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. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it 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 Terms & Conditions and the Ethical guidelines 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.

This article can be cited before page numbers have been issued, to do this please use: G. Wang, G. Chen, S. Yang, P. Zhang, F. Wang, A. Shaygan Nia, M. Yu and X. Feng. Faraday Discuss., 2019, DOI: 10.1039/C9FD00120D.
Facile assembly of layer-interlocked graphene heterostructures as flexible electrodes for Li-ion batteries

Gang Wang, Guangbo Chen, Sheng Yang, Panpan Zhang, Faxing Wang, Ali Shaygan Nia, Minghao Yu and Xinliang Feng*

Dr. G. Wang, G. Chen, Dr. S. Yang, Dr. P. Zhang, F. Wang, Dr. A. Nia, Dr. M. Yu, Prof. X. Feng
Center for Advancing Electronics Dresden (cfaed) & Department of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany
E-mail: xinliang.feng@tu-dresden.de

Abstract:
Flexible electrodes with robust mechanical properties and high electrochemical performance are of significance for practical implementation of flexible batteries. Here we demonstrate a general and straightforward co-assembly approach to prepare flexible electrodes, where electrochemically exfoliated graphene (EG) is exploited as the film former/conducting matrix and different binary metal oxides (Li$_4$Ti$_5$O$_{12}$, LiCoO$_2$, Li$_2$MnO$_4$, LiFePO$_4$) are incorporated. The resultant EG-metal oxide hybrids exhibit a unique layer-interlocked structure, where metal oxide is conformably wrapped by the highly flexible graphene. Due to numerous contact interphases generated between EG and intercalated material, the hybrid films show high flexibility, which can endure rolling, bending, folding and even twisting. When serving as the anode for Li-ion batteries, the freestanding EG-Li$_4$Ti$_5$O$_{12}$ hybrid presents a characteristic flat discharge plateau at 1.55 V (vs Li/Li$^+$), indicating transformation of Li$_4$Ti$_5$O$_{12}$ to Li$_7$Ti$_5$O$_{12}$. Small polarization, high rate capability and excellent cycling stability against mechanical bending are also demonstrated for the prepared EG-Li$_4$Ti$_5$O$_{12}$ hybrid. Finally, full cells composing of EG-Li$_4$Ti$_5$O$_{12}$ and EG-LiFePO$_4$ hybrids show impressive cycling (98% capacity retention after 100 cycles at 1C) and rate performance (84% capacity retained at 2.5C). The straightforward co-assembly approach based on EG can be extended to other two-dimensional layered materials for constructing high-efficient flexible energy storage devices.

KEYWORDS: graphene, heterostructures, flexible electrodes, Li-ion batteries, 2D
materials

Introduction

With the development of portable and wearable electronics, flexible energy storage devices are arousing tremendous attention due to their promising application in powering various foreseen new technology products, such as flexible cell phones, electronic skin and implantable medical products. Owing to the high energy density, long cycle life and environmental benign operation, Li-ion batteries (LIBs) are the first option for the above applications. However, the conventional LIBs with rigid package and large quantity of inactive components (binder, current collector and other additives) are not able to conform to device deformation and fail to maximize energy density. To this end, rationally designing electrodes with high flexibility and freestanding feature becomes a critical issue.

Various carbon materials like carbon nanotubes (CNTs), carbon cloth, reduced graphene oxide (rGO) and chemical vapor deposition graphene (CVDG), have been explored to prepare flexible electrodes due to their light weight and high electrical conductivity. The first reported flexible electrodes were fabricated on CNT paper, where active materials were loaded via a conventional slurry-coating method. In such electrodes, electrochemically inactive components like binder and conductive additives are ineluctable. Recently, the booming development of in-situ synthesis makes it possible to directly grow active materials on carbon substrates, largely reducing the content of inactive components and affording close contact between active materials and conductive host matrix. Even though significant progress has been achieved, the complicated fabrication procedures including repeated hydrothermal/solvothermal synthesis and calcination severely hinder its practical application. Further, the effectiveness of such method to specific materials is difficult to extend to other active electrodes, raising a practical compatibility issue. Therefore, it is highly appealing to develop a straightforward approach with wide material compatibility for flexible electrode fabrication.

