High-quality and low-cost three-dimensional graphene from graphite flakes via carbocation-induced interlayer oxygen releasing

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Materials:

Flake graphite was purchased from Sigma-Aldirch (Art. No. 332461). 30% H₂O₂, 98% H₂SO₄, absolute ethanol and N-Methyl pyrrolidone (NMP) were purchased from Sinopharm Chemical Reagent Co., L td. All of the chemicals were used as received without further purification.

Methods:

Calculation of Exfoliation Yields. Since dispersion concentration of graphene in NMP is limited, repeated centrifugation extraction was employed to take all of the exfoliated sheets out from the dispersion. Herein, the dispersion concentration of graphene sheets in NMP was about 0.2 mg/mL. Typically, we first centrifuged the dispersion at 1000 rpm for 30 minutes and separated the supernatant from the precipitate. The precipitate was redispersed in NMP with 30s sonication to form a suspension. The centrifugation extraction process was repeated until the supernatant was colorless. The yield was calculated according to the following equation where m_{up} is the total mass of graphene in all the collected supernatants, m_{down} is the mass of the residual precipitate after many time of centrifugation extraction process.

$$yield = \frac{m_{up}}{m_{up} + m_{down}} \ge 100\%$$

Methylene blue (MB) absorption experiments of CEG and CEG-o. The adsorption amounts of MB in CEG and CEG-o were calculated according to the following equation, where A_e (mg g⁻¹) is the amount of MB adsorbed at equilibrium, C_i (mg L⁻¹) is the initial solute concentration, C_e (mg L⁻¹) the equilibrium solute concentration, V the volume of MB solution, and m is the amount of CEG or CEO-o used as the adsorbate.

$$A_e = (C_i - C_e)V/m$$

The adsorption isotherms were fitted (correlation coefficients, $R_2 > 0.99$) using the Langmuir adsorption model, where A_e (mg g⁻¹) is the amount of MB adsorbed at equilibrium, C_e (mg L⁻¹) the equilibrium solute concentration, A_m the maximum adsorption capacity corresponding to complete monolayer coverage, and b

the equilibrium constant (l mg⁻¹).

 $A_e = A_m bC_e / (1 + bC_e)$

Preparation of graphene films. Graphene films were produced by vacuum-filtering of graphene dispersions through organic membranes (0.22 μm nominal pore size). Films were dried under vacuum condition at 90 °C for 48 hours. Conductivities of films were measured without annealing treatment.

Optical microscope. The spontaneous expansion process was monitored by optical microscope. After the mixing of H2O2 and H2SO4, small amount of pristine graphite was added into the mixture for observing the expansion process under transmission mode. Small bubbles released from the edge of graphite flakes after several minutes. The increasing of flake length and spontaneous exfoliation can be clearly seen during the expansion process.

Raman Spectrometry. The Raman data was taken on XploRA. CEG, CEG-o were loaded on glass substance for Raman characterization directly. As for exfoliation products, the dispersions were diluted with NMP and dropped onto clean Si substance for measurement. After absorbing most solvent by filter paper, the samples were dried in vacuum oven at 90 °C overnight. Raman spectra were recorded using a 532 nm excitation laser. No obvious D band can be observed in CEG and CEG-o while the I_D/I_G ratio of CEG-o is smaller than 0.15.

TEM characterization. TEM images were collected by Tecnai G2 20 TWIN an accelerating voltage of 200 kV. HRTEM images were collected by JEM -2100F advanced field emission electron microscope with an accelerating voltage of 200 kV. For TEM measurements, the suspensions were dropped onto micro grids without pre-treatment. After dropping a few drops of ethanol, the samples were dried in a vacuum oven at 90 °C overnight. After exfoliation, all samples show thin sheet morphology with the lateral size ranging from 1 μ m to over 6 μ m.

FESEM characterization. FESEM was carried out on Ultra 55. For observing 3D structures, the products containing deionized water were quenched in liquid nitrogen and freeze-dried. The dried samples were loaded on conductive carbon adhesive for FESEM characterization.

AFM characterization. Graphene suspensions were diluted with NMP and dropped onto fresh mica flakes. After absorbing most solvent by filter paper and washed with ethanol several times, the samples were dried under vacuum condition at 90 °C overnight. In AFM images, graphene flakes have lateral sizes about a few micrometers, which is similar to TEM and FESEM investigation. The height of graphene sheets from CEG-o is smaller than that from CEG.

