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Reduced Graphene Oxide/Boron Nitride Composite Film as a Novel Binder-Free Anode for Lithium Ion Batteries with Enhanced Performances

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Abstract

Reduced graphene oxide (rGO)/boron nitride (BN) composite films were successfully fabricated by facile vacuum filtration and subsequent thermal treatment. Their morphology, structure and electrochemical performance were systematically characterized by field emission scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, cyclic voltammetry, galvanostatic charge/discharge and

electrochemical impedance spectroscopy. Importantly, the as-prepared rGO/BN composite film with a 2 wt.% BN content as binder-free anode material for lithium ion batteries (LIBs) exhibited a high reversible capacity of $278 \text{ mAh}\cdot\text{g}^{-1}$ at a high current density of $100 \text{ mA}\cdot\text{g}^{-1}$, high rate capability, and high capacity retention over the first 200 cycles. The enhanced electrochemical performances of rGO/BN composite film are attributed to the unique structure and the synergistic effects between layered BN and graphene, which favored electrolyte penetration and buffered the volume expansion during the lithiation and delithiation process. In addition, this work not only provides a versatile strategy for fabrication of other graphene-based films, but also shows the potential promise of rGO/BN composite film for other energy storage devices.

Keywords: Reduced graphene oxide; Boron nitride; Composite film; Anode; Lithium-ion batteries

1. Introduction

Lithium ion batteries (LIBs), with high energy density, long cyclic life and environmental compatibility, have been recognized as the most promising energy storage devices not only used in portable electronics but also in clean and renewable energy [1-7]. Among the key components of LIBs, anode materials play an important role in the determination of the stability and cyclability, and thus considerable efforts have been devoted to the development of anode materials with improved electrochemical performance. To meet the increasing demand for higher reversible capacities, metal oxides as anode materials for LIBs have been extensively investigated because they have higher theoretical capacities than that of commercial graphite [8-18]. However, significant capacity fading with cycling is still one of the most commonly encountered issues due to large volume changes during the lithiation and delithiation process.

Therefore, it remains a challenge to develop electrochemically active and structurally stable anode materials for high performance LIBs which can buffer the volume expansion during the cycling process.

An effective strategy is to develop environmentally friendly, metal-free anode materials such as graphene, carbon nanotubes (CNTs), graphene/CNTs based composites, or doped graphene with N, B, or S atoms to further increase their electrochemical performances and electron transport abilities [19-26]. However, after the synthesis of composite powder an additional step of coating this electrode material on to the current collector is required for traditional battery fabrication, which results in poor electron transport and loss of electrical contact on extended cycling. Hence, to develop versatile, binder-free, thin film electrodes with superior performance is highly desirable for advanced micro-scale energy devices.

Graphene which exhibits outstanding electrical properties, remarkable mechanical flexibility and high chemical tolerance, has been extensively utilized in the design of various composite electrode materials [27-30]. Among them, layered graphene/transition metal sulfide (such as MoS_2 and WS_2) composites have been successfully prepared and widely used as anode material of LIBs with excellent electrochemical performances, due to their robust composite structure and the synergistic effects between layered transition metal sulfide and graphene [31-38]. Furthermore, as a structural analog of graphene, hexagonal boron nitride (h-BN) has also attracted great attention in many fields due to its high chemical stability, much higher oxidation resistance than that of graphene, high thermal conductivity, and excellent mechanical properties [39-43]. Recently, Yan and coworkers reported two-dimensional (2D) h-BN and graphene atomic crystals growing directly on Cu metal current collectors as a stable interfacial layer, respectively, which can suppress dendritic/mossy lithium formation and improve cycling

efficiency [44]. The improvement in the cycling stability is mainly attributed to their excellent chemical stability as well as mechanical strength and flexibility. The above-mentioned analyses and the previously reported results inspire us to investigate whether it is possible to select a proper approach, a proper structure, and a proper combination of graphene and BN to assemble them into the desired structures as an improved anode material of LIBs or not. Combining superior mechanical and chemical properties of BN with rGO, it is expected that the restacking of rGO layers in the composite film can be effectively inhibited, which will facilitate the access of the electrolytes to the electrode, allowing rapid diffusion of electrolytes and better utilization of active materials. Additionally, the excessive interlayer expansion in the rGO/BN composite film caused by lithiation can also be suppressed. Thus, assembling graphene and BN into a two-dimensional composite film is believed to be a promising way to improve the electrochemical performances of anode material for LIBs. However, to the best of our knowledge, there is little report on the fabrication of rGO/BN composite films as well as their lithium-storage properties [45]. Therefore, it is of great significance to develop the fabrication process of graphene/BN composite film, and to further investigate its potential application as the anode material for LIBs.

Reduced graphene oxide/boron nitride (rGO/BN) composite films with different BN contents were prepared by vacuum filtration and subsequent annealing process. The composite film based on graphene and BN can have significant technological advantages apart from the individual properties. Interestingly, the electrochemical performances of the as-prepared rGO/BN composite films showed a strong dependence towards the BN nanosheets doping level. Importantly, the rGO/BN composite film with an optimized amount of BN nanosheets exhibited superior electrochemical properties including high capacity/capacitance, good cycling stability and excellent rate performance. Furthermore, this strategy may be extended to synthesize other

graphene based nanoarchitectures, which are very promising in high performance LIBs, supercapacitors, and catalysts.

