SUBJECT AREAS:

SYNTHESIS OF
GRAPHENETWO-DIMENSIONAL
MATERIALS

BATTERIES

ELECTRONIC PROPERTIES
AND DEVICES

Interlayer catalytic exfoliation realizing scalable production of large-size pristine few-layer graphene

Xiumei Geng^{1†}, Yufen Guo^{1†}, Dongfang Li¹, Weiwei Li¹, Chao Zhu¹, Xiangfei Wei¹, Mingliang Chen¹, Song Gao¹, Shengqiang Qiu¹, Youpin Gong¹, Liqiong Wu¹, Mingsheng Long¹, Mengtao Sun², Gebo Pan¹ & Liwei Liu¹

¹Key Laboratory of Nanodevices and Applications, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, Jiangsu 215123, People's Republic of China, ²Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China.

Received

11 November 2012

Accepted

11 December 2012

Published

25 January 2013

Correspondence and
requests for materials
should be addressed to

L.W.L. (lwliu2007@
sinano.ac.cn)

† These authors
contributed equally to
this work.

Mass production of reduced graphene oxide and graphene nanoplatelets has recently been achieved. However, a great challenge still remains in realizing large-quantity and high-quality production of large-size thin few-layer graphene (FLG). Here, we create a novel route to solve the issue by employing one-time-only interlayer catalytic exfoliation (ICE) of salt-intercalated graphite. The typical FLG with a large lateral size of tens of microns and a thickness less than 2 nm have been obtained by a mild and durative ICE. The high-quality graphene layers preserve intact basal crystal planes owing to avoidance of the degradation reaction during both intercalation and ICE. Furthermore, we reveal that the high-quality FLG ensures a remarkable lithium-storage stability (>1,000 cycles) and a large reversible specific capacity (>600 mAh g⁻¹). This simple and scalable technique acquiring high-quality FLG offers considerable potential for future realistic applications.

Graphene is of considerable and fascinating physical and chemical properties, such as large theoretical specific surface area and high carrier mobility, which make graphene attractive for electrode materials in energy storage and conductive additives in composites^{1–7}. However, so far, it has remained elusive to create a convincing method producing both large-quantity and high-quality graphene layers that their structure and properties resemble pristine graphene layers. Thus it is also unrealistic to evaluate the applications of pristine graphene layers in industry. Considerable efforts have been devoted to producing large-quantity or high-quality graphene layers and a series of great progresses have been made for the past years. The scalable production has merely been realized in the preparations of thin reduced graphene oxides (rGOs) and thick graphene platelets. The rGOs are widely produced by oxidization or fluorination method, showing the promising applications in functional nanocomposites and supercapacitors^{8–10}. Unfortunately, the rGOs lost the remarkable electrical and mechanical properties that graphene layers possess since intrinsic graphene structures have been irreparably destroyed. In addition, high-quality graphene flakes can be produced by a simple liquid-phase exfoliation of graphite powder in organic solvents^{11,12}. Its drawbacks are that the yield is quite low (~1 wt%) and the small lateral size of graphene flakes is hard to be improved for the limitation of sonication method. Exfoliation of graphite intercalated compounds (GIC) is considered as a promising method to produce scalable and high-quality graphene since several pilot studies have been demonstrated^{13,14}. The initial acid intercalation graphite followed by the reintercalation of alkali metal has been used to fabricate graphene¹⁵. Another method, the expandable graphite combining the organic molecular reintercalation, could produce highly conductive graphene films¹⁶. Nevertheless, these GIC exfoliation methods of high-quality graphene layers either produce the finite yields and lateral sizes, or use expensive or environment unfriendly chemical agents.

Here, we report simultaneous achievement of high-quality and large-quantity few-layer graphene (FLG) by mild interlayer catalytic exfoliation (ICE). The resulting graphene layers are characterized by thin layers and large lateral size, in contrast to the thicker and small graphene platelets produced by the thermal and microwave expansion^{17,18}. High purity of the produced FLG ensures the stability and exceptional lithium-storage capacity, as opposed to the poor cyclic stability and reversible specific capacity of the previously reported rGOs¹⁹. Our approach provides an environmentally friendly route to prepare high-quality FLG on large scale.