UV-vis spectra characterization. Graphene suspensions were diluted with NMP for UV-vis spectra measurement using Lambda 750. The step size was settled at 1 nm during experiments.

TGA analysis. TGA analysis was carried out on Pyris 1 TGA-207 from 50 to 800 °C with a heating rate of 10 °C /min.

XRD analysis. The crystal structures were recorded using (X'pert PRO) with 2θ scan rate of 10 °/min.

Electrochemical study on the potential. The measurement of potential of graphite in admixture was taken on CHI660E, in a two-electrode system with a stainless iron tweezer as the current collector of working electrode and mercury-mercurous sulfate electrode (in saturated aqueous K_2SO_4) as the reference electrode. Pt electrode should not be used here due to its catalysis effect to the decomposition of H_2O_2 in this system. We measured the saturated (stable) potential of flake graphite (80 mesh) in an admixture of SA-98 and HP-30 with various σ . To keep the concentrations of each species constant in the expansion process, the volume of the admixture was largely excessive.

In the admixture, the concentration of H_2SO_4 , H_2O_2 and H_2O can be written as a function of σ as follows.

$$c(H_2SO_4) = 18.4 - 18.4 \div (\sigma + 1) (M)$$

$$c(H_2O_2) = 1.11 \times 30\% \div 34 \div (\sigma + 1) \times 1000 \quad (M)$$

$$c(H_2O) = (1.11 \times 70\% \div 18 \div (\sigma + 1) + 1.84 \times 2\% \div 18 \times \sigma \div (\sigma + 1)) \times 1000 \quad (M)$$

As seen, along the decrease of σ , $c(H_2SO_4)$ decreases.

The saturated potential induced by reaction of H_2O_2 and graphite is related to the equilibrium potential given by Nernst's equation. The half electrode reactions can be written as follows.

$$H_2 O_2 + 2e^- + 2H_3 O^+ \to 4H_{20} \tag{4}$$

$$O_2 + 2e^- + 2H_3O^+ \rightarrow H_2O_2 + 2H_{20}$$

The equilibrium concentrations of H_2O_2 , $H_3^+O_3$ and H_2O_3 are denoted as $[H_2O_2]$, $[H_3^+O]_3$ and $[H_2O]_3$

Equilibrium potential E_4 reached by the half reaction (4). The equilibrium potential E_4 reached by the half reaction (4) can be written as follows.

$$E_4 = E_{0-4} + \frac{RT}{2F} \times ln \frac{[H_2O_2][H_3O^+]^2}{[H_2O]^4}$$

In which, E_{0-4} is the standard electrode potential (1.776 V vs. SHE).

The first ionization equilibrium of H₂SO₄ can be written as follows.

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$

The equilibrium constant is as high as 2400000. In H_2SO_4 solution with high concentration in the range of 10-18.4 M, one can make an approximation that,

$$\begin{bmatrix} H_3 O^+ \end{bmatrix} = \begin{bmatrix} HSO_4^- \end{bmatrix} = c(H_2 O)$$
$$\begin{bmatrix} H_3 O^+ \end{bmatrix} = \begin{bmatrix} H_3 O^+ \end{bmatrix}^2 / 2400000 / (c(H_2 SO_4) - [HSO_4^-])$$

From the above equations, we can get the relationship between E_4 and $c(H_2SO_4)$ which was depicted in Fig. 1b (green dot line).

Equilibrium potential E_5 reached by the half reaction (5). The equilibrium potential E_5 reached by the half reaction (5) can be written as follows.

$$E_{5} = E_{0-5} + \frac{RT}{2F} \times ln \frac{(\frac{P_{0_{2}}}{P_{0}})[H_{3}^{+}O]^{2}}{[H_{2}O]^{2}[H_{2}O_{2}]} \equiv E_{0-5} + \frac{RT}{2F} \times ln \frac{[H_{3}^{+}O]^{2}}{[H_{2}O]^{2}[H_{2}O_{2}]}$$

In which, E_{0-5} is the standard electrode potential (0.695 V vs. SHE).

From the above equations, we can get the relationship between E_{σ} and $c(H_2SO_4)$, which was depicted in Fig. 1b (black dot line).



Fig. S1 Photo of (a) 0.3 g graphite fully expanded. (b) 160g CEG. (c) 1g CEG can absorb 120 mL concentrated sulfuric acid without any leakage.



Fig. S2 HRTEM images of TEG.



Fig. S3 HRTEM images of CEG.



