RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

ARTICLE



Nitrogen-Doped Holey Graphene Foams for High-Performance **Lithium Storage**

Jiaguang Sun,^a Lan Wang,^a Ranran Song,^a Shubin Yang^{*a}

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Although lithium ion batteries have gained commercial success in abundant portable devices, they still lack suitable electrode materials with high capacities and rate capabilities critical for broad applications. Herein, we demonstrate a facile and scalable approach toward nitrogen-doped holey graphene foams (NHGFs) via simultaneously etching and assembling of graphene oxide and subsequently annealing treatments. The resultant NHGFs possess some unique structural features su. as the hierarchically interconnected pores in the foams and nitrogen-doped holey structure in the basel plane of graphe walls, which facilite the fast diffusions of both lithium and electron through the NHGFs and meanwhile signficantly improved electrochemical activity. As a result, NHGFs exhibit excellent electrochemical performances for lithium storage, including high reversible capacity (1194 mAh g⁻), good high-rate capability (420 mAh g⁻1 at 5 C) and long cycle stability (negligible capacity loss after 1000 continuous cycles.

Introduction

Graphene nanosheets have attracted great interesting in the development of new anode materials for lithium ion batteries owing to their fascinating physical and chemical properties, such as high electrical conductivity, large surface area, good flexibility and high theoretical capacity (744 mAh g⁻¹)¹⁻³. However, due to the strong van der Waals interaction and large surface area, graphene nanosheets are prone to restack and aggregate during electrode fabrication process⁴⁻⁶. Moreover, the cross-plane diffusivity of lithium ions in graphene nanosheets is very low, leading to the predominant diffusion of lithium ions at the edges of restacked graphene nanosheets 7, despite of their high in-plane diffusivity of lithium ions (${\sim}10^{\text{-8}}$ cm² s⁻¹)⁸. This hampers severely the electrochemical performances of graphene for lithium storage, especially at high current rates9, 10.

To circumvent above obstacles of graphene nanosheets for lithium effective strategies including storage. several introducing defects, holes and heteroatoms (N, B, S)¹¹⁻¹³ into the basal plane of graphene, and assembling graphene into threedimensional (3D) foams or networks have be recently developed¹⁴. In the former, the presence of defects or holes in the graphene basal plane, also called holey graphene or graphene nanomesh¹⁵, can be beneficial to the easy access of electrolyte and rapid diffusion of lithium ions^{8, 9}. The introducing heteroatoms into graphene nanosheets can greatly

their energy barriers for lithium ion penetration, owing to the hybridization of heteroatom lone pair electrons with the Moreover, graphene aromatic system⁵. it has been demonstrated theoretically and experimentally that all the introductions of defects, holes and heteroatoms into graphene could improve their electrochemical active sites for lithium storage compared to pristine graphene nanosheets^{16, 17}. In the later, different from above chemically engineering in the basal plane of graphene, rational arrangement of individual graphene nanosheets into 3D forms or networks, in which physical spaces (multi-sized pores) are created between the intact nanosheets, can also reduce significantly the diffusion length of lithium ion migration during the charge-discharge processes and allow more graphene sheets available for lithium storage^{5, 18, 19} Although the separated strategy has been carefully investigated with the aid of various approaches such as chemical vapor deposition^{20,} 21, template-assisted lithography²² methods²³ hydrothermal in the recent years, facilely intergrating several strategies to maximize their merits into one graphene-based material and realizing excellent electrochemcial performances for lithium storage remain great challenge²⁴⁻²⁶. Herein, we develop a rational approach to facile and scalab.

fabrication of nitrogen-doped holey graphene foams (NHGFs) via a hydrothermal treatment of graphene oxide with hydrogen peroxide and subsequently annealing under ammonia gas. 📶 resultant NHGFs, the macroporous networks the constructed from abundant nitrogen-doped graphen nanosheets with in-plane holes, which can provide lar e amounts of cross-plane ion diffusion channels and meanwhile decrease the energy barriers for lithium ion penetratio Combining these with the 3D graphitic networks that maintain high electrical conductivity and structural integrity, a nov

^{a.} Key Laboratory of Aerospace Advanced Materials and Performance of Ministry of Education, School of Materials Science and Engineering, Beihang University, 100191. Beijing. Ching. E-mail: vangshubin@bugg.edu.cn

⁺Electronic Supplementary Information (ESI) available: (details of anv supplementary information be included here]. available should DOI: 10.1039/x0xx00000x

graphene-based electrode material with well intergrating the merits of several stratigies is generated, which exhibits a high reversible capacity of 1194 mAh g^{-1} , good high-rate capability (420 mAh g^{-1} at 5C) and long cycle stability for lithium storage.

