Nanoscale



Check for updates

Cite this: Nanoscale, 2019, 11, 12132

Received 22nd March 2019, Accepted 22nd May 2019 DOI: 10.1039/c9nr02480h

rsc.li/nanoscale

Introduction

Graphene, an atomically thin two-dimensional carbonaceous material, has attracted tremendous attention in the scientific community. Graphene is closely arranged in a two-dimensional crystal structure using sp² hybridized carbon atoms, similar to a honeycomb network.¹ Due to the special structure of graphene, it has many excellent physical and chemical properties,^{2,3} for example, very high carrier mobility, thermal conductivity and light transmittance, excellent impermeability, and superior mechanical stability.^{4–8} Therefore, graphene is very interesting in both science and technology and has wide applications in various fields, such as solar cells,⁹ supercapacitors,¹⁰ fuel cell catalysis,¹¹ photocatalysis,¹² and sensors.^{13–16}

Many recent reports on the preparation of graphene by chemical vapor deposition (CVD) have indicated that almost

A multilayer-graphene nanosheet film deposited on a ceramic substrate without a catalyst for constructing an electrochemiluminescence imaging platform[†]

Jiannan Wang, Pengxiang Shang, Jiangyan Zhong, Shan Lin and Yuwu Chi 🗈 *

Chemically and electrochemically stable conducting films are very desirable in the electrochemical industry and electrochemical sensing. In this work, ethanol was used as the carbon source to synthesize a multilayer-graphene nanosheet (MLGNS) film on ceramic substrates by a catalyst-free chemical vapor deposition (CVD) method at 900 °C and under ambient pressure. The developed CVD method is simple, economical and safe and avoids damage to the graphene nanosheet film during its transfer from the metal substrate to the non-metal substrate. The synthesized MLGNS film was well characterized by various techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Raman spectroscopy. The prepared MLGNS film has good chemical and electrochemical stability and satisfactory electrical conductivity thus can be used as a new type of electrode material. The MLGNS film on the ceramic substrate has been fabricated into an electrochemiluminescence (ECL) imaging platform to investigate the oxygen reduction reaction (ORR) and evaluate the activities of ORR catalysts, such as PtNPs. The established MLGNS film-based ECL imaging platform may have promising applications in the study of catalysts for fuel cells, high throughput immunoassay in the clinic, and fast screening of anti-cancer drugs.

> all transition metals in the periodic table can be used as catalysts for the preparation of graphene by CVD.¹⁷⁻²⁴ Therefore, for the CVD preparation, the growth of graphene is generally realized by using a metal or a plated metal as a substrate. However, transferring graphene from a metal substrate to a non-metallic substrate, such as glass, ceramic or plastic for further applications is a complicated and skilled job.^{25,26} Inappropriate operation may easily destroy graphene, and the residual metals may contaminate the graphene materials. Therefore, it is of considerable interest if graphene film can be prepared directly on chemically or electrochemically inert and insulating substrates, such as ceramic and glass chips rather than metallic substrates. Particularly, for the applications of graphene film in electrochemical studies and industry and electronics industry, metal-free and transfer-free CVD methods for preparing graphene film are highly desired.

> To overcome the drawbacks of the metal catalyst-based CVD methods mentioned above, thermal decomposition of SiC into graphene on its surface has been intensively studied lately as a promising method to obtain graphene film with high quality for electronic applications.^{27,28} Compared with the classic CVD methods, the SiC decomposition-based method has the obvious advantage that graphene film may be directly prepared on a semiconducting or semi-insulating substrate, such as SiC,



View Article Online

MOE Key Laboratory for Analytical Science of Food Safety and Biology, Fujian Provincial Key Laboratory of Analysis and Detection for Food Safety, and College of Chemistry, Fuzhou University, Fuzhou, Fujian, 350108, P. R. China. E-mail: y.w.chi@fzu.edu.cn; Fax: +86-591-22866137; Tel: +86-591-22866137 † Electronic supplementary information (ESI) available. See DOI: 10.1039/ c9nr02480h

Nanoscale

and thus no transfer operation is needed for further electrochemical applications. However, the method may suffer from the necessary use of very high temperature²⁹ or ultra-high vacuum (UHV),³⁰ and from high cost for using a special furnace and SiC material, which may limit the extensive studies and applications of graphene/SiC. Besides SiC, other insulating substrates, such as SiO₂,^{31–34} sepiolites,³⁵ and other insulating materials (Al₂O₃, sapphire and mica),³⁴ have been used to deposit and support graphene in the absence of catalysts. These graphene/insulating substrate composites may be very attractive in electrochemistry; however, they suffer from the drawback that easily explosive gas sources such as CH₄ and H₂ are still needed in most of these CVD preparation methods.