2. Experimental

2.1. Materials

All chemicals used were of analytical grade without further purification. Graphite powder (99.9995%, 325 mesh) was purchased from Alfa Aesar. Hexagonal boron nitride (grade AC6004) with lateral particle sizes in the range of 10–13 μm was purchased from Momentive Performance Materials, Inc. 25 μm thick Cu foils (99.8%, Alfa Aesar, item no. #13382) were used as substrates and were cleaned and degreased by sonication in isopropanol (IPA) and acetone before use.

2.2. Characterization

Field emission scanning electron microscopy (FESEM, LEO 1550 GEMINI) and transmission electron microscopy (TEM, Model JEM-2100) were used to characterize morphology and structure of the samples. Raman spectra were collected with a WITEC CRM200 Raman system (532 nm laser, 2.54 eV, WITec, Germany). X-ray photoelectron spectroscopy (XPS, Model PHI Quantera SXM) analysis was conducted for determining elemental chemical state of sample.

2.3. Synthesis of Graphene Oxide (GO) Dispersion

Graphene oxide was synthesized from natural graphite powder by a modified Hummers method [46,47]. The as-prepared GO was suspended in water to give a brown dispersion (0.5 wt.%), which was subjected to dialysis for one week to completely remove residual salts and acids. Then, exfoliated GO was obtained by ultrasound of the 0.5 wt.% GO dispersion for 30 min,

followed by a low-speed centrifugation to get rid of any aggregated GO nanosheets. The as-obtained GO supernatant was diluted further to form a stable GO suspension with a concentration of $0.1 \text{ mg}\cdot\text{mL}^{-1}$.

2.4. Preparation of Boron Nitride Nanosheets (BNNSs) Dispersion

A sonication–centrifugation technique was used for the preparation of BNNSs through exfoliation of h-BN micro-sized particles because liquid exfoliation is the most appropriate method for producing 2D materials. Moreover, this technique is extremely useful because it gives liquid-suspended nanosheets that can then be easily processed into films, composites, or other structures [48]. In a typical experimental process, BN powder (0.45 g, used as received) in IPA (150 mL) was tip-type sonicated to disperse the powder for 6 h. The as-prepared suspension was further centrifuged at 3000~5000 rpm in order to remove residual large-sized BN particles.

2.5. Fabrication of Reduced Graphene Oxide/Boron Nitride (rGO/BN) Composite Film

The rGO/BN composite films were prepared by a vacuum filtration film-formation process, as shown in Fig. 1. After sonication of a combined dispersion of graphene oxide and BN with a certain ratio, the GO/BN composite films were prepared by vacuum filtration of the as-synthesized GO/BN composite dispersions through cellulose esters filter membranes (45 mm in diameter, $0.22 \text{ }\mu\text{m}$ in pore size). The GO/BN composite film on cellulose esters filter membrane was then transferred onto a copper foil and subsequently annealed at $300 \text{ }^{\circ}\text{C}$ for 2 h under a constant flow of argon to obtain the rGO/BN composite film. The as-prepared rGO/BN composite films on copper foil were directly used as anode material and assembled into CR 2032 coin type cells. For comparison, pure GO film on cellulose esters filter membrane was also prepared using the same procedure without BN. The rGO/BN composite films on cellulose esters

filter membrane with a BN content of 0, 2 wt.%, 5 wt.% and 11 wt.% were denoted as rGO, rGO/BN-2%, rGO/BN-5% and rGO/BN-11%, respectively.

2.6. Electrochemical Measurements

The synthesized rGO/BN composite films on copper foils were directly used as working electrodes without any binder or additive. For electrochemical performance testing, the rGO/BN composite films on copper foils were assembled into CR 2032 coin type cells with lithium metal as counter electrodes. The assembly was carried out in a glove box filled with pure argon (Innovative Technology, Inc.). 1.0 M of LiPF_6 dissolved in a mixture of ethylene carbonate and diethyl carbonate (EC/DEC, 1:1 by volume) was used as the electrolyte. The specific capacity was calculated based on the total mass of the electrode. Cyclic voltammetry (CV) was carried out in the voltage range of 0.0–3.0 V with a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$. Charge/discharge capacities were measured by galvanostatic cycling the half cells over the potential range of 0.01–2.5 V (vs Li/Li^+) in a battery tester (NEWARE BTS-5 V, Neware Technology Co., Ltd.). The CV and electrochemical impedance spectroscopy (EIS) tests were performed using a Solartron (1287+1260) electrochemical work station.