Fig. S4 (a) TEM image of graphene sheets exfoliated from CEG. (b) The corresponding diffraction curve. (c) FESEM image of graphene sheets exfoliated from CEG. (d) AFM image of graphene sheets exfoliated from CEG. (e-f) The height and lateral size distribution of graphene sheets exfoliated from CEG.



Fig. S5 XRD patterns of graphite in admixture of σ = 100:1 (a), 9:1 (b), 9:2 (c), 9:3 (d) and 2:1 (e).

Table S1. Peak position in XRD patterns of graphite expanded in admixture of different σ and the corresponding stage index.

σ	Stage index	Peak positon (°) (002)	Peak positon (°) (003)	Peak positon (°) (004)	Peak positon (°) (005)
100:1	1	21.93	33.29	45.03	57.06
9:1	2	/	23.32	31.3	/
9:2	2	/	23.94	31.89	/
9:3	3	/	/	25.50	29.56
2:1	∞	26.77	55.45	/	/



Fig. S6 Raman spectra mapping of an mm-scale CEG. (a) digital photo under microscopy. Intensity image of D band (b) and G band (c).



Fig. S7 (a) Curves of potential of graphite vs. reaction time in different concentration of H_2SO_4 by galvanostatic oxidation. (b) Threshold potentials for the stage one, two H_2SO_4 –GIC.



Fig. S8 (a) Chemical potential of graphite in admixture of σ =100:5 at different expanding degree. (b) Photo of the blue particle state graphite. (c) Photo of fully expanded graphite state graphite.



Fig. S9 (a) Flake graphite, (b) SWNT and (c) carbon fiber in the admixture of s =9:2. SWNT was stirred in dilute sulfuric acid, washed by water and dried before added into the admixture. The carbon fiber is free of sizing agent. As seen, little bubbles were observed around carbon fiber. A lot bubbles emerged when SWNT was added.



Fig. S10 HRTEM images of CEG-o.



Fig. S11 (a) Thermal gravity analysis and (b) Raman spectra of graphene sheets derived from CEG and CEG-o.



Fig. S12 (a) Optical image of a graphene sheet exfoliated from CEG-o for Raman imaging. The corresponding two-dimensional images of D band (b) and G band (c) and I_D/I_G intensity.

 Table S2 Properties of CEG and CEG-o.

Sample	ID/IG	Residue weight at 800 °C	MB-SSA (m²/g)	Graphene yield (%)	Exfoliated graphene sheet film conductivit y (S/cm)
CEG	0.01	100%	354	41%	1150
CEG-o	0.15	93%	1245	100%	961



Fig. S13 SEM images of CEO-o from graphite foil with different magnifications.



Fig. S14 (a-c) Typical TEM images of a graphene sheet exfoliated from CEG-o by ultrasonic method.



Fig. S15 (a-c) FESEM images of CEG-o/MnO₂ composite. (d-g) SEM image and the corresponding EDS mapping of C, O and Mn in CEG-o/MnO₂ composite.



Fig. S16 (a) XRD pattern of CEG-o/MnO₂ composite. (b) Raman spectrum of CEG-o/MnO₂ composite. **Table S3** Different preparation methods of 3D graphene.

Ref	Methods	3D graphene sample	Raman spectra	Comments
1	CVD growth on Ni foam	Graphene foam	Strongly suppressed defect-related D band	High cost and low productivity
2	CVD growth on Ni foam and electrochemical deposition	Graphene foam	No obvious D band	High cost and low productivity

3	CVD growth on colloidal silica	Graphene network	I _D /I _G =0.15	High cost and low productivity
4	CVD growth on porous MgO layers	Graphene nanomesh	I _D /I _G >1	High cost and low productivity
5	Hydrothermal treatment and freeze drying	Graphene hydrogel	Not supplied	Containing a large amount of defects
6	Hydrothermal treatment and electrodeposition	Graphene foam	Strong D band	Containing a large amount of defects
7	Hydrothermal treatment and freeze drying	Graphene aerogel	I _D /I _G >1	Containing a large amount of defects
8	Chemical reduction and freeze drying	Graphene aerogel	I _D /I _G >1	Containing a large amount of defects
9	Chemical reduction and filtration	Macroporous graphene frameworks	Not supplied	Containing a large amount of defects
10	Chemical reduction	Graphene/CNT composites	I _D /I _G >1	Containing a large amount of defects
11	Solvent-exchange approach	Graphene frameworks	I _D /I _G >1	Containing a large amount of defects

 Table S4 Different preparation methods of graphene.