Recently, we have tried to synthesize graphene conducting film on insulting substrates for use in electrochemistry by an easy, economical and safe method. Herein, we have found that multilayer-graphene nanosheet (MLGNS) film can be well deposited on a ceramic substrate by the CVD method without using a catalyst, by using ethanol/Ar gas as the carbon source, and under relatively gentle CVD conditions (900 °C and ambient pressure). The developed CVD method is simple, economical and safe because easily available and relatively safe ethanol acts as the carbon source, and very cheap ceramic is used as the substrate. The prepared MLGNS film/ceramic has excellent chemical and electrochemical stability, satisfactory conductivity, and excellent electrochemical responses when used as working electrodes. Finally, the MLGNS film/ceramic has been fabricated into electrochemical and electrochemiluminescent (ECL)^{36,37} cells with bipolar array electrodes to construct an ECL imaging platform for investigating the oxygen reduction reaction (ORR), and evaluating the activities of the ORR catalysts, such as PtNPs. It is envisioned that the MLGNS film-based ECL imaging platform may have promising applications in high throughput screening of fuel cell catalysts and anti-cancer drugs, and in clinic immunoassay.

Results and discussion

Synthesis and characterization of MLGNS

The CVD preparation of the MLGNS film on a ceramic substrate from ethanol was carried out by a device as described in Fig. S1,† which was composed of an ethanol/Ar gas source (section (A) in Fig. S1†) and a quartz tube furnace (section (B) in Fig. S1†). The ethanol/Ar gas was provided by bubbling ultrapure Ar gas into absolute ethanol. CVD was operated using the following procedures.

Firstly, a ceramic boat was cleaned by being ultrasonically washed in acetone, ethanol and double-distilled water each for 10 min and was then dried in a vacuum oven at 70 °C before use. The quartz tube for CVD was first physically cleaned by a brush at room temperature to remove dust on the inner wall, then it was heat-treated in air at 950 °C until any possible organic impurity was burned out, and was naturally cooled to room temperature for further use.

Then, the cleaned ceramic boat was placed in the middle of the quartz tube, followed by blocking two ends of the quartz tube to ensure that the CVD system is airtight. The quartz tube was initially heated at 80 °C under vacuum for 80 min followed by slowly introducing ultrapure Ar into the chamber for CVD. The temperature program of the tube furnace was set as follows: 25 °C to 80 °C for 30 min, 80 °C for 30 min, to 500 °C within 60 min, to 900 °C within 25 min, 900 °C for 30 min, to room temperature by natural cooling. During the temperature programming, an ethanol/Ar gas stream was introduced into a quartz tube after the temperature reached 500 °C to cause graphitization,³⁸ and the ethanol/Ar stream at a flow rate of 100 mL min⁻¹ (under 1 atm) was continuously passed through the quartz tube for 45 min, after which ultra-pure argon was again introduced into the CVD chamber until the temperature fell to room temperature. Thus, the deposition of the MLGNS film on the ceramic substrate was completed.

After the CVD treatment with ethanol/Ar, the white ceramic boat (Fig. 1a) was deposited with a uniform, smooth and black film with somewhat metallic luster (Fig. 1b). The film is quite dense and difficult to be wiped off by soft objects such as rubber and a finger. MLGNS/ceramic chips with a desired shape and scale can be obtained by cutting them from the ceramic boat with a 355 nm laser beam (Fig. 1c). The MLGNS film is very stable to all organic solvents and inorganic solvents, such as concentrated H_2SO_4 , HNO_3 , and mixed acids (*e.g.* H_2SO_4 + HNO_3 or HNO_3 + HCl), even upon heating.