Herein we demonstrate facile assembly of flexible graphene-metal oxide hybrids
and explore their applications in Li-ion batteries. Electrochemically exfoliated graphene (EG) with remarkable solution processability and high quality (low oxygen content and low defect) is used as the film former and conductive matrix. No additional reduction procedure is involved, which largely simplifies the preparation of graphene-metal oxide hybrids. Due to large lateral size and flexibility of EG, various metal oxides with multidimensional size, shape and diverse composition can be readily incorporated to fabricate thin-film EG-metal oxide electrodes via a straightforward flow-directed assembly process. The constructed EG-metal oxide hybrids manifest a unique layer-interlocked heterostructure, where metal oxides are well intercalated between graphene layers, thus exhibiting outstanding mechanical stability and flexibility. When serving as the LIB anode, the flexible EG-Li$_4$Ti$_5$O$_{12}$ (EG-LTO) hybrid electrodes show excellent cycling stability and bending stability with high capacity retention of 98% (after 500 cycles at 2.5C) and 94% (after 500 bending cycles), respectively. Similar impressive cycling stability can be achieved in the full cells.

Experimental section

**Preparation of EG:** EG was prepared by electrochemical exfoliation of graphite, where commercial graphite foil (Alfa Aesar) was used as both the working electrode and the counter electrode in 0.1 M ammonium sulfate aqueous solution.$^{24,25}$ A positive voltage of 10 V was applied to initiate the electrochemical exfoliation of graphite. When the exfoliation was finished, the product was filtered and washed several times with deionized water and ethanol. The resultant product was dispersed in dimethylformamide (DMF) via 15 min mild sonication. After standing for 24 h to precipitate thick flakes, the stable supernatant containing EG (designated as EG dispersion) with specific concentration of 0.1-1.0 mg/ml was taken for further material synthesis.

**Preparation of EG-metal oxide hybrids:** EG-metal oxide hybrids were prepared via a flow-directed assembly approach. Typically, a certain amount of the metal oxide was dispersed into DMF by sonication and then mixed the above EG dispersion, followed by another 30 min sonication to produce stable hybrid dispersion. Then the
hybrid dispersion was filtered through a polytetrafluoroethylene filtration membrane (0.2 µm) and washed with ethanol. A free-standing EG-based hybrid film could be directly peeled off from the membrane when the filter cake was dry. The resultant hybrid film was further dried at 200 °C for 12 h in vacuum to remove the residual solvent. The film was cut into specific size for different experiments. The metal oxides used for hybrid films included LTO (<200nm), LiCoO2 (LCO), LiFePO4 (LFP), Li2MnO4 particles (LMO).

Preparation of control sample rGO-LTO hybrid: GO prepared via a modified Hummers’ method26-28 was used instead of EG to fabricate GO-LTO in a similar flow-directed assembly approach. The obtained GO-LTO hybrid film was subjected to hydrazine vapor reduction at 100 °C for 8h within a sealed autoclave, where the hybrid film was separated from direct contact with liquid hydrazine hydrate (N₂H₄ 50-60 %), leading to the formation of rGO-LTO hybrid.

Characterization: Scanning electron microscope (SEM) images were collected on Zeiss Gemini LEO 1530. Atomic force microscopy (AFM) measurement was performed on Veeco Nanoscope-IIIa Multimode Tuna (Digital Instruments). The powder X-ray powder diffraction (XRD) patterns were taken on Brucker D8 ADVANCE X-ray diffractometer using Cu-Kα radiation (λ=1.54178Å). The X-ray photoelectron spectroscopy (XPS) spectra were performed on Kratos X-ray Photoelectron Spectrometer-Axis Ultra DLD using Al Kα radiation. Raman analysis was carried out on a Raman Spectrometer Reinshaw inVia.