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Ref	Method	Yield	Raman spectrum	Lateral size or thickness	XPS spectrum	Comments
12	Sonication exfoliation in organic solvents.	7-12%	The D peak is only visible in the spectrum of small flakes.	A monolayer yield of ~1 wt%.	No C-O peak is observable in XPS spectrum.	

13	Exfoliation in surfactant/wat er solutions.		No D-band is observed in the spectrum associate with the large flake.	Thickness: ~43 % of flakes <5 layers. lateral size: ~1µm	The main C-C peak makes up 86% of the spectrum.	
14	Exfoliation- reintercalation -expansion of graphite.		Not supplied.	Thickness: single layer ; lateral size: 250 nm.		Complex preparation process.
15	Shear exfoliation in solvents.	low	I _D /I _G =0.17-0.37			
16	Electrochemic al exfoliation in aqueous solutions of inorganic salts	>85%	$I_D/I_G = 0.42$	Over 80% are larger than 5.0 μ m with a mean thickness of ~0.72 nm	C/O=17.2	The electrode size limit the scalability.
17	Electrochemic al exfoliation in inorganic solvents with TEMPO	~75%	I _D /I _G <0.1	Primarily 5-10 μm with 52% 1-3 layers.	C/O=25.3	The electrode size limit the scalability.
18	Spontaneous exfoliation in chlorosulphon ic acid.		A higher D-peak in the top than in the bottom phase.	70% of graphene flakes are single layer.	C/O = 2.03 -35.9	corrosive acid was used.
19	Ball milling of graphite nanosheets with a thickness of 30-80 nm.		Showing a single and symmetric low frequency 2D peak at 2693 cm ⁻¹ .	thickness: 0.8-1.8 nm lateral size: <100 nm.	Not supplied.	long time of milling
20	Direct exfoliation and dispersion in pure water.	low.	negligible D band	thickness: 2-3 layers Flake size: ~200-300 nm.		
21	FeCl ₃ - intercation- expansion and sonication		I _D /I _G =~1	Mostly <6 layers.	C: 99.08 atom%	High energy consumption.

	exfoliation.					
22	Ternary KCl- NaCl-ZnCl2 eutectic salt intercalation and sonication exfoliation.	60%	I _D /I _G =~0.15	thickness: 0.4-10 nm lateral size: 0.5 μm	O: 2.9 atom%	High energy consumption.
23	Microwave expansion with ionic liquid.	93%	$I_{D}/I_{G}=0.14$	Lateral size in the range of 1 to 5 μ m with 95% single layer.	C/O=30	HF releasing
24	Ball milling with dry ice.		I _D /I _G =1.16	Typically less than 5 layers.	C/O=3.63	
25	Ionic compounds ICl and IBr intercalation.		Low D band.	Controlled layers.		cost ineffective
26	Room temperature intercalation of CrO3 and mild sonication exfoliation.	70%	I _D /I _G <0.1	Lateral size: 5-15 μm.	C/O=28	Cl ₂ releases Toxic CrO3 is used

Table S5 The yields of mass of the products divided by the mass of starting graphite.

Samples	CEG	CEG-o	Graphene from CEG	Graphene from CEG-0	Graphene from dried CEG	Graphene from dried CEG-o
Yields (divided by the mass of starting	100%	106%	41%	102%	13%	37%

graphite)			