Fig. 1 Photos of the ceramic boat before (a) and after (b) deposition with the MLGNS film by the CVD method. Photo of an MLGNS/ceramic chip cut from the MLGNS/ceramic boat with a 355 nm laser (c). Photo of a 1064 nm laser-fabricated MLGNS/ceramic chip (d).

Paper

However, the MLGNS film can be peeled off from the ceramic substrate by being immersed in HF solution for 12 h (Fig. S2†), which should be due to the reaction between SiO_2 contained in the ceramic substrate and HF. The MLGNS film can be easily fabricated into the desired patterns such as electronic circuits and electrodes by a 1064 nm laser beam without cutting the ceramic substrate (Fig. 1d).

The SEM images were obtained for the MLGNS film, which was peeled off from the ceramic substrate by HF-etching (Fig. $S2\dagger$).

Under low-magnification conditions, the MLGNS film loaded on a piece of Si wafer is very uniform in thickness and has some narrow wrinkles in the middle (Fig. 2A), implying that the film is guite thin. The thickness of the MLGNS film was found to be (501.0 ± 1.0) nm from the SEM images obtained for the fracture surfaces of the MLGNS film/ceramic substrate blocks (Fig. S5[†]). At a higher magnification, the MLGNS film is flat and smooth (Fig. 2B) and consists of particles with a lateral size of around 80 nm (Fig. S3[†]). The AFM images show that the prepared MLGNS film is composed of multilayer nanoparticles (sections (a) and (c) in Fig. S4[†]), with a lateral size less than 100 nm. The average thickness of the nanoparticles can be estimated to be ca. 7 nm by the data of the height profile (section (b) in Fig. S4[†]). Apparently, the thickness (several micrometers) of the obtained MLGNS film is too large for TEM measurement. Therefore, the site at the edge rather than that in the middle of the MLGNS film was chosen for TEM imaging (Fig. 2C). The recorded high-resolution TEM image shows that the nanoparticles in the MLGNS film have clear crystal structures with a lattice spacing of 0.34 nm (Fig. 2D), which is associated with the (002) facet of multi-



Fig. 2 SEM images of the peeled MLGNS film placed on a Si wafer with low-magnification (A) and high-magnification (B). TEM images of the MLGNS film with low-resolution (C) and high-resolution (D).

layered graphene, *i.e.* the distance between two graphene layers. Moreover, Fig. 2D indicates that one MLGNS particle may have tens of graphene layers. No lattice spacing of 0.24 nm corresponding to the (1120) facet of graphene can be found,³⁹ which might result from the fact that the MLGNS film is too thick to observe the (1120) facet of MLGNS therein. Overall, the above morphology characterization studies by SEM, AFM and TEM suggest that the prepared MLGNS film consists of multilayers of graphene nanosheets with a lateral size less than 100 nm and a thickness of around 7 nm.

In addition to the morphology characterization studies, various spectroscopic technologies were used to analyze the components and structures of the MLGNS film. The XPS survey spectrum of the MLGNS film/ceramic substrate shown in Fig. 3(A) indicates that the MLGNS film/ceramic composite material mainly contains C and O elements and has a small amount of Si element. All Si element and some O element should be from the ceramic substrate under the MLGNS film. No metal elements, such as Fe, Co, Ni and Cu are found, indicating that no metal element participates in the growth process of the MLGNS film, *i.e.* graphene nanosheets can be directly prepared on a ceramic substrate without any metal as a catalyst. The high-resolution XPS spectra (Fig. 3(B)) show that the MLGNS film has three types of binding carbons, including a large amount of SP² C-C (284.7 eV), and relatively small amounts of C-O (286.4 eV) and C=O (288.4 eV). It is verified that the MLGNS film mainly consists of graphitic carbon (*i.e.* SP^2 C–C) with some C–O and C=O groups on the surfaces. The XRD data shown in Fig. 3C verify that the MLGNS film consists of multilayer-graphene nanosheets since a very broad (002) peak appearing at around 25° can be found. Apparently, the (002) facet observed by XRD is consistent with that found in the HRTEM image (Fig. 2D). The Raman spectrum of the MLGNS film/ceramic substrate shows a strong D band (related to the defects in graphene) at 1345 cm⁻¹, a strong G band



Fig. 3 XPS survey spectrum (A); high resolution XPS spectra (B); XRD pattern (C); and Raman spectrum (D) of the MLGNS film/ceramic substrate.