3. Results and discussion

3.1. Morphological and Structural Characterization

To study the morphologies and microstructures of the as-prepared BN, GO and rGO/BN composite materials, FESEM and TEM were first employed. The starting BN powder has representative lateral particle sizes in the range of 10–13 μm that are stacked together (Fig. S1) while the exfoliated BNNSs have dimensions of several micrometers and are highly bent and

scrolled (Fig. 2a), similar to what has been reported for graphene [49]. Compared with the initial h-BN powder, the average size of BNNSs is smaller and the thickness is obviously reduced, which makes it almost transparent. Fig. 2b reveals BNNSs with a lattice distance of 0.21 nm, corresponding to the (100) crystal planes of h-BN. Further insights into the number of layers in the BN sheets can be achieved by examining the edges. The insets in Fig. 2b show that the BN sheets range from one to several layers, and most of which have a thickness of less than 5 nm. Fig. 2c and 2d show the typical TEM images of as-prepared GO which exhibit crumpled and folded sheets, similar to previous report [29]. SEM top-view and cross-section view together with the TEM images (Fig. 2e and 2f) of as prepared rGO/BN-2% composite film show that the thin 2D nanosheets morphologies of rGO and BN were well preserved after their combination. As observed from the cross-section image, the average thickness of the rGO/BN-2% composite film is about 0.8 μm . In addition, pure rGO and rGO/BN composite films with other BN contents exhibit similar morphologies to that of the rGO/BN-2% composite film (Fig. S2).

XPS and Raman measurements were further employed to identify the chemical composition and electronic state of the rGO/BN composite films, respectively. Fig. 3a shows a typical survey XPS spectrum of the rGO/BN-2% composite film which confirms the existence of C, O, N, and B in the composite film, in contrast to only C and O elements observed in XPS spectrum of the pure rGO film (Fig. S3). The peak in high resolution C 1s spectrum (Fig. 3b) is mainly deconvoluted into three peaks at 284.5 eV for graphitic carbon, 286.1 eV for C–O, and 287.8 eV for C=O. Among them, the peaks for the C–O and C=O are relatively weaker than that of the graphitic carbon, suggesting the reduction of GO. Fig. 3c exhibits high resolution N 1s peak of the composite film, which can be fitted to two components at 398.6 eV (N–B), and 400.2 eV (N–C). Raman scattering is strongly sensitive to the electronic structure and therefore the structural

changes of GO during the preparation of the rGO/BN composites are reflected in their Raman spectra. As shown in Fig. 3d, the pure exfoliated h-BN exhibits a characteristic peak at 1362 cm^{-1} , whereas rGO/BN composites with different BN contents show typical D band around 1347 cm^{-1} and G band around 1600 cm^{-1} . The G band usually corresponds to the graphitic hexagon-pinch mode (C sp^2 atoms), while the D band is associated with structural defects and staging disorders that can break the symmetry and selection rules [50,51]. Due to the overlap of the D band of rGO and the 1362 cm^{-1} band in h-BN [45], the intensity ratios of D band to G band (I_D/I_G) increase from 0.78 to 0.97 with the increase of the BN doping contents, which indicates an increase in disordered structures after the wedging of BNNSs into few-layer reduced graphene nanosheet stacks.

3.2. Li Ion Batteries Performance

To reveal the advantages of rGO/BN composite film as Li ion storage media in comparison to pure rGO film, comprehensive electrochemical measurements were conducted systematically. First, CV experiments were carried out to evaluate the electrochemical performance of pure rGO film and rGO/BN composite films with different BN contents at a scanning rate of $0.1\text{ mV}\cdot\text{s}^{-1}$ (Fig. 4). All samples exhibit similar current response in an electrochemical window of 0.0 V to 3.0 V. In the first cathodic process, three peaks at around 1.5, 0.5 and 0.0 V can be observed for both pure rGO film and rGO/BN composite films with different BN contents. Here, the weak peak at about 1.5 V is attributed to lithium interactions with the residual functional groups on the surface or on the edge sites of graphene sheets [52-55]. The obvious peak around 0.5 V is due to the decomposition of the electrolyte and the formation of a solid electrolyte interface (SEI) [56]. Notably, the integrated peak area around 0.5 V for rGO/BN composite films with different BN contents is larger than that for the pure rGO film, indicating that the amount of Li ions for the

formation of the SEI in the rGO/BN composite films is larger than that in the pure rGO film. Therefore, the irreversible capacity of the rGO/BN composite film is found to be larger than that of the pure rGO. Additionally, a large irreversible cathodic peak around 0.0 V corresponds to the intercalation of lithium into the graphene film, which becomes weaker after the first cycle due to the lithium intercalation reaction being partially reversible [31,56,57]. In the first anodic process, the peaks around 1.25 and 2.25 V are observed for both pure rGO film and rGO/BN composite films, respectively. The peak at 1.25V is attributed to the extraction of Li ions between the graphene layers. Also, the peak around 2.25 V corresponds to the extraction of Li ions bonded to the surface functional groups in the pure rGO film and rGO/BN composite films. Besides, the redox peaks in the second and third charge and discharge cycles are overlapped after the first cycle, implying an excellent cycle ability of pure rGO film and rGO/BN composite film electrodes.