Results

Interlayer catalytic exfoliation. Our strategy is clearly illustrated in the schematic diagram (Fig. 1a and ICE process see Movie S1.). The preparation is accomplished by the interlayer catalytic reaction of the stage-1 FeCl_3 -intercalated graphite (FeCl_3 -GIC) with H_2O_2 (see Methods), in which interlayer FeCl_3 serves as effective catalyst and H_2O_2 as both reductant and oxidant. FeCl_3 -GIC and highly expanded product after ICE show a striking contrast in volume and shape (Fig. 1b,c). Different exfoliation extents are characterized with increasing amount of additive H_2O_2 (see Supplementary Information, Fig. S3). Through gentle and short-time sonication, the volume of the freeze-dried FLG increases explosively compared to that of the raw graphite flake, as shown in Fig. 1d.

The morphologies and structures of the large-quantity FLG. The large area and ultra-thin thickness of the scalable FLG are

characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM), respectively (Fig. 2). Mass production of graphene powders can be achieved by the ICE strategy. Tens of gram FLG can be readily exfoliated per batch in a vessel with a few liters capacity. A photograph shows 10 g raw graphite flakes and exfoliated FLG suspension by ICE in Fig. 2a. The volume-expanded FLG can suspend in water which plays a role in preventing the further restacking of graphene layers (see Supplementary Information, Fig. S4). Figure 2b shows a 10 g FLG powder made by freeze-dried graphene layer suspension. The morphologies of the as-prepared FLG are flexible and gauze-like, shown in Fig. 2c,d. The larger area FLG are preserved by the gentle ICE sustaining a few hours than that produced by sonication and thermal expansion methods^{20,21}. The SEM image shows a graphene layer with a typical area as large as $40 \times 60 \mu\text{m}^2$ (Fig. 2e), which is comparable with that of large-area rGOs. The ultra-thin thickness and layer numbers are identified by

Figure 1 | FLG fabricated by interlayer catalytic exfoliation. (a) Schematic illustration of the process from stage-1 FeCl_3 intercalated graphite (FeCl_3 -GIC) to ICE graphene layers. (b, c) Photographs of the FeCl_3 -GIC powder and the highly expanded products consisting of interconnected graphene layers upon ICE. (d) Comparison images of the raw graphite (left) and the FLG (right).

Figure 2 | Typical photographs, SEM, AFM and TEM images of the FLG. (a) Large volume of the FLG suspension (right), graphite flakes (bottom left). (b) The ~10 g FLG powder. (c,d) SEM image of the FLG at different magnifications shows the thin and soft morphologies. (e) SEM image of an isolated few-layer graphene with a large area ($40 \times 60 \mu\text{m}^2$) on a TEM grid. (f) AFM image shows the height profile of the soft wrinkled surface morphology of the FLG, and the highlight step height is ~ 1.94 nm. (g) Low-resolution TEM images of the FLG. (h–k), HRTEM images of the folded edges, indicating single-layer, bilayer, trilayer and few-layer graphene.

AFM and TEM, respectively. AFM image shows a thickness of 1.94 nm, calculated from the height difference between the surface of the graphene layer and the SiO_2 substrate, corresponding to an approximately four-layer thickness¹ (Fig. 2f). Ultra-thin thickness was further proved by HRTEM observation. The single-layer, bilayer, trilayer and few-layers graphene are determined by the dark lines in the folded regions from interior and edges of the typical large area graphene layers (Fig. 2g–k). Most FLG are predominately less than 6 layers using TEM analysis. Currently, we estimate conservatively that the thickness of the FLG is less than 2 nm.