(associated with order structures of graphene) at 1589 cm⁻¹ and a small 2D band at 2689cm⁻¹ (Fig. 3D). The intensity of the D band is almost the same as that of the G band, suggesting that there are many disorder or defect structures in the MLGNS film. The abundant disorder structures can be explained by the fact that the MLGNS film consists of multilayer graphene sheets, thus it has many edges or defect states.⁴⁰ In addition, there is a weak peak at 791 cm⁻¹ corresponding to SiC,⁴¹ which means that a small amount of SiC may form at the interface between the MLGNS film and ceramic substrate during the CVD process.

Electroconductivity and electrochemical performances

Before evaluating the electrochemistry of the prepared MLGNS film, it is necessary to investigate the electroconductivity of the MLGNS film with metallic luster on the ceramic substrate. The sheet resistance was found to be $(360.3 \pm 4.0) \Omega \square^{-1}$, and thus the electroconductivity was calculated to be $(5541 \pm 73) \text{ S m}^{-1}$, by knowing the thickness of the MLGNS film $(501.0 \pm 1.0 \text{ nm})$ (Fig. S5†).

Then, the MLGNS film was fabricated into a working electrode (Fig. 4A), followed by the investigation of the cyclic voltammetric (CV) response for the MLGNS film working electrode immersed in K_3 [Fe(CN)₆] solution (Fig. 4B). The obtained cyclic voltammograms have one electroreduction peak and one electrooxidation peak respectively at potentials of +0.17 V and +0.32 V, and almost the same oxidation and reduction peak currents, showing a basically reversible redox process of [Fe (CN)₆]³⁻ at the MLGNS film electrode. Additionally, the cyclic voltammograms are almost the same at the following continuous potential scans, suggesting very stable electrochemistry of the MLGNS film. The above CV investigation indicates that the MLGNS film is suitable for acting as electrodes in electrochemical cells.

Compared with other types of electroconductive films, such as an indium tin oxide (ITO) film, Au film, and Pt film, our



Fig. 4 (A) The fabricated MLGNS film working electrode; (B) cyclic voltammogram of K_3 [Fe(CN)₆] (1 mM) in 0.5 M KCl obtained at the MLGNS film working electrode at a scan rate of 20 mV s⁻¹. The reference electrode and counter electrode were a Ag/AgCl (3 M KCl) electrode and Pt wire electrode, respectively.

prepared MLGNS film may have the following advantages of being used as electrodes: first, the MLGNS film is very stable in various solutions, whereas ITO can be dissolved by acid, and Au and Pt film can be destroyed by mixed acid (e.g. HNO₃ + HCl). Second, the MLGNS film is electrochemically stable, while ITO may be degraded under electroreduction conditions, and Au and Pt film may be electrochemically oxidized and even dissolved in the presence of halogen anions (e.g. Cl⁻ and Br⁻). Third, a MLGNS film-based electrode may have a relatively large potential window, *i.e.* -2.0 to +2.0 V in a neutral medium (Fig. S6[†]). Therefore, the MLGNS film may become ideal electrode material in various electrochemical applications.

Electrochemiluminescence (ECL) imaging platform based on MLGNS electrode arrays

Apparently, the MLGNS film with satisfactory conductivity, very nice chemical and electrochemical stabilities, and good electrochemical performances is very suitable to be fabricated into electrode arrays for high throughput electrochemical sensing. Herein, we demonstrate a potential application of the MLGNS electrode array in the ECL imaging platform for investigating the catalysis of Pt nanoparticles (PtNPs) towards the oxygen-reduction reaction (ORR). First, the MLGNS electrode array-based ECL imaging platform for the catalytic ORR is designed and shown in Fig. 5A, in which 4 bipolar array electrodes named as "H", "A", "C" and "B" are fabricated with cathodic ends (labeled as E_{catal}) immersed in the electrolyte solution of the investigated electrochemical (EC) reaction cell, and anodic ends (labeled as $E_{Ru(II)}$) immersed in the ECL imaging cell containing Ru(bpy)₃²⁺ and TPrA. A shared anode with a "cross" shape (labeled with E_{anode}) is fabricated in the EC reaction cell, while a shared cathode with a "right bracket" shape (labeled as E_{cathode}) is fabricated and placed in the ECL imaging cell. The EC reaction cell is connected serially with an ECL imaging cell by the bipolar array electrodes. At the cathodic ends of the bipolar electrode array, O₂ is electroreduced into H₂O₂ and then into H₂O by two-step two-electron transfer in the absence of a catalyst $(eqn (1a) and (1b)):^{42}$