Flexibility test of EG-metal oxide hybrid films: The flexibility evaluation of the EG-metal oxide hybrid films was conducted on a homemade movable stage, where the hybrid film was fixed at its two terminals and gap distance could be adjusted. In order to test the resistance variation and conductive feature of EG hybrid films at different bending states, the two terminals of hybrid films were connected to a multimeter or a circuit with or without a polyethylene terephthalate substrate.

Electrochemical measurements: the electrochemical performance of flexible EG-metal oxide hybrids was tested in both CR2032 coin cells and pouch cells with transparent package. The batteries were assembled in an Ar-filled glove box with
moisture and oxygen level <0.1 ppm. The hybrids were cut into small pieces (1 cm*1 cm or 3 cm*1 cm) and directly used as working electrodes. In assembling CR2032 half cells, Li foil was used as the counter electrode; while for full cells, both EG-LFP or EG-LMO hybrids were used and cathode capacity was kept 1.2 times anode capacity. Celgard 2400 (polypropylene membrane) was used as the separator. The electrolyte was 1 M LiPF$_6$ in ethylene carbonate/ethyl methyl carbonate (volume ratio of 1:1). To assemble the pouch cell, a gel-type solid electrolyte, including 0.7 g poly(ethylene oxide), 0.7 g succinonitrile, and 0.6 g lithium bis(trifluoromethane) sulfonimide (LiTFSI) in a mixture of methylene chloride and acetone, was used. The cycling performance of the cells was tested on LAND CT2001A battery system at various current densities. The specific capacity was calculated based on the whole mass of EG-metal oxide hybrids. The CV was measured on a CHI760E electrochemical workstation.

Results and discussion

To fabricate EG-metal oxide hybrids, EG was firstly prepared by electrochemical exfoliation of graphite, which can produce processable EG sheets in large quantities and high quality. The as-formed EG exhibited distinct morphology anisotropy with a large lateral size of 1.0~10 µm and a thin thickness of ~2.0 nm (3-layer graphene) (Figure S1a-c). The oxygen content on EG was estimated to be as low as 4.16 at%, leading to a high C/O ratio of 23 (Figure S1d). No tedious oxidation/reduction or etching procedures are required as that for rGO or CVDG. The Raman spectroscopy of EG in Figure S1e showed a low D peak at 1346 cm$^{-1}$ (the breathing mode of sp$^3$ carbon atoms), a strong G peak at 1568 cm$^{-1}$ (the in-plane vibrations of the graphene lattice) and a 2D peak at 2692 cm$^{-1}$ (overtones of the D band). The $I_D/I_G$ ratio was around 0.13, which is much lower than that (>1.0) of rGO and indicates low defect content on EG basal plane. Under directional flow induced by vacuum filtration, the shear force will make anisotropic EG nanosheets perpendicular to the flow direction. The capillary force associated with solvent between EG interlayers will further closely stack EG nanosheets during
drying process, restoring π-π stacking and yielding an ultra-flexible EG paper with well-packed sheet orientation (Figure S2). Unlike time-consuming vacuum filtration (hours or even days) of GO dispersion, the filtration process of EG dispersion took much shorter time (30 min; including wash process). This can be explained by the structure difference between GO and EG. GO contains substantial oxygen functional groups and will form hydrogen bond with water32; while EG with limited oxygen functional group interacts with DMF just because of surface tension match34. During filtration, the hydrogen bond between GO and water hinders fast removal of water molecular, which, however, will not be a problem for EG dispersion. Moreover, due to high quality of EG, the fabricated EG paper generally shows a high electrical conductivity of 9000 S/m (measured by a four-point probe system), which is superior to 7200 S/m of hydrazine reduced GO.35

In the presence of guest components (metal oxides), EG with large lateral size and high flexibility will conformably wrap and intercalate guest materials between EG layers, forming a layer-interlocked heterostructure (Scheme 1). Within the heterostructure, the guest materials are well connected and confined between EG nanosheets, ensuring excellent electrical contact of guest species throughout the hybrid film. In addition, the porous channels in the heterostructure can facilitate fast ion diffusion and alleviate strain during electrode deformation, endowing EG hybrids with high mechanical and electrochemical stability. Because of simplicity of our co-assembly process, the EG-based hybrid films could be tailored in size, shape and thickness by changing filtration molds and adjusting dispersion concentration or volume.
Scheme 1. The flow-directed assembly process of EG-metal oxide hybrids and the proposed layer-interlocked structure.