The quality and purity of the FLG. The high quality and intact structure toward pristine graphene layers are determined by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and X-ray diffraction (XRD). FTIR experiments reveal that there are no discernable functional groups in as-prepared FLG (Fig. 3a). XPS

results of FLG are in good agreement with natural graphite, and oxidized groups and impurities is insignificant (Fig. 3b). The high consistence of C 1s peaks between graphite and the FLG, locating at ~ 284.5 eV associated with C–C bonds, implies the high quality of FLG (the inset of Fig. 3b). The little amount of oxygen in XPS originates from the raw graphite and the reactive process (see Supplementary Information, Fig. S5). The peaks of Fe 2p, Cl 2s and Cl 2p appearing in FeCl_3 -GIC (see Supplementary Information, Fig. S6) mainly in the form of Fe–Cl bond²² almost disappear in the FLG (Fig. 3b). A quite small amount of residual Cl element is ~ 0.2 atom% in the form of C–Cl bond in the FLG (see Supplementary Information, Fig. S7). The low defect concentration of the FLG is further confirmed by the comparisons of Raman spectra of the FLG and the natural graphite (Fig. 3c). A small D peak and the low ratio of D to G ($I_D/I_G \sim 0.1$) of graphene layers are similar to those of the natural graphite, suggesting that our process hardly generates structural defects. The D peak of the FLG is quite different from that of rGOs with the prominent D peak^{23–25}. The

Figure 3 | Spectrum characterizations of high quality FLG. (a) IR spectra of graphite and the FLG. The absence of functional groups includes in the range (500–4,000 cm^{-1}). (b) XPS spectra of the FLG. The inset is comparison C 1s spectra of graphite and the FLG, showing the perfect structure of the resulting FLG. (c) Raman spectra of graphite and the FLG, showing the low peak intensity ratios of D to G. (d) XRD spectra of graphite and FLG, displaying well consistent peak positions.

Raman spectroscopy and XRD pattern of the FeCl_3 -GIC confirm the complete stage-I intercalation (See Supplementary Information, Figs. S8 and S9)²⁶. The high quality and purity of the ICE graphene layers are determined by the recovering of a single (002) peak and the absence of other impurities peaks in XRD pattern. The (002) peak of the ICE graphene layers (26.58) shifts slightly relative to the natural graphite (26.69), which is ascribed to increasing the interlayer spacing of the FLG (Fig. 3d). The perfect structure and the trace amount of impurities indicate that the ICE reaction does not bring degradation of FLG. We assume that the weak oxidation ability at room temperature (see Supplementary Information, Figs. S5 and S10), short reaction duration and the catalytic reaction with Fe^{3+} effectively restrict the damage of H_2O_2 to graphene layers.

We measured the specific surface area (SSA) of the few-layer graphene by the N_2 gas absorption Brunauer-Emmett-Teller (BET) and methylene blue (MB) adsorption^{27–29} in solution. The SSA is found to be up to $\sim 545 \text{ m}^2 \text{ g}^{-1}$ of the few-layer graphene in alcohol solution by MB method, and $\sim 184 \text{ m}^2 \text{ g}^{-1}$ of the freeze-dried few-layer graphene powder by BET (The details see Supplementary Information). The component analysis showed that carbon element content of the resulting few-layer graphene is $\sim 99.08 \text{ atom\%}$ by the experiments of the combustion-based elemental analysis and the energy-dispersive X-ray spectroscopy (EDX) (see Supplementary Information, Fig. S11).

Remarkable lithium-storage performance of the FLG. We further investigate the electrical properties and lithium-storage performance of the FLG (Fig. 4). The conductivities are measured by a four-point method on a thin and compact disc of few-layer graphene pressed by

a pressure of 20 MPa. The disc diameter is 25.4 mm and the film thickness is $\sim 8 \mu\text{m}$ (see cross-section SEM image in Fig. S12). The semiconductor parameter analyzer B1500A (Agilent) is used with the probe spacing of 1 mm. The order of magnitude of the conductivities ($2.3 \times 10^5 \text{ S m}^{-1}$) of our samples is approximate to that of our natural raw graphite ($6.6 \times 10^5 \text{ S m}^{-1}$) and around two orders of magnitude higher than that of the previous reported reduced graphene oxide^{24,29,30}, which implies that in-plane defects are least significant. (The details see Supplementary Information).