Experimental

ARTICLE

Synthesis of nitrogen-doped holey graphene foams

In a typical experiment, graphene oxide was first synthesized from natural graphite flakes by a modified Hummers method²⁷, and then diluted to a concentration of 2 mg mL⁻¹ by milli-Q water. 10 mL as-synthesized graphene oxide aqueous dispersion was then mixed with 1 mL hydrogen peroxide (3 wt. %) by sonication for 10 min. The resulting mixture was then sealed in a Telfon-lined autoclave and hydrothermally treated at 180 °C for 6h, in which graphene oxide nanosheets were chemically etched to holey graphene oxide and simultaneously assembled into a 3D holey graphene oxide foam. Finally, the asprepared foam was freeze- or critical point-dried to preserve the 3D network formed during synthesis process. Finally, 3D holey graphene oxide foams were annealed under a mixed atmosphere of ammonia gas (150 sccm) and nitrogen gas (450 sccm) at 1000 $^\circ\!\mathrm{C}$ for 45 mins, generating nitrogen-doped holey graphene foams, denoted as NHGFs. For comparison, a slightly etched nitrogen-doped graphene foam (se-NGFs) and nonetched nitrogen-doped graphene foam (ne-NGFs) were also farbicated under the similar synthesis conditions except for adding 1 mL 0.3 wt.% H₂O₂ and no adding H₂O₂, respectively. Meanwhile, NHGFs-800 and NHGFs-900 were fabricated by adjusting the anealing at different temperature at 800 $^\circ\!\!\mathbb{C}$ and 900 °C, respectively. Pure holey graphene foam (denoted as HGFs) was also fabricated via the directly annealing of graphene oxide foam in N_2 at 1000 $\,^{\rm o}\text{C}.$

Assembly of Lithium ion cells

The working electrodes were prepared by spreading the slurry of the active materials (80 *wt*. %), acetylene black (10 *wt*. %) and the polyvinylidene fluoride (10 *wt*. %) binder on copper foil with N-methyl-2- pyrrolidone (NMP) as the mixture solvent. The asprepared electrodes were then dried at 120 $^{\circ}$ C under vacuum for 12 h. For testing lithium ion battery assembly, metallic lithium foil was used as the counter-electrode, 1 M LiPF6 in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 by volume) as the electrolyte, and a glassy fiber film as the separator. All the coin-type (CR2032) cells were assembled in an argon-filled glove box (H₂O, O₂ level<0.1 ppm).

Characterizations

The morphology and microstructure of NHGFs were investigated by transmission electron microscopy (TEM: JEOL-2100F), field-emission scanning electron (FE-SEM: JEOL-7500). X-ray diffraction (XRD, Rigaku D/max2500PC) using Cu K α radiation over the range 10–60° (two-theta) at room temperature (XRD partterns shown in Fig. S1). X-ray photoelectron spectroscopy (XPS: Thermo Electron Corporation ESCALAB 250) measurements. XPS spectrometer was used a monochromatized Al K α radiation with 200 eV pass energy in 30

eV step over an area of 500 μ m × 500 μ m to the sample. Nitrogen sorption isotherms, BET surface area, porous volume and pore size distribution were measured at 77K with Qudrasorb (Quatachrome, USA).

The charge-discharge measurements were carried out on a Land CT2001A battery test system over a voltage range of 0.01– 3V at different current rates (theoretical capacity of graphene: 1C=744 mAh g⁻¹) under room temperature. Electrochemical impedance spectroscopy (EIS) measurements of the electrodes were carried out on an electrochemical workstation (Autolab). The impedance spectra were recorded by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 0.01 Hz.