Table S6 MnO ₂ /3D g	graphene as	anode materials	for Li-ior	batteries.
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Ref	Current densities	Reversible capacity	Rate performance	Cycling stability
27	100 mA g ⁻¹	595 mA h g ⁻¹	380 mA h g ⁻¹ at 1 A g ⁻¹	416 mA h g ⁻¹ at 100 mA g ⁻¹ after 60 cycles
28	100 mA g ⁻¹	1132 mA h g ⁻¹	248 mA h g-1 at 10 A g ⁻¹	300 mA h g ⁻¹ at 1A g ⁻¹ after 2400 cycles
29	100 mA g ⁻¹	1173 mA h g ⁻¹	481 mA h g-1 at 2 A g ⁻¹	949 mA h g ⁻¹ at 200 mA g ⁻¹ after 300 cycles
30	100 mA g ⁻¹	880 mA h g ⁻¹	460 mA h g-1 at 5 A g ⁻¹	600 mA h g ⁻¹ at 3 A g ⁻¹ after 80 cycles
31	60 mA g ⁻¹	998 mA h g ⁻¹	590 mA h g ⁻¹ at 12 A g ⁻¹	Not supplied
32	50 mA g ⁻¹	1105 mA h g ⁻¹	698 mA h g-1 at 400 mA g ⁻¹	421 mA h g ⁻¹ at 50 mA g ⁻¹ after 15 cycles
33	100 mA g ⁻¹	482 mA h g ⁻¹	168 mA h g-1 at 5 A g ⁻¹	600 mA h g ⁻¹ at 500 mA g ⁻¹ after 650 cycles
34	100 mA g ⁻¹	634 mA h g ⁻¹	222 mA h g-1 at 5 A g ⁻¹	1574 mA h g ⁻¹ at 2 A g ⁻¹ after 500 cycles
35	100 mA g ⁻¹	977 mA h g ⁻¹	684 mA h g ⁻¹ at 750 mA g ⁻¹	89% retention after 50 cycles
36	100 mA g ⁻¹	1003 mA h g ⁻¹	846mA h g ⁻¹ at 400 mA g ⁻¹	909 mA h g ⁻¹ at 400 mA g ⁻¹ after 200 cycles
this work	2 A g ⁻¹	1082 mA h g ⁻¹	483 mA h g ⁻¹ at 5 A g ⁻¹	98% capacity at 2 A g ⁻¹ after 1000 cycles

References

[1] Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei and H.-M. Cheng, *Nat. Mater.*, **2011**, 10, 424-428.

[2] Y. He, W. Chen, X. Li, Z. Zhang, J. Fu, C. Zhao and E. Xie, *ACS Nano*, **2013**, 7, 174-182.

- [3] J.-C. Yoon, J.-S. Lee, S.-I. Kim, K.-H. Kim and J.-H. Jang, *Sci. Rep.*, **2013**, 3.
- [4] G. Ning, Z. Fan, G. Wang, J. Gao, W. Qian and F. Wei, *Chem. Commun.*, **2011**, 47, 5976-5978.
- [5] Y. Xu, K. Sheng, C. Li and G. Shi, *ACS Nano*, **2010**, 4, 4324-4330.
- [6] Y. Zhao, J. Liu, Y. Hu, H. Cheng, C. Hu, C. Jiang, L. Jiang, A. Cao and L. Qu, Adv. Mater., 2013, 25, 591-595.
- [7] Z.-S. Wu, A. Winter, L. Chen, Y. Sun, A. Turchanin, X. Feng and K. Muellen, *Adv. Mater.*, 2012, 24, 5130-5135.
- [8] W. Chen, S. Li, C. Chen and L. Yan, *Adv. Mater.*, **2011**, 23, 5679-5683.
- [9] B. G. Choi, M. Yang, W. H. Hong, J. W. Choi and Y. S. Huh, ACS Nano, 2012, 6, 4020-4028.
- [10] S.-Y. Yang, K.-H. Chang, H.-W. Tien, Y.-F. Lee, S.-M. Li, Y.-S. Wang, J. Y. Wang, C. C. M. Ma and C.-C. Hu, J. Mater. Chem., 2011, 21, 2374-2380.
- [11] Y. Xu, Z. Lin, X. Zhong, B. Papandrea, Y. Huang and X. Duan, *Angew. Chem. Int. Ed.*, 2015, 54, 5345-5350.
- 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, J. N. Coleman, *Nat. Nanotechnol.* 2008, 3, 563.
- M. Lotya, Y. Hernandez, P. J. King, R. J. Smith, V. Nicolosi, L. S. Karlsson, F. M. Blighe, S. De, Z.
 Wang, I. T. McGovern, G. S. Duesberg, J. N. Coleman, J. Am. Chem. Soc. 2009, 131, 3611.
- [14] X. Li, G. Zhang, X. Bai, X. Sun, X. Wang, E. Wang, H. Dai, *Nat. Nanotechnol.* 2008, 3, 538.
- [15] 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, S. 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, J. N. Coleman, *Nat. Mater.* 2014, 13, 624.
- [16] K. Parvez, Z.-S. Wu, R. Li, X. Liu, R. Graf, X. Feng, K. Muellen, J. Am. Chem. Soc. 2014, 136, 6083.
- [17] S. Yang, S. Brueller, Z.-S. Wu, Z. Liu, K. Parvez, R. Dong, F. Richard, P. Samori, X. Feng, K. Muellen, J. Am. Chem. Soc. 2015, 137, 13927.
- [18] N. Behabtu, J. R. Lomeda, M. J. Green, A. L. Higginbotham, A. Sinitskii, D. V. Kosynkin, D. Tsentalovich, A. N. G. Parra-Vasquez, J. Schmidt, E. Kesselman, Y. Cohen, Y. Talmon, J. M. Tour, M. Pasquali, *Nat. Nanotechnol.* 2010, 5, 406.
- [19] W. Zhao, M. Fang, F. Wu, H. Wu, L. Wang, G. Chen, J. Mater. Chem. 2010, 20, 5817.
- [20] J. Kim, S. Kwon, D.-H. Cho, B. Kang, H. Kwon, Y. Kim, S. O. Park, G. Y. Jung, E. Shin, W.-G. Kim, H. Lee, G. H. Ryu, M. Choi, T. H. Kim, J. Oh, S. Park, S. K. Kwak, S. W. Yoon, D. Byun, Z. Lee, C. Lee, *Nat. Commun.* 2015, 6.
- [21] X. Geng, Y. Guo, D. Li, W. Li, C. Zhu, X. Wei, M. Chen, S. Gao, S. Qiu, Y. Gong, L. Wu, M. Long, M. Sun, G. Pan, L. Liu, *Sci. Rep.* 2013, 3.
- [22] K. H. Park, B. H. Kim, S. H. Song, J. Kwon, B. S. Kong, K. Kang, S. Jeon, *Nano Lett.* 2012, 12, 2871.
- [23] M. Matsumoto, Y. Saito, C. Park, T. Fukushima, T. Aida, Nat. Chem. 2015, 7, 730.
- [24] I.-Y. Jeon, Y.-R. Shin, G.-J. Sohn, H.-J. Choi, S.-Y. Bae, J. Mahmood, S.-M. Jung, J.-M. Seo, M.-J.
 Kim, D. W. Chang, L. Dai, J.-B. Baek, *P. Natl. Acad. Sci. USA* 2012, 109, 5588.