Further, we demonstrate that the FLG as the electrode material in lithium-ion batteries show the advantages of the cyclic stability and high specific capacity. The reversible cycles can be more than 1,000 (Fig. 4b, c). The first discharge curve shows a specific capacity of $1,243 \text{ mAh g}^{-1}$ at a current density of 0.1 A g^{-1} . The solid electrolyte interface (SEI) layer is formed at a potential plateau of 0.77 V, which leads to the degradation of the initial specific capacity. The second discharge curve shows a reversible specific capacity of 619 mAh g^{-1} (Fig. 4b), which is almost twice as much as that of commercial graphite. During the 1,000 cycles, the battery undergoes the charging and discharging at a large current density of 1 A g^{-1} from 24 to 1,000 cycles with an average reversible specific capacity of 480 mAh g^{-1} (Fig. 4c). The reversible specific capacity increases from 619 to 712 mAh g^{-1} after 1,000 cycles when the current density is returned to 0.1 A g^{-1} . A possible origin of the increment is the slow infiltration process of the electrolyte through the compact film of graphene layers. So far, there are a lot of reports about the lithium storage based on the rGOs and its composites. Very recently, the excellent cyclic stability has been demonstrated on the binder-free photothermally reduced graphene film with the steady capacity of

Figure 4 | Conductivity and lithium storage properties of the FLG.

(a) Conductivity of the FLG, and inset is the schematic diagram of the four-point measurement. (b) Charge and discharge curves of the FLG. The inset displays the dispersion of the FLG in N-methyl-2-pyrrolidone. (c) The highly cyclic stability of the FLG in lithium storage. The inset is a photograph of a lithium-ion coin cell.

$\sim 156 \text{ mAh g}^{-1}$ over 1,000 cycles at large charge/discharge rates of $\sim 40 \text{ C}^{31}$. In addition, the rGOs-composites are also a promising candidate as new lithium-ion battery electrode materials. For instance, ultrathin CoO/graphene hybrid nanosheets show the capacity of $\sim 1,018 \text{ mAh g}^{-1}$ after ~ 520 cycles³². However, as for the lithium storage properties of rGOs electrodes formed by rGOs power with binder, the moderate reversible specific capacity rapidly degrades with cycling. To our knowledge, most of them suffer from the poor cyclic stability and no stable cycles more than 1,000 have been reported^{33,34}. The film method using graphene powder with

binder is compatible with the conventional technique, although the reversible capacity and cyclic stability are required to be greatly improved. Our work demonstrated the significance of the high conductivity and high purities for the good cyclic stability with the compatible coating technique through the polymer binder.

Discussion

Among GICs, the FeCl_3 -GIC is quite unique for its thermal and soluble stability. Even through ICE, graphene layers still maintain their pristine intact structures due to the weak interaction between graphene layers and FeCl_3 molecules. Furthermore, another advantage is that FeCl_3 is an available catalyst of ICE reaction. The interlayer catalytic reaction of FeCl_3 and H_2O_2 provides mild and durable gas exfoliation and produces environment-friendly by-products of water and oxygen. The control experiments show the advantages of ICE approach in thin thickness and large size over thermal expansion exfoliation and common chemical reaction³⁵ (see Supplementary Information, Figs. S13 and S14).

Next we consider the source of the excellent lithium-storage capacity of our ICE graphene layers. The observed enhanced interlayer spacing and the high conductivity of the FLG are assumed to be the origins of the excellent capacity in the lithium storage. The increment of interlayer spacings with the reducing layer numbers of the graphene layers has been observed by the statistic results of TEM (see Supplementary Information, Fig. S15). The average interlayer spacings are 0.419, 0.393, 0.372, 0.346 nm, corresponding to 2, 3, 4 and 5 layers, respectively. The similar results have also been reported in polyacenic semiconductor materials and the hybrid system of rGOs and carbon nanotubes^{36,37}.