Results and discussion

As illustrated in Fig. 1, the overall synthetic procedure on nitrogen-doped holey graphene foams involves two steps: to first is hydrothermal treatment of graphene oxide with hydrogen peroxide at 180 °C, in which graphene oxide and simultaneously assembled into a 3D foam; the second is annealing of as-prepared 3D holey graphene oxide foams at different temperatures under ammonia gas. The morphology and structure of the resulting NHGFs were elucidated by SEM, TEM, and HRTEM measurements (Fig. 1 and 2). Apparently, a 3D porous configuration with interconnected pores ranging from sub-micrometer to several micrometers is clearly visible (Fig. 1), which is similar to those reported for graphene and graphene oxide hydrogels ^{28, 29}. A typical TEM image (Fig. 2a) discloses that the nanosheet walls of these pores are highly transparent to



Fig. 1 Schematic illustration of the fabrication of nitrogen-doped holey graphene foams (NHGFs). It mainly involves two steps: 1) hydrotherr¹ treatment of graphene oxide with hydrogen peroxide at 180 °C, in wh. h graphene oxide nanosheets were chemically etched to holey graphene oxide and simultaneously assembled into a 3D foam; 2) anealing the ho' y graphene oxide foam at high temperatures under ammonia gas. The type SEM image of NHGFs (Left down) reveals 3D porous configuration with interconnected pores ranging from sub-micrometer to several micrometer rs.



Fig. 2 Morphological and structural analysis of nitrogen-doped holey graphene foams. a) Typical TEM and b) HRTEM images of NHGFs, revealing the holey structure with a uniform pore size of ca. 2 nm in the nanosheets. Elemental mapping images of c) nitrogen, d) carbon and e) oxygen, indicating the homogeneous dispersion of N, C and O in the holey graphene. Electron beams, demonstrating their ultrathin nature. Close inspection further reveals the holey structure with a uniform pore size of ca. 2 nm in the nanosheets (Fig. 2b). This clearly demonstrates that some oxidants like hydrogen peroxide could effectively make holes in the base plane of graphene nanosheet during the hydrothemal process as we expected. The elemental mapping images further reveal that carbon, nitrogen, oxygen atoms are homogenerously dispersed in the walls of NHGFs (Fig. 2c-2e).

The porous nature of NHGFs is further confirmed by nitrogen physisorption measurements. Their adsorption-desorption isotherms exhibit a typical IV hysteresis loop (Fig. 3a), which is characteristic to mesopores with different pore sizes. Barrett-Joyner-Halenda (BJH) calculations disclose that the pore size distribution is in the range of 5-15 nm (Fig. 3b), except for the open macropores identified from the SEM images (Fig. 2a). A high BET surface area of up to 623 m^2g^1 is observed for NHGFs, which is much higher than those for slightly etched nitrogendoped graphene foam (507 m² g⁻¹) and pure holey graphene foam (131 m^2 g¹). This clearly demonstrates that the BET surface areas of NHGFs are strongly dependent on the



Fig. 3 a) Nitrogen adsorption/desorption isotherms of NHGFs, se-NGFs, ne-NGFs and NGFs, confirming the porous structure with different pore sizes b) BJH calculation discloses that the pore sizes in 3D Nitrogen-doped holey graphene architectures are mainly in the range of 5–20 nm.



Fig. 4 a) XPS survey spectra of NHGFs, se-NGFs, ne-NGFs and NGFs. Highresolution XPS spectra of a) Survey, b) C1s, c) N1s and d) O1s. These N___ peaks are fitted to three energy components centered at around 398.2 eV, 399.7 eV, and 401.3 eV, corresponding to pyridinic-N (N1), pyrrolic-N (N and graphitic-N (N3), respectively.

concetrations of hydrogen peroxide during our fabrication process. Because BET surface area are mainly origniated from the mesopores and micropores, we further conducted methylene blue (MB) adsorption method to evaluate the macroporous surface area of NHGFs 29. According to this method (Fig. S2)³⁰, the surface area of NHGFs is 863 m2 g⁻¹, which is also much higher than those of slightly etched nitrogendoped graphene foam (495 m² g¹) and pure holey graphene foam (206 m² g¹), well consistant to the above BET analysis. In combination with the analysis based on SEM and TEM images, it is reasonable to believe that the high surface area of 3D NHGFs attributes to both the holy graphene nanosheets and their constructed porous structures. Thus, this unique hierarchically porous structure should greatly facilitate the access of electrolyte and the fast diffusion of lithium ions during lithium storage.