- [25] C.-J. Shih, A. Vijayaraghavan, R. Krishnan, R. Sharma, J.-H. Han, M.-H. Ham, Z. Jin, S. Lin, G. L.
 C. Paulus, N. F. Reuel, Q. H. Wang, D. Blankschtein, M. S. Strano, *Nat. Nanotechnol.* 2011, 6, 439.
- [26] S. Lin, L. Dong, J. Zhang, H. Lu, *Chem. Mater.* **2016**, 28, 2138.
- [27] H. Liu, Z. Hu, Y. Su, H. Ruan, R. Hu and L. Zhang, Appl. Surf. Sci., 2017, 392, 777-784.
- [28] C. Jiang, C. Yuan, P. Li, H.-g. Wang, Y. Li and Q. Duan, J Mater. Chem. A, 2016, 4, 7251-7256.
- [29] Y. Li, D. Ye, B. Shi, W. Liu, R. Guo, H. Pei and J. Xie, *Phys. Chem. Chem. Phys*, **2017**, 19, 7498-7505.
- [30] C. Chae, K. W. Kim, Y. J. Yun, D. Lee, J. Moon, Y. Choi, S. S. Lee, S. Choi and S. Jeong, ACS Appl. Mater. Inter., 2016, 8, 11499-11506.
- [31] Y. Zhang, H. Liu, Z. Zhu, K.-w. Wong, R. Mi, J. Mei and W.-m. Lau, *Electrochim. Acta*, 2013, 108, 465-471.
- [32] C. X. Guo, M. Wang, T. Chen, X. W. Lou and C. M. Li, Adv. Energy Mater., 2011, 1, 736-741.
- [33] Z. Ma and T. Zhao, *Electrochim. Acta*, **2016**, 201, 165-171.
- [34] S.-W. Lee, C.-W. Lee, S.-B. Yoon, M. S. Kim, J. H. Jeong, K.-W. Nam, K. C. Roh and K. B. Kim, J. Power Sources, 2016, 312, 207-215.
- [35] X. Jiang, X. Zhu, X. Liu, L. Xiao, X. Ai, H. Yang and Y. Cao, *Electrochim. Acta*, **2016**, 196, 431-439.
- [36] Z.-Y. Sui, C. Wang, K. Shu, Q.-S. Yang, Y. Ge, G. G. Wallace and B.-H. Han, *J Mater. Chem. A*, 2015, 3, 10403-10412.