The electrochemical properties of pure rGO film and rGO/BN composite films as binder-free electrodes for LIBs were further evaluated by galvanostatic charge/discharge in the potential range from 0.01 to 2.5 V. The first three cycle charge/discharge profiles of the pure rGO film and the rGO/BN composite film electrodes at a current density of $100 \text{ mA}\cdot\text{g}^{-1}$ are shown in Fig. 5, which match well with the shape of the CV curves. The capacity between 0.5–1.5 V may be ascribed to the faradic capacitance on the surface or on the edge sites of graphene sheets. The irreversible capacity near 0.5 V is attributed to the formation of a solid electrolyte interface (SEI) layer in the first cycle, while the reversible capacity below 0.5 V should be due to the lithium binding on the basal plane of the graphene sheets [58]. They deliver a first discharge capacity of $480 \text{ mAh}\cdot\text{g}^{-1}$, $620 \text{ mAh}\cdot\text{g}^{-1}$, $751 \text{ mAh}\cdot\text{g}^{-1}$, and $1162 \text{ mAh}\cdot\text{g}^{-1}$, then the discharge capacity drops to $296 \text{ mAh}\cdot\text{g}^{-1}$, $357 \text{ mAh}\cdot\text{g}^{-1}$, $292 \text{ mAh}\cdot\text{g}^{-1}$, and $253 \text{ mAh}\cdot\text{g}^{-1}$ in the second cycle for pure rGO film

and rGO/BN composite films, respectively. The coulombic efficiency of the pure rGO film and rGO/BN composite films with different BN contents is about 61%, 58%, 39%, and 20% during the initial charge/discharge cycle, respectively. Obviously, all of them demonstrate an irreversible capacity between the first and the second discharge cycle. Especially, the more content of BN nanosheets in the rGO/BN composite film, the larger irreversible capacity the film produces, which is consistent to the results obtained from the CV tests. The irreversible capacity may result from the incomplete conversion reaction and the irreversible lithium loss due to the formation of a solid electrolyte interphase (SEI) layer [59,60]. Notably, the reversible capacities of the rGO/BN-2% composite film electrode are always higher than that of the pure rGO. These results indicate that BN nanosheets doping levels in the composite materials have a significant role in improving specific capacity.

Further, the rate performances of the pure rGO film and the rGO/BN composite films with different BN contents were examined at various current densities. As shown in Fig. 6a, the rGO/BN-2% composite film electrode demonstrates better rate performance. Even at a high current density of $1000 \text{ mA}\cdot\text{g}^{-1}$, the specific capacity remains at $121 \text{ mAh}\cdot\text{g}^{-1}$ which is still higher than that of rGO film electrode at the same current density. Interestingly, with further increasing the BN content, the rate performances of the rGO/BN composite film electrodes become worse. It is deduced that proper weight ratio of rGO and BN nanosheets is beneficial to enable a synergistic structure which further improves the rate performance. This can be attributed to a combination of the following two main reasons: (a) Due to the insulating property of BN, the higher content of BN in the composite film leads to lower conductivity of the rGO/BN composite film, resulting in poorer electrochemical performances; (b) BN as an inactive component, a higher BN content will also decrease the specific capacity of the composite film electrodes to

some extent. In addition, it is observed that the measured capacity values of the rGO/BN-2% composite film electrode are 278 $\text{mAh}\cdot\text{g}^{-1}$, 221 $\text{mAh}\cdot\text{g}^{-1}$, 172 $\text{mAh}\cdot\text{g}^{-1}$, 138 $\text{mAh}\cdot\text{g}^{-1}$, and 121 $\text{mAh}\cdot\text{g}^{-1}$ at the current densities of 100 $\text{mA}\cdot\text{g}^{-1}$, 200 $\text{mA}\cdot\text{g}^{-1}$, 500 $\text{mA}\cdot\text{g}^{-1}$, 800 $\text{mA}\cdot\text{g}^{-1}$, and 1000 $\text{mA}\cdot\text{g}^{-1}$, respectively. Furthermore, when the current density is back to 100 $\text{mA}\cdot\text{g}^{-1}$, the specific capacity is recovered from 121 $\text{mAh}\cdot\text{g}^{-1}$ to 247 $\text{mAh}\cdot\text{g}^{-1}$, demonstrating good rate performance of the rGO/BN-2% composite film electrode. For practical applications, the cycling stability of the electrode materials is a very important parameter. The cycling stabilities of the pure rGO film and rGO/BN composite films at a current density of 200 $\text{mA}\cdot\text{g}^{-1}$ are shown in Fig. 6b. The rGO/BN-2% composite film electrode maintains a high reversible capacity of 197 $\text{mAh}\cdot\text{g}^{-1}$ after 200 cycles, which is significantly higher than that of rGO film electrode (127 $\text{mAh}\cdot\text{g}^{-1}$) and those of the other two rGO/BN composite film electrodes. Meanwhile, the columbic efficiency of the rGO/BN-2% composite film electrode after the second cycle remains close to 100% until the 200th cycle, indicating good cycling stability.