The morphology of hybrid films was first investigated by SEM with EG-LTO as an example. Spinel LTO NPs with uniform size (~55 nm) and cubic shape were selected (Figure S4). As shown in top-view SEM images of EG-LTO hybrid (Figure 1a-b), transparent and crumpled EG nanosheets fully covered on clusters of LTO NPs. And the cross section-view images (Figure 1c-d) evidenced the formation of the layered-interlocked heterostructure throughout the hybrid film, where LTO NPs were well confined between EG nanosheets. The thickness of compact EG-LTO hybrid film was determined to be ~17 µm. Further, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurements conducted on EG-LTO hybrid indicated that both the chemical composition and crystallinity (JCPDS No. 49-0207) of LTO were well preserved during the assembly process (Figure S5a-e). The broad peak centered at 26.3° on XRD patterns of EG-LTO derives from few-layer EG sheets. In addition, the sheet resistance of EG-LTO hybrid film with 70 wt% LTO was determined as 143 Ω/sq, which are 3.7 times the value of pristine EG film (38 Ω/sq, Figure S5f). For comparison, a control sample rGO-LTO was prepared by replacing EG with GO and hydrazine vapor reduction at 100 °C for 8 h (see experimental section for preparation details). The LTO content in rGO-LTO and thickness of hybrid films are comparable to those of EG-LTO. In sharp contrast, the sheet resistance of rGO-LTO hybrid was as
high as 585 Ω/sq, over 4 times of that for EG-LTO.

Figure 1. SEM images of EG-LTO hybrid in top view (a, b) and edge view (c, d). Inset is an optical image of the EG-LTO hybrid film.

The flexibility of the resultant hybrid films was then investigated under different bending state or after certain bending cycles. Due to the unique layer-interlocked heterostructure, the free-standing EG-LTO hybrid film showed impressive flexibility, which could endure rolling, bending, folding and even twisting (Figure 2a). Since the resistance of the EG hybrid films could affect their electrochemical performance in Li-ion batteries, the resistance of EG hybrid films under different bending states was evaluated. There was nearly no change in their resistance when the distance between the two ends of EG hybrid films was adjusted from 1 to 0.1 of their original length (Figure 2b). And the bending curvature radius at 0.1 L/L₀ was around 1 mm. The EG-LTO hybrid film remained electrically conductive to connect a circuit even at a high bending state, well similar to the pure EG film (Figure 2c and S6). Furthermore, only 8% resistance increase was detected after 500 continuous bending cycles (L/L₀=0.1-1; Figure 2d), indicating high mechanical stability and flexibility of our EG hybrid films.
Figure 2. Flexibility test of EG-LTO hybrids. (a) Flexibility of EG-LTO hybrid film. (b) Resistance variation of EG paper and EG-LTO hybrid under different bending states. (c) EG-LTO hybrid film connected a circuit at different bending states. (d) Resistance variation of EG-LTO hybrid after various bending cycles.

The co-assembly process plays an important role on the mechanical property of the resultant EG-based hybrid films. When a mix filtration approach was adopted, the pre-formed stable hybrid dispersion directionally flowed through the filtration membrane, forming the layer-interlocked heterostructure with numerous contact interphases between EG and guest materials (Figure S7). As a consequence, the strong EG hybrid films can be directly peeled off from the filtration membrane. On the contrary, no interlocked structure can be guaranteed by a layer-by-layer (LBL) filtration approach. The formed LBL-hybrid films are fragile along the vertical direction and always fail to be peeled off.