$$O_2 + 2H^+ + 2e^- \to H_2O_2$$
 (1a)

$$H_2O_2 + 2H^+ + 2e^- \to 2H_2O$$
 (1b)

or O_2 is directly electroreduced into H_2O by one-step fourelectron transfer in the presence of a catalyst, such as PtNPs (eqn (2)):⁴³

$$O_2 + 4H^+ + 4e^- \xrightarrow{PtNPs} 2H_2O$$
 (2)

At the anodic ends, ECL reactions happen when the currents of the ORR in the EC cell flow through the ECL imaging cell (Fig. 5B, and eqn (3)-(6)):⁴⁴

$$\operatorname{Ru}(\operatorname{bpy})_{3}^{2+} - e^{-} \to \operatorname{Ru}(\operatorname{bpy})_{3}^{3+}$$
(3)

$$\text{TPrA} - e^- \rightarrow \text{TPrA}^{\bullet} + \text{H}^+$$
 (4)



Fig. 5 (A) Design of the MLGNS electrode array-based ECL imaging platform for the catalytic ORR; (B) principle of ECL imaging for the PtNP-catalyzed ORR.; (C) fabricated MLGNS electrode array-based ECL imaging platform.

$$\operatorname{Ru}(\operatorname{bpy})_{3}^{3+} + \operatorname{TPrA}^{\bullet} \to \operatorname{Ru}(\operatorname{bpy})_{3}^{2+*} + \operatorname{Product}$$
 (5)

$$\operatorname{Ru}(\operatorname{bpy})_{3}^{2+*} \to \operatorname{Ru}(\operatorname{bpy})_{3}^{2+} + \operatorname{hv}$$
(6)

According to our previous study on the ECL imaging platform,⁴⁵ in which Cu wire-connected glassy carbon disk electrodes and Pt disk electrodes were used as the bipolar electrode array, the applied potential (E_{app}) on the two cells can be used to evaluate the catalytic activity of Pt NPs towards the ORR:

$$E_{\rm app} = E_{\rm anode} - E_{\rm catal} + E_{\rm Ru(II)} - E_{\rm cathode} + E_{\rm IR}$$
(7)

where E_{anode} and $E_{cathode}$ are the potentials of the anode and cathode in the EC reaction cell and ECL imaging cell, respectively. E_{catal} is the potential of the catalytic ORR at the cathodic end of a bipolar electrode, while $E_{Ru(II)}$ is the potential of the $Ru(bpy)_3^{2+}$ -TPrA ECL system at its maximum ECL emission. E_{IR} is the IR drop. Under certain experimental conditions, E_{anode} , $E_{cathode}$, $E_{Ru(II)}$, and E_{IR} can be all regarded as constants, then we can obtain a simple relationship between E_{app} and E_{catal} (as shown in eqn (8)):

$$E_{\rm app} = K - E_{\rm catal} \tag{8}$$

where $K = E_{anode} - E_{cathode} + E_{Ru(II)} + E_{IR}$

Apparently, eqn (8) can be used to evaluate the catalysis activity of catalysts such as PtNPs. The smaller the E_{app} value, the larger the E_{catal} value, *i.e.* the easier the reduction of O₂. This means that the catalysis activity of an ORR catalyst can be evaluated by the applied potential turning on ECL.