To identify the chemical composition of 3D NHGFs, XPS measurements and elemental analysis were carried out. As shown in Fig. 4, C1s, N1s and O1s peaks are observed clearly in the survey curves. In the case of NHGFs, an obvious N1s signal is evident, and the corresponding N content was measured to be 3.4 at.%, close to that analyzed by Organic Elements Analyzer (3.6 at.%). This value is higher than those of slightly etched nitrogen-doped graphene foam (3.0 at.%) and non-etched nitrogen-doped foam (1.3 at.%), as well as comparable to those reported for N-doped graphene foams or networks (2-4 at.%) The high nitrogen content in NHGFs should arise from more accessible heteroatoms doping at the holes and defects of graphene compared with pristine graphene. The complex N15 spectrum can be fitted to three different peaks (Fig. 4c), located at the binding energies of 398.2 eV, 399.7 eV, and 401.3 e corresponding to the pyridinic, pyrrolic and graphitic nitrogen respectively. The corresponding O1s spectrum (Fig. 4d) shows O-C=O, C=O and C-O peaks at 531.9 eV, 533.0 eV, 534 e /, respectively.



Fig. 5 Electrochemical performances of 3D nitrogen-doped holey graphene foams. a) Representative discharge-charge curves of NHGFs at a current rate of 0.1C, b) Representative discharge-charge curves of ne-NGFs at 0.1C. c) Cycle performances of NHGFs, se-NGFs, ne-NGFs and NGFs at 0.1C.d) Rate capacities of NHGFs, se-NGFs, ne-NGFs and NGFs at different current rates from 0.25C to 5C. e) Cycle performance of NHGFs at 5 C for 1000 cycles.

The electrochemical performances of 3D NHGFs were systematically evaluated by galvanostatic discharge (lithium insertion)-charge (lithium extraction) measurements at various rates (1C = 744 mA h g^{-1}) over a voltage range from 0.01 to 3.0V. It is striking that a very high capacity of 2847 mAh g⁻¹ is achieved during the initial discharge process at a current rate of 0.1C (Fig. 5a), corresponding to a lithium insertion coefficient of 7.7 in Li7.7C6. This value is much higher than the theoretical capacity of graphene (744 mAh g⁻¹) with the maximum coefficient of 2 $(Li_2C_6)^{30}$, suggesting the existence of extra lithium storage sites in our 3D NHGFs. The detailed discharge-charge curve analysis (Fig. 5a, b) reveals that two domains including an approximate plateau and a slope mainly contribute to the overall capacity of 3D NHGFs during the discharge process. Obviously, the plateau at ~ 0.9 V is similar to that reported for carbonaceous materials³¹, characteristic for the formation of solid electrolyte interface (SEI) layer on the surface of NHGFs electrode. The typical cyclic voltammograms of NHGFs, se-NGFs, ne-NGFs and NGFs are compared in Figure S3 (See Supporting Information). As shown in the Figure S3a, in the case of NHGFs, there is a main reduction peak centred at 0.8V in the first cathodic scanning process, corresponding to the discharge flat plateau at around 0.85V in the first dicharge curve, which is disappeared from the second cycle. This should be ascribed to the formation of solid electrolyte interphase (SEI) layers on the surface of NHGFs. The other cathodic peak ranged from 0.5V to 0.05V, which is clearly

Page 4 of 6

different from that of graphite with a narrow peak at 0.05V. Associated with slope below 0.5 V in discharge curves, it reasonable to belive that this should attribute to lithium adsorption onto both sides of graphene owing to the large surface area, similar to the reported graphene nanosheets. It is also indicated that the severe re-stacking and aggregation of graphene nanosheets were effectively avoided during our fabrication process since the re-stacked graphene sheets commonly have a long plateau at \sim 0.15V for lithium storage. The first charge curve further shows that the reversible capacity of NHGFs is mainly in the voltage range of above 0.2V. This demonstrates that the severe re-stacking and aggregation of graphene nanosheets were effectively avoided during our fabrication process since the re-stacked graphene sheets commonly have a long plateau at \sim 0.15V for lithium storage³² Moreover, this phenomenon with high reversible capaicty at above 0.2V is similar to those reported for holey graphene graphene nanomesh and other nanostructured carbons wi high capacities, in which additional micro and mesporous lithium storage mechanisms exists³³. There is worth to notice that foams' reversible capacity exceeds the theoretical capacity of graphene, 744 mAh g⁻¹, which could ascribed to the synergistic effect of porous lithium storage mechanism and nitrogen-doped, which improved BET surface area of foam Thereby, such porous lithium storage mechanism combined with the common surface storage on graphene gives rise to a very high capacity of 1194 mAh g⁻¹ for NHGFs during the initial charge process.