Electrochemical impedance spectroscopy (EIS) was employed to further understand the enhanced electrochemical performance of the rGO/BN composite electrodes in comparison with the pure rGO electrode. The typical Nyquist plots recorded for the four electrodes are presented in Fig. 7. All Nyquist plots display a broad depressed semicircle at high-medium frequency region and a slopping line at low frequency region. In general, the semicircle in the high frequency region is related to the formation of solid electrolyte interface (SEI) film and corresponding impedance between active material and electrolyte, while the semicircle in the medium frequency region is associated with the charge transfer impedance through the electrode-electrolyte interface, which is a large proportion of the overall kinetic impedance of the cell [61]. And the straight line at low-frequency region represents the Warburg impedance, which is

related to the diffusion-controlled process in the solid state electrodes [62]. Obviously, with increase of BN content, the diameters of the semicircle for the rGO/BN composite film electrodes become larger, indicating higher contact and charge-transfer resistances. The equivalent circuit model of the studied system is also shown in the inset of Fig. 7 [60]. R_e represents the internal resistance of the test battery, R_f and C_f are associated with the SEI layer resistance and dielectric relaxation capacitance respectively, R_{ct} and C_{dl} are associated with the charge transfer resistance and the associated double-layer capacitance, and Z_w is referred as the ion diffusion resistance in the solution, also known as Warburg impedance [31,33,37]. The R_{ct} for rGO, rGO/BN-2%, rGO/BN-5%, and rGO/BN-11% composite film electrodes are 90.2, 151.3, 172.5 and 203.2 Ω , respectively, which indicates that the charge-transfer resistances increase with the increase of BN contents. The possible reason is that the rGO/BN composite film with a higher BN content will have a poor conductivity due to the insulating property of BN.

The abovementioned electrochemical performance measurement results of the rGO/BN composite film electrodes indicate that suitable amount of BN nanosheets in the composite materials plays a significant role in improving the electrode rate performance and specific capacity. The enhanced performances can be attributed to the synergistic effect between rGO and BN nanosheets: (a) the addition of proper amount of BN nanosheets can inhibit the restacking of rGO layers and contribute to more accessible Li adsorption and diffusion, leading to an effective material utilization during the charging/discharging processes; (b) the excessive expansion at the rGO/BN interlayer distance caused by lithiation can be highly facilitated by the weak van der Waals and electrostatic interactions of the two materials.

4. Conclusions

In summary, we have demonstrated a facile approach for the fabrication of rGO/BN composite films by vacuum filtration and subsequent thermal annealing. In addition, the effects of BN nanosheets doping level in the rGO/BN composite film on the electrochemical performances are systematically investigated. When used as binder-free anode materials of LIBs, the rGO/BN composite film with a 2 wt.% BN content exhibits a high reversible capacity of $278 \text{ mAh}\cdot\text{g}^{-1}$ at a high current density of $100 \text{ mA}\cdot\text{g}^{-1}$, high rate capability, and excellent cycling stability (no obvious decay after 200 cycles), which can be attributed to the synergistic effect between rGO and BN nanosheets. The synthesis strategy presented in this work holds promise in general fabrication of other graphene-based composite films for high-performance energy storage devices without any binder or additive.

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References

- [1] J.-M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, *Nature* 414 (2001) 359.
- [2] K. Kang, Y.S. Meng, J. Breger, C.P. Grey, G. Ceder, Electrodes with high power and high capacity for rechargeable lithium batteries, *Science* 311 (2006) 977.
- [3] M. Armand, J.-M. Tarascon, Building better batteries, *Nature* 451 (2008) 652.
- [4] A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala, G. Yushin, High-performance lithium-ion anodes using a hierarchical bottom-up approach, *Nat. Mater.* 9 (2010) 353.

- [5] B. Kang, G. Ceder, Battery materials for ultrafast charging and discharging, *Nature* 458 (2009) 190.
- [6] M.V. Reddy, G.V. SubbaRao, B.V.R. Chowdari, Metal oxides and oxysalts as anode materials for li ion batteries, *Chem. Rev.* 113 (2013) 5364.
- [7] B. Dunn, H. Kamath, J.M. Tarascon, Electrical energy storage for the grid: a battery of choices, *Science* 334 (2011) 928.
- [8] Z.-S. Wu, W. Ren, L. Wen, L. Gao, J. Zhao, Graphene anchored with Co_3O_4 nanoparticles as anode of lithium ion batteries with enhanced reversible capacity and cyclic performance, *ACS Nano* 4 (2010) 3187.
- [9] J.M. Jeong, B.G. Choi, S.C. Lee, K.G. Lee, S.J. Chang, Y.K. Han, Y.B. Lee, H.U. Lee, S. Kwon, G. Lee, C.S. Lee, Y.S. Huh, Hierarchical hollow spheres of Fe_2O_3 @polyaniline for lithium ion battery anodes, *Adv. Mater.* 25 (2013) 6250.
- [10] X. Lang, A. Hirata, T. Fujita, M. Chen, Nanoporous metal/oxide hybrid electrodes for electrochemical supercapacitors, *Nat. Nanotechnol.* 6 (2011) 232.
- [11] L. Ji, Z. Lin, M. Alcoutlabi, X. Zhang, Recent developments in nanostructured anode materials for rechargeable lithium-ion batteries, *Energy Environ. Sci.* 4 (2011) 2682.
- [12] R.H. Wang, C.H. Xu, J. Sun, L. Gao, C.C. Lin, Flexible free-standing hollow Fe_3O_4 /graphene hybrid films for lithium-ion batteries, *J. Mater. Chem. A* 1 (2013) 1794.
- [13] Y. Chen, B.H. Song, L. Lu, J.M. Xue, Ultra-small Fe_3O_4 nanoparticle decorated graphene nanosheets with superior cyclic performance and rate capability, *Nanoscale* 5 (2013) 6797.
- [14] S.J.R. Prabakar, Y.H. Hwang, E.G. Bae, S. Shim, D. Kim, M.S. LAh, K.S. Sohn, M. Pyo, SnO_2 /graphene composites with self-assembled alternating oxide and amine layers for high Li-storage and excellent stability, *Adv. Mater.* 25 (2013) 3307.