In summary, the scalable ICE method has a significant ability to produce pure few-layer graphene with a large lateral size. The intact structure, thin thickness and excellent conductance of the produced FLG ensure the exceptional cyclic stability and specific capacity in the lithium storage. The results represent important breakthroughs in scalable fabrication and lithium-storage application of high-quality FLG, to date, which have been the two awkward challenges. The novel technique presented here opens a way to bring the best graphene layers to the broad applications.

Methods

Preparation of the FLG. Ferric chloride-graphite intercalation compounds were synthesized via a conventional two-zone vapour transport technique. Natural graphite flakes (0.5 g, 99.8%, ABCR Karlsruhe, Germany) and anhydrous ferric chloride powders (2.8 g, Alfa Aesar) were put in a two-zone reactive container and then the reactants were sealed, which was carried out in a nitrogen filled glove box ($\text{H}_2\text{O} < 1 \text{ ppm}$ and $\text{O}_2 < 1 \text{ ppm}$). The mixture was heated at 380°C for 24 h in a furnace. As-synthesized FeCl_3 -intercalated graphite and H_2O_2 (30%) was loaded into a reactive bottle at room temperature for 2 h. The graphite was exfoliated into long worm-like graphite consisting of interconnecting graphene layers and then a gentle and short time (5 min) sonication is performed to obtain the FLG.

Fourier transform infrared spectroscopy. The IR ($500\text{--}4,000 \text{ cm}^{-1}$) was measured using a Nicolet 6700 FT-IR spectrometer with pure KBr as the background. Graphite and graphene layers were ground with KBr, respectively. These mixtures were dried and compressed into transparent tablets for measurements.

Transmission electron microscopy observations. TEM and HRTEM imaging and electron diffraction were performed on a FEI Tecnai G2 F20 S-Twin microscope operated at an accelerating voltage of up to 200 kV. The TEM samples were prepared by sonicating at 500 W for $\sim 5 \text{ min}$, and 25 μL supernatant was dropped onto holey carbon grids.

Scanning electron microscopy observations. SEM images were obtained with a field emission gun scanning electron microscope (Quanta 400 FEG FEI). The samples were dispersed in ethanol, and then dropped onto the Si/SiO_2 substrates.

X-ray photoelectron spectroscopy. XPS was conducted with an Axis Ultra DLD (Kratos) system. The vacuum of chamber was 1×10^{-9} torr. A monochromatic aluminium K_{α} source was used with source power 150 W ($15 \text{ kV} \times 10 \text{ mA}$). The pass energy was 160 eV for wide scans and 40 eV for narrow scans.

Raman spectroscopy. Raman spectroscopy was recorded at a LabRam HR800 UV NIR using a 633 nm laser excitation with working distances on a $\times 50$ lens. Raman spectra of the natural graphite, the FeCl₃-GIC and the graphene layers were taken by depositing the samples on glass slides.

XRD patterns. XRD patterns of the natural graphite, the FeCl₃-GIC and the FLG were recorded for two theta values from 4° to 60° in order to characterize the interlayer spacings. The characterization was done in a Bruker AXS-D8 Advance powder X-ray diffractometer using Cu/K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a step size of 0.02° and a dwell time of 3.0 seconds.

Battery. Electrochemical testing was carried out by using the FLG as anodes in lithium-ion cells. The graphene layers were mixed with binder poly(vinylidene fluoride) (PVDF) at the weight ratio of 8:2 in N-methyl-2-pyrrolidone (NMP) solvent. After that, the resultant slurries were shaken for 12 h, and then pasted on Cu foil uniformly. The prepared working electrode sheets were dried in a vacuum oven at 120°C for 24 h. Li metal foil was used as the counter electrode. LIR2032-type coin cells were assembled in an argon-filled glove box for electrochemistry characterization. The electrolyte was 1 M LiPF₆ dissolved in a 1:1:1 volume ratio mixture of ethylene carbonate, diethylene carbonate and dimethyl carbonate. The coin cells were galvanostatically charged and discharged at current densities of 0.1 A g⁻¹ and 1 A g⁻¹ within the range of 0.001–3.0 V.