As the fabricated EG-metal oxide hybrid films were flexible, freestanding and conductive, they could be cut into desired shapes and directly used as battery electrodes, where no additional current collector, binder or additive was needed. The electrochemical activity of the EG hybrid films was first evaluated in coin cells with Li foil as the counter electrode. The cyclic voltammetry (CV) curve of the EG-LTO hybrid film was presented in Figure S8. A cathodic peak located at 1.47 V (vs Li/Li⁺) is ascribed to lithiation of LTO into Li₇Ti₅O₁₂ (Li₄Ti₅O₁₂ + 3Li⁺ + 3e⁻ → Li₇Ti₅O₁₂), and
an anodic peak at 1.65 V (vs Li/Li\(^+\)) corresponds to the delithiation of Li\(_7\)Ti\(_5\)O\(_{12}\) back to LTO\(^{36, 37}\), suggesting that the electrochemical performance of EG-LTO hybrid films mainly derived from active material LTO. Then we investigated the lithium insertion/extraction properties of the EG-LTO hybrid films by a galvanostatic charge-discharge measurement (Figure 3). At a small current of 0.15 C (1 C=0.14 A/g), the EG-LTO anode displays a long, flat potential plateau at 1.55 V (vs Li/Li\(^+\)) on the discharge curve (Figure 3a), which is a characteristic of phase transition from LTO to Li\(_7\)Ti\(_5\)O\(_{12}\).\(^{20}\) The voltage gap between charge plateau and discharge plateau is only 24 mV, indicating negligible polarization. Based on the total mass, the EG-LTO anode delivered a specific capacity of 137 mAh/g. In the light of LTO content (70 wt%) in EG-LTO hybrid and its theoretical capacity (175 mAh/g), LTO should contribute a capacity of 122.5 mAh/g to the EG-LTO hybrid. An excess capacity of 14.5 mAh/g is ascribed to EG nanosheets in the hybrid. In contrast, the control sample rGO-LTO showed a large voltage gap of 72 mV and an inferior capacity of 125 mAh/g at 0.15C (Figure S9), which can be attributed to the high resistance of rGO-LTO hybrid.

Besides, the rate performance of EG-LTO hybrid film was analyzed under accelerated current rates (Figure 3a, b). When the current increased from 0.15 C to 2.5 C, slight potential polarization was noticed, accompanied by the capacity decrease from 137 mAh/g to 108 mAh/g. Regarding the charge-discharge curves, the charge-discharge plateaus were retained at all rates, implying highly reversible and fast two-phase equilibrium of EG-LTO.\(^{20}\) Figure 3c-d further shows the cycling stability of EG-LTO hybrid films at 1 C and 2.5 C. After 200 and 500 cycles, the capacity decreased less than 1.8% of the initial value, demonstrating the excellent electrochemical stability of the freestanding and flexible EG hybrid electrode. The effect of bending on the capacity of EG-LTO hybrid films was also investigated (Figure 3e, f). Before collecting electrochemical performance at 0.15 C, the EG-LTO hybrid films were pre-bended for certain cycles (0, 100, 200, 300, 400 and 500) in the range of 0.1-1 of its original length. We found that after 500 bending cycles, only ~6% capacity fading was observed, highlighting the remarkable mechanical and electrochemical stability of the formed EG hybrids.
Figure 3. Half-cell electrochemical performance of EG-LTO anode. (a, b) Rate performance and the corresponding charge-discharge curves of EG-LTO anode at different rates; (c, d) Cycling performance at 1 C and 2.5 C and the corresponding charge-discharge curves at 2.5 C. (e, f) Bending effect on the battery performance of EG-LTO anode. CE represents Coulombic efficiency.

To confirm the structure stability of EG-LTO hybrids, the product morphology of EG-LTO after 100 cycles at 1 C was examined by SEM (Figure S10). After cycling, a thick polymeric film was formed on the EG-LTO outer surface, which can be assigned to the formed solid-electrolyte interphase (SEI). Nevertheless, LTO NPs were still well encapsulated by EG without detachment. From the cross section view, it was found that the LTO NPs remained confined between EG nanosheets without unexpected aggregation, that is, the layer-interlocked heterostructure was well preserved throughout the electrodes after cycling.