The rate capabilities and cycle performances of NHGFs were investigated via galvanostatic discharge-charge measurements at various current rates from 0.1C to 5C (Fig. 5c and 5d). For comparison, the slightly etched and non-etched nitrogen-doped graphene foams as well as pure holey graphene foam (the rat performance of NHGFs-800 and NHGFs-900 shown in Fig. S6) were also tested under the same electrochemical conditions. Remarkably, in the case of 3D NHGFs, the reversible capacities are retained at 1150 and 900 mAh g⁻¹ after 50 cycles at 0.1 C and 0.25 C, respectively, and the Coulombic efficiencies (calculated from the discharge and charge capacities) approach almost 100% (Fig. S4 in Supporting Information). In contrast, the capacities of slightly etched and non-etched nitrogen-doped graphene foams rapidly decreases to 610 and 320 mAh g⁻¹ even at the lowest current rate of 0.1C, although these values are higher than that of pure holey graphene foam (450 mAh g⁻¹). Such a prominent difference strongly validates the efficiency of our protocol to improve the electrochemical performance of graphene by incorporation of the strategies of doping nitrogen and creating holes or defects. More importantly, 3D NHGFs exhibit excellent cycle performance at high current rates, indicating the ultrafast diffusion of lithium ions in electrode material owing to the short diffusion path length and the stable structure. Apparently, such high-rate performances of 3D NHGFs nanosheets are superi to those reported for the most previously graphene-based materials including graphene nanosheets, holey graphene graphene nanomesh, nitrogen-doped hollow graphene spher s and 3D graphene foams obtained under similar testing conditions 34, 35.



Fig. 6 a) Nyquist plots of NHGFs, se-NGFs, ne-NGFs and NGFs electrodes obtained by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 0.01 Hz. b) Relationship between Z_{Re} and $\omega_{\cdot 1/2}$ at low freuencies, the slope of each line corresponds to the Warburg impedane coefficient, σ_w .

In addition, from Fig. 5d, it can be seen that the capacity has a tendency of slight decrease at a high current rate of 5C, whereas that increases steadily at the same rate during long chargedischarge processes (Fig. 5e). Close inspection of the cycle performance in Fig. 5e, it is visible that the capacity is fluctuated and slightly increased during the long testing processes. This should be related to two influence factors: (1) testing room temperature, and (2) effective availability of active materials at high current rates. During our testing processes, we find that the capacity of a cell is sentive to the testing room temperates during day and night; higher temperature commonly leads to the higher capacity. More importantly, at high current rates, the charge-discharge time is very short, which significantly affects the effective availabitiy of active materials (less than 100%). Thus, with increasing the cycles, the holey structure and nitrogen-doping should be more favorable for the fast diffusions of both lithium and electron, lead to higher effective availabitiy of active materials during charge-discharge processes.

To further gain insight into the reason why 3D NHGFs possess the excellent electrochemical performance, we carried out AC impedance spectra measurements after 50 cycles at the rate of 0.1 C. As presented in Fig. 6a (and Fig. S7), the Nyquist plot of NHGFs consists of a broad semicircle at the high frequencies for the charge-transfer kinetic-controlled region and a straight lineat the low frequencies for the mass transfer-controlled Warburg region (Warburg impedance coefficient, σ_w , calculated in Table S1 ^{8, 36}. The diffusion coefficient of lithium ions in 3D NHGFs is estimated to \sim 1.4×10⁻⁸ cm²•s⁻¹ from the impedance spectra (for details, see Supporting Information). This value is much higher than those of slightly etched and non-etched nitrogen- doped graphene foams ($1.3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) and even comparable to that reported for vertically aligned graphene sheets (\sim 1.5 \times 10⁻⁸ cm² s⁻¹)³⁷, demonstrating that the holey structure of graphene and the hierarchically porous structure of the NHGFs can significantly improve the diffusivity of lithium ions in the electrode. This can be further confirmed by the low electrolyte resistance (R_e) of 4.0 Ohm (Table S2) calculated on the basis of a modified Randles equivalent circuit shown in Fig. S5. Meanwhile, the charge-transfer resistance (R_{ct}) of NHGFs is only 26.7 Ohm, prominently lower than those of slightly etched and non-etched nitrogen-doped graphene foams (32.0-45.8 Ohms), holey graphene foam (39.4 Ohm) and those