- Novoselov, K. S. *et al.* Electric field effect in atomically thin carbon films. *Science* **306**, 666–669 (2004).
- Stankovich, S. *et al.* Graphene-based composite materials. *Nature* **442**, 282–286 (2006).
- Emtsev, K. V. *et al.* Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide. *Nature Mater.* **8**, 203–207 (2009).
- Ramanathan, T. *et al.* Functionalized graphene sheets for polymer nanocomposites. *Nature Nanotech.* **3**, 327–331 (2008).
- Stoller, M. D., Park, S. J., Zhu, Y. W., An, J. H. & Ruoff, R. S. Graphene-based ultracapacitors. *Nano Lett.* **8**, 3498–3502 (2008).
- Wang, H. L. *et al.* LiMn_{1-x}Fe_xPO₄ nanorods grown on graphene sheets for ultrahigh-rate-performance lithium ion batteries. *Angew. Chem. Int. Ed.* **50**, 7364–7368 (2011).
- Wang, H. L. *et al.* Graphene-wrapped sulfur particles as a rechargeable lithium-sulfur battery cathode material with high capacity and cycling stability. *Nano Lett.* **11**, 2644–2647 (2011).
- Li, D., Muller, M. B., Gilje, S., Kaner, R. B. & Wallace, G. G. Processable aqueous dispersions of graphene nanosheets. *Nature Nanotech.* **3**, 101–105 (2008).
- Liu, L. H., Lerner, M. M. & Yan, M. D. Derivatization of pristine graphene with well-defined chemical functionalities. *Nano Lett.* **10**, 3754–3756 (2010).
- Zhu, Y. W. *et al.* Carbon-based supercapacitors produced by activation of graphene. *Science* **332**, 1537–1541 (2011).
- Blake, P. *et al.* Graphene-based liquid crystal device. *Nano Lett.* **8**, 1704–1708 (2008).
- Hernandez, Y. *et al.* High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature Nanotech.* **3**, 563–568 (2008).
- Park, S. & Ruoff, R. S. Chemical methods for the production of graphenes. *Nature Nanotech.* **4**, 217–224 (2009).
- Park, K. H. *et al.* Exfoliation of non-oxidized graphene flakes for scalable conductive film. *Nano Lett.* **12**, 2871–2876 (2012).
- Viculis, L. M., Mack, J. J., Mayer, O. M., Hahn, H. T. & Kaner, R. B. Intercalation and exfoliation routes to graphite nanoplatelets. *J. Mater. Chem.* **15**, 974–978 (2005).
- Li, X. L. *et al.* Highly conducting graphene sheets and Langmuir-Blodgett films. *Nature Nanotech.* **3**, 538–542 (2008).
- Chiu, P. L. *et al.* Microwave- and nitronium ion-enabled rapid and direct production of highly conductive low-oxygen graphene. *J. Am. Chem. Soc.* **134**, 5850–5856 (2012).
- Safavi, A., Tohidi, M., Mahyari, F. A. & Shahbaazi, H. One-pot synthesis of large scale graphene nanosheets from graphite-liquid crystal composite via thermal treatment. *J. Mater. Chem.* **22**, 3825–3831 (2012).
- Pan, D. Y. *et al.* Li storage properties of disordered graphene nanosheets. *Chem. Mater.* **21**, 3136–3142 (2009).
- Gilje, S., Han, S., Wang, M. S., Wang, K. L. & Kaner, R. B. A chemical route to graphene for device applications. *Nano Lett.* **7**, 3394–3398 (2007).
- Tung, V. C., Allen, M. J., Yang, Y. & Kaner, R. B. High-throughput solution processing of large-scale graphene. *Nature Nanotech.* **4**, 25–29 (2009).
- Li, B. *et al.* Photochemical chlorination of graphene. *ACS Nano* **5**, 5957–5961 (2011).
- Kudin, K. N. *et al.* Raman spectra of graphite oxide and functionalized graphene sheets. *Nano Lett.* **8**, 36–41 (2008).