In addition, other flexible EG-metal oxide hybrid films like EG-LCO, EG-LMO and EG-LFP can also be prepared by the similar assembly approach with 90 wt% active materials incorporated (Figure S11). The EG-LMO and EG-LFP exhibited impressive battery performance (cycling stability and rate performance) as LIB cathodes at potential windows of 3-4.3 V and 3.5-4.0 V (Figure S12). For EG-LMO electrodes, two characteristic charge plateaus were observed at 4.0 and 4.15 V. The specific capacity was 106.7 mAh/g for the first cycle and retained 85.3% after 50
cycles at 0.2 C (Figure S12a-c). The EG-LFP electrodes with a typical discharge plateau at 3.4 V delivered a stable cycling capacity of 80 mAh/g. No capacity fading was observed after 50 cycles at 0.25 C, which can be ascribed to the better structural stability of LFP over LMO during lithiation and delithiation processes (Figure S12d-f).

To construct full cells, the EG-LTO hybrid was used as the anode and EG-LFP or EG-LMO hybrids as the cathode. The cathode capacity was kept 1.2 times anode capacity, and the specific capacity of the entire battery was calculated based on the mass of the EG-LTO hybrid anode. Figure 4 shows the full cell performance in both coin cells and pouch cells. Typical charge-discharge curves of EG-LTO//EG-LFP full cells present two charge/discharge plateaus around 1.9/1.85 V (Figure 4a), which was highly consistent with the potential difference between EG-LFP and EG-LTO electrodes. The full battery exhibited a reversible capacity of 119 mAh/g at 0.3 C, a little lower than 130 mAh/g of EG-LTO in half cells. Increasing the current rates from 0.3 C to 2.5 C, slight potential polarization was observed as well and the specific capacity decreased to 100 mAh/g (Figure 4a, b), corresponding to 84% of capacity at 0.3 C. When the current was reversed back to 0.3 C, the capacity was completely recovered, indicating superb rate performance of EG-LTO//EG-LFP full cells. The cycling performance of EG-LTO//EG-LFP full cells was further investigated at 0.3 C and 1 C (Figure 4c, d). After 100 cycles, 99.6 % and 98% of the initial capacity was maintained, respectively, demonstrating excellent cycling stability. Similar rate capability and cycling stability were achieved in EG-LTO//EG-LMO full cells, except that the capacity was slightly lower than that in EG-LTO//EG-LFP full cells (Figure S13). The areal capacity of full cells was around 0.5 mAh/cm² and the energy density of EG-LTO//EG-LFP and EG-LTO//EG-LMO was determined as 80 and 120 Wh/kg, respectively, based on the total mass of both electrodes. To further enhance the energy density of full cells, Si anode will be explored in the future due to its high theoretical capacity (3579 mAh/g) and low working potential (<0.25V vs Li/Li⁺). The initial half-cell results indicate that the EG-Si hybrid performed efficiently with a high capacity of 2005 mAh/g (Figure S14).
Finally, a pouch cell EG-LTO//EG-LFP was assembled with a transparent package and a gel-type solid electrolyte (see Experimental section for preparation details). As shown in Figure 4e, the cell was able to power a red light-emitting diode (LED). Under 0.3 C, the pouch cell delivered a capacity of 75 mAh/g after 20 cycles (Figure 4f). This value was much lower than 119 mAh/g of EG-LTO//EG-LFP in coin cells at 0.3C, which can be attributed to the lower ion conductivity of the used solid electrolyte than liquid electrolyte. Due to the use of solid electrolyte, the demonstration of flexible LIBs at current stage is not successful. Further optimization on the electrolyte and hybrid composition will be conducted in the future to enhance the electrochemical performance and flexibility of the pouch cell.

**Figure 4.** Full-cell electrochemical performance of EG-LTO and EG-LFP. (a, b) Rate performance, (c, d) cycling stability and corresponding charge-discharge curves in coin cells. (e, f) An image of a pouch-type full cell with transparent package and its battery performance at 0.3C.