- [15] G. Zhao, L. Jiang, Y. He, J. Li, H. Dong, X. Wang, W. Hu, Sulfonated graphene for persistent aromatic pollutant management, *Adv. Mater.* 23 (2011) 3959.
- [16] Z.-S. Wu, W. Ren, L. Xu, F. Li, H.-M. Cheng, Doped graphene sheets as anode materials with superhigh rate and large capacity for lithium ion batteries, *ACS Nano* 5 (2011) 5463.
- [17] L. Pan, K.X. Wang, X.D. Zhu, X.M. Xie, Y.T. Liu, Hierarchical assembly of SnO₂ nanowires on MnO₂ nanosheets: a novel 1/2D hybrid architecture for high-capacity, reversible lithium storage, *J. Mater. Chem. A* 3 (2015) 6477.
- [18] L. Pan, X.D. Zhu, X.M. Xie, Y.T. Liu, Delicate ternary heterostructures achieved by hierarchical co-assembly of Ag and Fe₃O₄ nanoparticles on MoS₂ nanosheets: morphological and compositional synergy in reversible lithium storage, *J. Mater. Chem. A* 3 (2015) 2726.
- [19] M. He, L. Yuan, X. Hu, W. Zhang, J. Shu, Y. Huang, A SnO₂@carbon nanocluster anode material with superior cyclability and rate capability for lithium-ion batteries, *Nanoscale* 5 (2013) 3298.
- [20] A.L.M. Reddy, A. Srivastava, S.R. Gowda, H. Gullapalli, M. Dubey, P.M. Ajayan, Synthesis of nitrogen-doped graphene films for lithium battery application, *ACS Nano* 4 (2010) 6337.
- [21] X.W. Lou, C.M. Li, L.A. Archer, Designed synthesis of coaxial SnO₂@carbon hollow nanospheres for highly reversible lithium storage, *Adv. Mater.* 21 (2009) 2536.
- [22] A. Ambrosi, C.K. Chua, A. Bonanni, M. Pumera, Electrochemistry of graphene and related materials, *Chem. Rev.* 114 (2014) 7150.
- [23] N. Mahmood, C.Z. Zhang, H. Yin, Y.L. Hou, Graphene-based nanocomposites for energy storage and conversion in lithium batteries, supercapacitors and fuel cells, *J. Mater. Chem.*

A 2 (2014) 15.

- [24] J. Luo, J. Liu, Z. Zeng, C.F. Ng, L. Ma, H. Zhang, J. Lin, Z. Shen, H.J. Fan, Three-dimensional graphene foam supported Fe_3O_4 lithium battery anodes with long cycle life and high rate capability, *Nano Lett.* 13 (2013) 6136.
- [25] J. Liu, J. Jiang, D. Qian, G. Tan, S. Peng, H. Yuan, D. Luo, Q. Wang, Y. Liu, Facile assembly of a 3D rGO/MWCNTs/ Fe_2O_3 ternary composite as the anode material for high-performance lithium ion batteries, *RSC Adv.* 3 (2013) 15457.
- [26] S.Y. Kim, J. Hong, R. Kaviani, S.W. Lee, M.N. Hyder, Y. Shao-Horn, P.T. Hammond, Rapid fabrication of thick spray-layer-by-layer carbon nanotube electrodes for high power and energy devices, *Energy Environ. Sci.* 6 (2013) 888.
- [27] X. Huang, Z. Zeng, Z. Fan, J. Liu, H. Zhang, Graphene-based electrodes, *Adv. Mater.* 24 (2012) 5979.
- [28] C. Xu, B. Xu, Y. Gu, Z. Xiong, J. Sun, X.S. Zhao, Graphene-based electrodes for electrochemical energy storage, *Energy Environ. Sci.* 6 (2013) 1388.
- [29] M. Xu, T. Liang, M. Shi, H. Chen, Graphene-like two-dimensional materials, *Chem. Rev.* 113 (2013) 3766.
- [30] B. Zhang, G. Cui, K. Zhang, L. Zhang, P. Han, S. Dong, Molybdenum nitride/nitrogen-doped graphene hybrid material for lithium storage in lithium ion batteries, *Electrochim. Acta* 150 (2014) 15.
- [31] K. Chang, W. Chen, L-cysteine-assisted synthesis of layered MoS_2 /graphene composites with excellent electrochemical performances for lithium ion batteries, *ACS Nano* 5 (2011) 4720.

