Li, Y. Feng, M. C. Li, W. Li, H. Wei and D. D. Song, *Adv. Funct. Mater.*, 2015, **25**, 6858-6866.
8. S. H. Choi, J. H. Kim, Y. J. Choi and Y. C. Kang, *Electrochim. Acta*, 2016, **190**, 766-774.
9. H. H. Li, X. L. Wu, L. L. Zhang, C. Y. Fan, H. F. Wang, X. Y. Li, H. Z. Sun, J. P. Zhang and Q.

Yan, *ACS Appl. Mater. Inter.*, 2016, **8**, 31722-31728.

10. Y. R. Lim, C. S. Jung, H. S. Im, K. Park, J. Park, W. I. Cho and E. H. Cha, *J. Mater. Chem. A*, 2016, **4**, 10691-10699.
11. X. Peng, X. Zhang, L. Wang, M. Xu, D. Zhao, Y. Rui, J. Xu and K. Tang, *Mater. Lett.*, 2016, **185**, 307-310.
12. W. Wang, J. W. Qin and M. H. Cao, *ACS Appl. Mater. Inter.*, 2016, **8**, 1388-1397.
13. X. Z. Zhang, L. L. Wang, Y. Zou, X. Peng, M. Zhang, S. A. Gao, J. L. Xu, K. B. Tang and D. L. Zhao, *Mater. Lett.*, 2016, **166**, 243-246.
14. W. Liu, T. Zhou, Y. Zheng, J. Liu, C. Feng, Y. Shen, Y. Huang and Z. Guo, *ACS Appl. Mater. Inter.*, 2017, **9**, 9778-9784.
15. C. Ding, Y. Zhao, D. Yan, D. Su, Y. Zhao, H. Zhou, J. Li and H. Jin, *Electrochim. Acta*, 2017, DOI: http://dx.doi.org/10.1016/j.electacta.2017.07.163.