In summary, we have demonstrated a straightforward co-assembly approach to prepare flexible EG-metal oxide hybrids for Li-ion batteries. The use of chemically and mechanically stable EG largely simplifies the preparation procedures for flexible electrodes. No metal current collector, binder or other additive was needed. Due to the presence of the unique layer-interlocked heterostructure, the resultant EG hybrids showed high flexibility, mechanical properties and electrochemical performance. When serving as flexible electrodes in LIBs, our EG hybrid films exhibited excellent...
cycling stability and rate performance in both half cells and full cells. It is worth to note that the co-assembly approach is not limited to particle-like materials. Other dimensional materials like 1D CNT can also be integrated for EG-based hybrid (Figure S15). Our approach may inspire new flexible heterostructure designs based on emerging 2D materials for various energy-related applications.

Electronic Supplementary Information
Supplementary Information is available.

ACKNOWLEDGEMENTS
This work was financially supported by the ERC grant for HIPER-G (Project ID 768930), the Federal State of Saxony (ESF-Project “GRAPHD”, TU Dresden) and the EC under the Graphene Flagship (GrapheneCore2 785219). The authors acknowledge the CFAED and the Dresden Center for Nanoanalysis (DCN) at TU Dresden.

References
1. H. Gwon, H.-S. Kim, K. U. Lee, D.-H. Seo, Y. C. Park, Y.-S. Lee, B. T. Ahn and K. Kang, *Energy Environ. Sci.*, 2011, 4, 1277-1283.
2. G. Zhou, F. Li and H.-M. Cheng, *Energy Environ. Sci.*, 2014, 7, 1307-1338.
3. W. Liu, M.-S. Song, B. Kong and Y. Cui, *Adv. Mater.*, 2016, n/a-n/a.
4. L. Wen, F. Li and H.-M. Cheng, *Adv. Mater.*, 2016, 28, 4306-4337.
5. H. Kim and J.-H. Ahn, *Carbon*, 2017, 120, 244-257.
6. Y. Hu and X. Sun, *J. Mater. Chem. A*, 2014, 2, 10712-10738.
7. Y. Huang, M. Zhu, Y. Huang, Z. Pei, H. Li, Z. Wang, Q. Xue and C. Zhi, *Adv. Mater.*, 2016, 28, 8344-8364.
8. M. Armand and J. M. Tarascon, *Nature*, 2008, 451, 652-657.
9. G. Wang, Y. Sun, D. Li, W. Wei, X. Feng and K. Müllen, *Small*, 2016, 12, 3914-3919.
10. G. Wang, J. Zhang, S. Yang, F. Wang, X. Zhuang, K. Müllen and X. Feng, *Adv. Energy Mater.*, 2018, 8, 1702254.
11. L. Hu, J. W. Choi, Y. Yang, S. Jeong, F. La Mantia, L.-F. Cui and Y. Cui, *Proc. Natl. Acad. Sci. U.S.A.*, 2009, 106, 21490-21494.
12. L. Hu, H. Wu, F. La Mantia, Y. Yang and Y. Cui, *ACS Nano*, 2010, 4, 5843-5848.
13. H. Lin, W. Weng, J. Ren, L. Qiu, Z. Zhang, P. Chen, X. Chen, J. Deng, Y. Wang and H. Peng, *Adv. Mater.*, 2014, 26, 1217-1222.
14. Y. Zhang, W. Bai, X. Cheng, J. Ren, W. Weng, P. Chen, X. Fang, Z. Zhang and H. Peng, *Angew. Chem.*, 2014, 126, 14792-14796.
15. Y. H. Kwon, S.-W. Woo, H.-R. Jung, H. K. Yu, K. Kim, B. H. Oh, S. Ahn, S.-Y. Lee, S.-W. Song, J. Cho, H.-C. Shin and J. Y. Kim, *Adv. Mater.*, 2012, 24, 5192-5197.