- Stankovich, S. *et al.* Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* **45**, 1558–1565 (2007).
- Eda, G., Fanchini, G. & Chhowalla, M. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nature Nanotech.* **3**, 270–274 (2008).
- Underhill, C., Leung, S. Y., Dresselhaus, G. & Dresselhaus, M. S. Infrared and raman spectroscopy of graphite-ferric chloride. *Solid State Commun.* **29**, 769–774 (1979).
- Choucair, M., Thordarson, P. & Stride, J. A. Gram-scale production of graphene based on solvothermal synthesis and sonication. *Nature Nanotech.* **4**, 30–33 (2009).
- El-Kady, M. F., Strong, V., Dubin, S. & Kaner, R. B. Laser scribing of high-performance and flexible graphene-based electrochemical capacitors. *Science* **335**, 1326–1330 (2012).
- McAllister, M. J. *et al.* Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chem. Mater.* **19**, 4396–4404 (2007).
- Schniepp, H. C. *et al.* Functionalized single graphene sheets derived from splitting graphite oxide. *J. Phys. Chem. B* **110**, 8535–8539 (2006).
- Mukherjee, R., Thomas, A. V., Krishnamurthy, A. & Koratkar, N. Photothermally reduced graphene as high-power anodes for lithium-ion batteries. *ACS Nano* **6**, 7867–7878 (2012).
- Sun, Y. M., Hu, X. L., Luo, W. & Huang, Y. H. Ultrathin CoO/graphene hybrid nanosheets: A highly stable anode material for lithium-ion batteries. *J. Phys. Chem. C* **116**, 20794–20799 (2012).
- Wang, G. X., Shen, X. P., Yao, J. & Park, J. Graphene nanosheets for enhanced lithium storage in lithium ion batteries. *Carbon* **47**, 2049–2053 (2009).
- Wang, C. Y., Li, D., Too, C. O. & Wallace, G. G. Electrochemical properties of graphene paper electrodes used in lithium batteries. *Chem. Mater.* **21**, 2604–2606 (2009).
- Viculis, L. M., Mack, J. J. & Kaner, R. B. A chemical route to carbon nanoscrolls. *Science* **299**, 1361 (2003).
- Yata, S. *et al.* Characteristics of deeply Li-doped polyacenic semiconductor material and fabrication of a Li secondary battery. *Synth. Met.* **73**, 273–277 (1995).
- Yoo, E. J. *et al.* Large reversible Li storage of graphene nanosheet families for use in rechargeable lithium ion batteries. *Nano Lett.* **8**, 2277–2282 (2008).

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 10834004, 10974141, 90923003, 51102273), Ministry of National Science and Technology Projects of China (Grants Nos. 2010CB934700, 2012CB722708), and KGZD-EW-303. Prof. L. W. Liu thanks the Platforms of Characterization & Test and Nanofabrication Facility at Sinano for experimental assistance.

Author contributions

L.L. and X.G. conceived and designed the experiments. X.G., Yu.G., D.L. and W.L. performed the sample preparation, characterizations. C.Z., L.W., Y.G., X.W., M.L., M.C., S.Q., S.G., G.P. and M.S. performed the measurement experiments and data analysis. X.G. and L.L. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

License: This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported License. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc-nd/3.0/>

How to cite this article: Geng, X. *et al.* Interlayer catalytic exfoliation realizing scalable production of large-size pristine few-layer graphene. *Sci. Rep.* **3**, 1134; DOI:10.1038/srep01134 (2013).