ARTICLE

reported for graphene-based materials (40-70 Ohms). Those value (R_e , R_f) are slightly decrease accompanied with the degree of chemical etched by hydrogen peroxide, the charge-transfer resistance (R_{ct}) became notable downturn, corresponding to resistance of 26.7 Ohms is lower than the other slightly or no etched ones, which indicated charger transfer and mass transfer of lithium ions much more conductivity. Such low charge-transfer resistance indicates the high electrochemical activity of NHGFs for lithium storage since the exchange current density is inversely proportional to the charge-transfer resistance. Associated with the unique structures of NHGFs as discussed above, it is reasonable to believe that the pronounced electrochemical performances of NHGFs attribute to their favorable structures for fast diffusions of both lithium ion and electron during the charge-discharge processes, well satisfying the kinetics requirements of high-power lithium ion batteries.

Conclusions

In summary, we have demonstrated an efficient fabrication U nitrogen-doped holey graphene foams via a hydrothermal treatment of graphene oxide with hydrogen peroxide and subsequently annealing under ammonia gas. The unique textural features of NHGFs including the hierarchicality interconnected pores and nitrogen-doped holey structure in the base plane of graphene walls not only allow for the fast diffusions of lithium and electron through the NHGFs, but also render significantly improved electrochemical activity for lithium storage. As a consequence, NHGFs exhibit superior electrochemical performances in terms of the high reversible capacity, good high-rate capability, and long cyclability when they are used as anode material for lithium storage. We believe that such a facile and scalable synthesis protocol can be furth extended to the fabrication of other heteroatoms (B, S, BN) doped holey graphene foams, with wide applications in catalysis sensors, supercapacitors, batteries, and fuel cells.

Acknowledgements

This work was financially supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars (No.37-7290-01), State Education Ministry, the "Recruitment Program of Global Experts", and the Fundamental Research Funds for the Central Universities (Nos. 30-4233-01 and 30-4041-02).

References

- A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, 6, 18 -191.
 D. Chen, J. Tang and J. Li, *Chem. Soc. Rev.*, 2010, 39, 3157-
 - D. Chen, L. Tang and J. Li, *Chem. Soc. Rev.*, 2010, **39**, 3157-3180.
 - M. M. Thackeray, C. Wolverton and E. D. Isaacs, Ener Y. Environ. Sci., 2012, **5**, 7854-7863.
 - Z. Fan, J. Yan, L. Zhi, Q. Zhang, T. Wei, J. Feng, M. Zhang, V. Qian and F. Wei, *Adv. Mater.*, 2010, **22**, 3723-3728.