16. Y. Zhang, L. Wang, Z. Guo, Y. Xu, Y. Wang and H. Peng, *Angew. Chem. Int. Ed.*, 2016, 55,
17. L. Shen, B. Ding, P. Nie, G. Cao and X. Zhang, *Adv. Energy Mater.*, 2013, 3, 1484-1489.
18. Q.-C. Liu, J.-J. Xu, D. Xu and X.-B. Zhang, *Nat. Commun.*, 2015, 6, 7892.
19. H. Yu, C. Zhu, K. Zhang, Y. Chen, C. Li, P. Gao, P. Yang and Q. Ouyang, *J. Mater. Chem. A*, 2014, 2, 4551-4557.
20. N. Li, Z. Chen, W. Ren, F. Li and H.-M. Cheng, *Proc. Natl. Acad. Sci. U.S.A.*, 2012, 109, 17360-17365.
21. R. Mo, D. Rooney, K. Sun and H. Y. Yang, 2017, 8, 13949.
22. T. Jiang, F. Bu, X. Feng, I. Shakir, G. Hao and Y. Xu, *ACS Nano*, 2017, 11, 5140-5147.
23. Y. Chao, R. Jalili, Y. Ge, C. Wang, T. Zheng, K. Shu and G. G. Wallace, *Adv. Funct. Mater.*, 2017, 27, 1700234-n/a.
24. K. Parvez, Z.-S. Wu, R. Li, X. Liu, R. Graf, X. Feng and K. Müllen, *J. Am. Chem. Soc.*, 2014, 136, 6083-6091.
25. S. Yang, S. Brüller, Z.-S. Wu, Z. Liu, K. Parvez, R. Dong, F. Richard, P. Samori, X. Feng and K. Müllen, *J. Am. Chem. Soc.*, 2015, 137, 13927-13932.
26. Y. Xu, K. Sheng, C. Li and G. Shi, *ACS Nano*, 2010, 4, 4324-4330.
27. G. Wang, L.-T. Jia, Y. Zhu, B. Hou, D.-B. Li and Y.-H. Sun, *RSC Adv.*, 2012, 2, 11249-11252.
28. G. Wang, L.-T. Jia, B. Hou, D.-B. Li, J.-G. Wang and Y.-H. Sun, *New Carbon Materials*, 2015, 30, 30-40.
29. T.-T. Shan, S. Xin, Y. You, H.-P. Cong, S.-H. Yu and A. Manthiram, *Angew. Chem.*, 2016, 128, 12975-12980.
30. K. R. Paton, E. Varrla, C. Backes, R. J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya, O. M. Istrate, P. King, T. Higgins, P. Barwich, P. May, P. Puczkarski, I. Ahmed, M. Moebius, H. Pettersson, E. Long, J. Coelho, S. E. O'Brien, E. K. McGuire, B. M. Sanchez, G. S. Duesberg, N. McEvoy, T. J. Pennycook, C. Downing, A. Crossley, V. Nicolosi and J. N. Coleman, *Nat. Mater.*, 2014, 13, 624.
31. I. K. Moon, J. Lee, R. S. Ruoff and H. Lee, *Nat. Commun.*, 2010, 1, 73.
32. D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen and R. S. Ruoff, *Nature*, 2007, 448, 457-460.
33. H. Chen, M. B. Müller, K. J. Gilmore, G. G. Wallace and D. Li, *Adv. Mater.*, 2008, 20, 3557-3561.
34. Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari and J. N. Coleman, *Nat. Nanotechnol.*, 2008, 3, 563-568.
35. D. Li, M. B. Müller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nat. Nanotechnol.*, 2008, 3, 101.
36. M. Odziomek, F. Chaput, A. Rutkowska, K. Świerczek, D. Olszewska, M. Sitarz, F. Lerouge and S. Parola, 2017, 8, 15636.
37. S. Mao, X. Huang, J. Chang, S. Cui, G. Zhou and J. Chen, *NPG Asia Mater.*, 2015, 7, e224.
38. Y.-B. He, B. Li, M. Liu, C. Zhang, W. Lv, C. Yang, J. Li, H. Du, B. Zhang, Q.-H. Yang, J.-K. Kim and F. Kang, *Sci. Rep.*, 2012, 2, 913.
39. W. Weng, Q. Sun, Y. Zhang, S. He, Q. Wu, J. Deng, X. Fang, G. Guan, J. Ren and H. Peng, *Adv. Mater.*, 2015, 27, 1363-1369.