- [32] K. Chang, W. Chen, In situ synthesis of MoS₂/graphene nanosheet composites with extraordinarily high electrochemical performance for lithium ion batteries, *Chem. Commun.* 47 (2011) 4252.
- [33] K. Chang, W. Chen, Single-layer MoS₂/graphene dispersed in amorphous carbon: towards high electrochemical performances in rechargeable lithium ion batteries, *J. Mater. Chem.* 21 (2011) 17175.
- [34] X.S. Zhou, L.J. Wan, Y.G. Guo, Synthesis of MoS₂ nanosheet–graphene nanosheet hybrid materials for stable lithium storage, *Chem. Commun.* 49 (2013) 1838.
- [35] Y.T. Liu, X.D. Zhu, Z.Q. Duan, X.M. Xie, Flexible and robust MoS₂–graphene hybrid paper cross-linked by a polymer ligand: a high-performance anode material for thin film lithium-ion batteries, *Chem. Commun.* 49 (2013) 10305.
- [36] K. Shiva, H.S.S.R. Matte, H.B. Rajendra, A.J. Bhattacharyya, C.N.R. Rao, Employing synergistic interactions between few-layer WS₂ and reduced graphene oxide to improve lithium storage cyclability and rate capability of Li-ion batteries, *Nano Energy* 2 (2013) 787.
- [37] Y. Liu, W. Wang, Y.W. Wang, X.S. Peng, Homogeneously assembling like-charged WS₂ and GO nanosheets lamellar composite films by filtration for highly efficient lithium ion batteries, *Nano Energy* 7 (2014) 25.
- [38] Z.Q. Duan, Y.C. Sun, Y.T. Liu, X.M. Xie, X.D. Zhu, Scalable production of transition metal disulphide/graphite nanoflake composites for high-performance lithium storage, *RSC Adv.* 4 (2014) 41543.
- [39] R.Y. Tay, M.H. Griep, G. Mallick, S.H. Tsang, R.S. Singh, T. Tumlin, E.H.T. Teo, S.P. Karna, Growth of large single-crystalline two-dimensional boron nitride hexagons on electropolished copper, *Nano Lett.* 14 (2014) 839.

- [40] K.S. Kim, C.T. Kingston, A. Hrdina, M.B. Jakubinek, J. Guan, M. Plunkett, B. Simard, Hydrogen-catalyzed, pilot-scale production of small-diameter boron nitride nanotubes and their macroscopic assemblies, *ACS Nano* 8 (2014) 6211.
- [41] Y. Liao, Z. Chen, J.W. Connell, C.C. Fay, C. Park, J.W. Kim, Y. Lin, Chemical sharpening, shortening, and unzipping of boron nitride nanotubes, *Adv. Funct. Mater.* 24 (2014) 4497.
- [42] R.Y. Tay, X. Wang, S.H. Tsang, G.C. Loh, R.S. Singh, H. Li, G. Mallick, E.H.T. Teo, A systematic study of the atmospheric pressure growth of large-area hexagonal crystalline boron nitride film, *J. Mater. Chem. C* 2 (2014) 1650.
- [43] Y.T. Liu, X.M. Xie, X.Y. Ye, Tuning the solubility of boron nitride nanosheets in organic solvents by using block copolymer as a “Janus” modifier, *Chem. Commun.* 49 (2013) 388.
- [44] K. Yan, H.-W. Lee, T. Gao, G.Y. Zheng, H.B. Yao, H.T. Wang, Z.D. Lu, Y. Zhou, Z. Liang, Z.F. Liu, S. Chu, Y. Cui, Ultrathin two-dimensional atomic crystals as stable interfacial layer for improvement of lithium metal anode, *Nano Lett.* 14 (2014) 6016.
- [45] G. Gao, W. Gao, E. Cannuccia, J. Taha-Tijerina, L. Balicas, A. Mathkar, T.N. Narayanan, Z. Liu, B.K. Gupta, J. Peng, Y. Yin, A. Rubio, P.M. Ajayan. Artificially stacked atomic layers: toward new van der Waals solids, *Nano Lett.* 12 (2012) 3518.
- [46] Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets, *J. Am. Chem. Soc.* 130 (2008) 5856.
- [47] W.S. Hummers, R.E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.* 80 (1958) 1339.
- [48] C.Y. Zhi, Y. Bando, C.C. Tang, H. Kuwahara, D. Golberg, Large-scale fabrication of boron nitride nanosheets and their utilization in polymeric composites with improved thermal and mechanical properties, *Adv. Mater.* 21 (2009) 2889.