3

4

36

37

ARTICLE

- 5 Y. Fang, Y. Lv, R. Che, H. Wu, X. Zhang, D. Gu, G. Zheng and D. Zhao, *J. Am. Chem. Soc.*, 2013, **135**, 1524-1530.
- 6 D. Li, M. B. Muller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nat. Nano.*, 2008, **3**, 101-105.
- 7 Z. Fan, J. Yan, T. Wei, L. Zhi, G. Ning, T. Li and F. Wei, *Adv. Funct. Mater.*, 2011, **21**, 2366-2375.
- Z. Jiang, B. Pei and A. Manthiram, J. Mater. Chem. A, 2013, 1, 7775-7781.
- 9 W. Yuan, Y. Zhou, Y. Li, C. Li, H. Peng, J. Zhang, Z. Liu, L Dai and G. Shi, *Sci. Rep.*, 2013, **3**.
- 10 Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts and R. S. Ruoff, *Adv. Mater.*, 2010, **22**, 3906-3924.
- 11 D. Yu, L. Wei, W. Jiang, H. Wang, B. Sun, Q. Zhang, K. Goh, R. Si and Y. Chen, *Nanoscale*, 2013, **5**, 3457-3464.
- 12 X. Zhao, C. M. Hayner, M. C. Kung and H. H. Kung, ACS Nano, 2011, **5**, 8739-8749.
- J. Liang, Y. Jiao, M. Jaroniec and S. Z. Qiao, Angew. Chem. Int. Ed., 2012, 51, 11496-11500.
- 14 Z. Wu, G. Zhou, L. Yin, W. Ren, F. Li and H. Cheng, *Nano Energy*, 2012, **1**, 107-131.
- J. Bai, X. Zhong, S. Jiang, Y. Huang and X. Duan, *Nat. Nano.*, 2010, 5, 190-194.
- 16 X. Zhao, C. M. Hayner, M. C. Kung and H. H. Kung, *Adv. Energy Mater.*, 2011, **1**, 1079-1084.
- 17 Y. Gong, S. Yang, Z. Liu, L. Ma, R. Vajtai and P. M. Ajayan, *Adv. Mater.*, 2013, **25**, 3979-3984.
- M. D. Levi and D. Aurbach, J. Phys. Chem. B, 1997, 101, 4641-4647.
- 19 Z. L. Wang, D. Xu, H. G. Wang, Z. Wu and X. B. Zhang, ACS Nano, 2013, 7, 2422-2430.
- S. C. O'Hern, C. A. Stewart, M. S. H. Boutilier, J. C. Idrobo, S.
 Bhaviripudi, S. K. Das, J. Kong, T. Laoui, M. Atieh and R.
 Karnik, ACS Nano, 2012, 6, 10130-10138.
- Z. J. Fan, J. Yan, T. Wei, G. Q. Ning, L. J. Zhi, J. C. Liu, D. X.
 Cao, G. L. Wang and F. Wei, ACS Nano, 2011, 5, 2787-2794.
- 22 S. Yang, L. Zhan, X. Xu, Y. Wang, L. Ling and X. Feng, *Adv. Mater.*, 2013, **25**, 2130-2134.
- Y. Sun, Q. Wu and G. Shi, Energy Environ. Sci., 2011, 4, 1113-1132.
- S. Yang, X. Fengand K. Müllen, Adv. Mater., 2011, 23, 3575-3579.
- 25 B. Kang and G. Ceder, *Nature*, 2009, **458**, 190-193.
- 26 Y. T. Liu, X. D. Zhu, Z. Q. Duan and X. M. Xie, *Chem. Commun.*, 2013, **49**, 10305-10307.
- 27 R. Offeman and W. Hummers, J. Am. Chem. Soc., 1958, 80, 1339-1339.
- Y. Xu, K. Sheng, C. Li and G. Shi, ACS Nano, 2010, 4, 4324 4330.
- A. L. M. Reddy, A. Srivastava, S. R. Gowda, H. Gullapalli, M.
 Dubey and P. M. Ajayan, *ACS Nano*, 2010, 4, 6337-6342.
- L. Pan, X. D. Zhu, X. M. Xie and Y. T. Liu, J. Mater. Chem. A, 2015, 3, 2726-2733.
- Z. Q. Duan, Y. C. Sun, Y. T. Liu, X. M. Xie and X. D. Zhu, RSC Adv., 2014, 4, 41543-41550.
- 32 L. Pan, X. D. Zhu, X. M. Xie and Y. T. Liu, *Adv. Funct. Mater.*, 2015.
- 33 S. L. Kuo, W. R. Liu, C. P. Kuo, N. L. Wu and H. C. Wu, J Power Sources, 2013, 244, 552-556.
- 34 Y. Zhao, C. Hu, L. Song, L. Wang, G. Shi, L. Dai and L. Qu, Energy Environ. Sci., 2014, 7, 1913-1918.
- Y. Zhao, C. Hu, Y. Hu, H. Cheng, G. Shi and L. Qu, Angew. Chem., 2012, 124, 11533-11537.

Journal Name

- C. Uthaisar and V. Barone, *Nano Lett.*, 2010, **10**, 2838-2842.
- L. Pan, K. X. Wang, X. D. Zhu, X. M. Xie and Y. T. Liu, *J. Mater Chem. A*, 2015, **3**, 6477-6483.