- [49] N.G. Shang, P. Papakonstantinou, M. McMullan, M. Chu, A. Stamboulis, A. Potenza, S.S. Dhesi, H. Marchetto, Catalyst-free efficient growth, orientation and biosensing properties of multilayer graphene nanoflake films with sharp edge planes, *Adv. Funct. Mater.* 18 (2008) 3506.
- [50] S. Park, R.S. Ruoff, Chemical methods for the production of graphenes, *Nat. Nanotechnol.* 4 (2009) 217.
- [51] M. Sprinkle, D. Siegel, Y. Hu, J. Hicks, A. Tejeda, A. Taleb-Ibrahimi, P. Le Fèvre, F. Bertran, S. Vizzini, H. Enriquez, S. Chiang, P. Soukiassian, C. Berger, W.A. de Heer, A. Lanzara, E.H. Conrad, First direct observation of a nearly ideal graphene band structure, *Phys. Rev. Lett.* 103 (2009) 226803.
- [52] H. Zhou, S. Zhu, M. Hibino, I. Honma, M. Ichihara, Lithium storage in ordered mesoporous carbon (CMK-3) with high reversible specific energy capacity and good cycling performance, *Adv. Mater.* 15 (2003) 2107.
- [53] D. Aurbach, Review of selected electrode–solution interactions which determine the performance of Li and Li ion batteries, *J. Power Sources* 89 (2000) 206.
- [54] Y. Wu, C. Jiang, C. Wan, E. Tsuchida, Effects of catalytic oxidation on the electrochemical performance of common natural graphite as an anode material for lithium ion batteries, *Electrochem. Commun.* 2 (2000) 272.
- [55] J.R. Dahn, T. Zheng, Y. Liu, J.S. Xue, Mechanisms for lithium insertion in carbonaceous materials, *Science* 270 (1995) 590.
- [56] M. Itagaki, S. Yotsuda, N. Kobari, K. Watanabe, S. Kinoshita, M. Ue, Electrochemical impedance of electrolyte/electrode interfaces of lithium-ion rechargeable batteries: Effects of additives to the electrolyte on negative electrode, *Electrochim. Acta* 51 (2006) 1629.

- [57] J. Xiao, X. Wang, X.-Q. Yang, S. Xun, G. Liu, P.K. Koech, J. Liu, J.P. Lemmon, Electrochemically induced high capacity displacement reaction of PEO/MoS₂/graphene nanocomposites with lithium, *Adv. Funct. Mater.* 21 (2011) 2840.
- [58] P. Lian, X. Zhu, S. Liang, Z. Li, W. Yang, H. Wang, Large reversible capacity of high quality graphene sheets as an anode material for lithium-ion batteries, *Electrochim. Acta* 55 (2010) 3909.
- [59] S.-L. Chou, J.-Z. Wang, D. Wexler, K. Konstantinov, C. Zhong, H.-K. Liu, S.-X. Dou, High-surface-area-Fe₂O₃/carbon nanocomposite: one-step synthesis and its highly reversible and enhanced high-rate lithium storage properties, *J. Mater. Chem.* 20 (2010) 2092.
- [60] K.H. Park, D. Lee, J. Kim, J. Song, Y.M. Lee, H.-T. Kim, J.-K. Park, Defect-free, size-tunable graphene for high-performance lithium ion battery, *Nano Lett.* 14 (2014) 4306.
- [61] R. Ruffo, S.S. Hong, C.K. Chan, R.A. Huggins, Y. Cui, Impedance analysis of silicon nanowire lithium ion battery anodes, *J. Phys. Chem. C*, 113 (2009) 11390.
- [62] I. Sultana, M.M. Rahman, S. Li, J. Wang, C. Wang, G.G. Wallace, H.K. Liu, Electrodeposited polypyrrole (PPy)/para (toluene sulfonic acid) (pTS) free-standing film for lithium secondary battery application, *Electrochim. Acta* 60 (2012) 201.

Figure captions

Fig. 1 (a) Fabrication process of GO/BN composite film by vacuum filtration, (b) schematic illustration for the preparation of rGO/BN composite film electrode on copper foil, (c) the assembled coin cell using the rGO/BN composite film electrode as anode material.

Fig. 2 (a-b) Typical TEM images of as-prepared BNNSs, the insets in (b) show the edge folding, (c-d) typical TEM images of GO, (e) top-view and cross-section SEM images of rGO/BN-2% composite film, (f) TEM image of as-prepared rGO/BN-2% composite film.

Fig. 3 XPS spectra of as-prepared rGO/BN-2% composite film: (a) survey scan, (b) C 1s scan, (c) N 1s scan, and (d) Raman spectra of as-prepared BN, rGO, and rGO/BN composite films.

Fig. 4 Cyclic voltammogram (CV) curves of the as-prepared film electrode for the first three cycles at a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$ in the voltage range of 0.0-3.0 V: (a) pure rGO film, (b) rGO/BN-2% composite film, (c) rGO/BN-5% composite film, and (d) rGO/BN-11% composite film.

Fig. 5 Galvanostatic charge/discharge curves of the as-prepared film electrode for the first three cycles at a current density of $100 \text{ mA}\cdot\text{g}^{-1}$ in the voltage range of 0.01-2.5 V: (a) pure rGO film, (b) rGO/BN-2% composite film, (c) rGO/BN-5% composite film, and (d) rGO/BN-11% composite film.

Fig. 6 (a) Rate performances at different current densities and (b) cycling stabilities for pure rGO film and rGO/BN composite films at the current density of $200 \text{ mA}\cdot\text{g}^{-1}$.

Fig. 7 Nyquist plots of rGO, rGO/BN-2%, rGO/BN-5% and rGO/BN-11% film electrodes. The scatter dots and solid lines are experimental and fitted results, respectively. Inset is the corresponding equivalent circuit model.

Fig. 1

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