According to the schematic structure of the ECL imaging platform shown in Fig. 5A, bipolar array electrodes and an anode and a cathode were fabricated on a piece of the MLGNS/ ceramic substrate (Fig. 5C). After modifying the PtNPs (Fig. S7[†]) on the cathodic ends of the bipolar array electrodes and adding pH 7.0 PBS solution on the EC reaction cell, and adding the $Ru(bpy)_2^{2+}$ -TPrA-PBS solution on the ECL imaging cell, the ECL imaging platform for the PtNP-catalyzed ORR was tested. First, the four bipolar array electrodes, i.e. "H", "A", "C" and "B" were investigated without the modification of the PtNPs at their cathodic ends. The four bipolar electrodes give the brightest red ECL at an applied DC potential (E_{app}) of 5.8 V (Fig. 6a) and have similar brightness at the potential, indicating that the four MLGNS film bipolar electrodes have the same performances in ECL imaging for the ORR in the absence of the PtNPs. Subsequently, the four bipolar electrodes were divided into two groups: two electrodes (i.e. "A" and "C") were modified with the PtNPs, while the other two electrodes (i.e. "H" and "B") were unmodified. The experimental results show that both of the two PtNP-modified bipolar electrodes have maximum ECL emission at E_{app} of 4.6 V, whereas none of the unmodified bipolar electrodes give visible ECL emission (Fig. 6b). Apparently, in the presence of the PtNPs, the ORR is obviously catalyzed with a 1.2 V decrease in the reduction



Fig. 6 The MLGNS film-based ECL imaging platform for investigating the oxygen reduction reaction (ORR) in the presence and absence of the PtNPs. (a) The four bipolar electrodes were all unmodified, and the applied potential was 5.8 V; (b) bipolar electrodes "A" and "C" were modified with the PtNPs, while bipolar electrodes "H" and "B" were unmodified, and the applied potential was 4.6 V; (c) experimental conditions were the same as those of (b) except that the applied potential was raised from 4.6 V to 5.8 V; (d) experimental conditions were the same as those of (b) except that the applied potential was decreased from 5.8 V to 4.5 V. On the EC reaction cell, a drop of 20 mM pH 7.4 PBS solution was used, while on the ECL imaging cell, a drop of 5.0 mM Ru (bpy)₃²⁺ and 25.0 mM TPA in 0.1 M pH 7.4 PBS was used.

potential. Further raising the applied potential to a higher value (*e.g.* 5.8 V) can turn on the unmodified bipolar electrodes of "H" and "B" (Fig. 6c). Finally, when the applied potential is decreased from 5.8 V to a lower value (*e.g.* 4.5 V), the ECL of the unmodified polar electrodes is turned off, while the PtNP-modified polar electrodes are still at "turn on" states (Fig. 6d). It is evident from the above experimental results that the MLGNS film-based ECL imaging platform can be used to investigate the ORR and evaluate the catalytic activities of the ORR catalysts, such as PtNPs, and the ECL imaging is reproducible and reversible.

Conclusions

Without a catalyst, and using easily obtained ethanol as the carbon source, the multilayer-graphene nanosheet (MLGNS) film on the ceramic substrate has been prepared by a CVD method at 900 °C and under ambient pressure. The MLGNS film is smooth and uniform in thickness, very stable in terms of chemistry and electrochemistry and has good electroconductivity, thus it can be used as a new type of electrode material. With the laser beams, it is easy to fabricate the MLGNS film/ceramic substrate composites into electrode arrays, electrochemical cells, conducting wires, and ECL imaging cells for electrochemical sensing. The MLGNS filmbased ECL imaging platform can be applied in investigating the ORR, and evaluating the activities of ORR catalysts, such as PtNPs. It is envisioned that the MLGNS film-based ECL imaging platform may have promising applications in screening catalysts for fuel cells, carrying out high throughput immunoassay, and studying cancers and related anti-cancer drugs, and the attractive chemical, electrical, and mechanical properties of the MLGNS film enable its various applications other than sensing, such as in the electrochemical industry, modern electronics, and anti-corrosion coating.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (21675027), the Program for Scientific and Technological Innovation Leading Talents in Fujian Province, and the Program for Changjiang Scholars and Innovative Research Team in University (No. IRT_15R11).

Notes and references

1 C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam and A. Govindaraj, *Angew. Chem., Int. Ed.*, 2009, **48**, 7752–7777.

- 2 H. Kim, A. A. Abdala and C. W. Macosko, *Macromolecules*, 2010, **43**, 6515–6530.
- 3 J. Luo, J. Kim and J. Huang, Acc. Chem. Res., 2013, 46, 2225-2234.
- 4 A. S. Mayorov, R. V. Gorbachev, S. V. Morozov, L. Britnell, R. Jalil, L. A. Ponomarenko, P. Blake, K. S. Novoselov, K. Watanabe, T. Taniguchi and A. K. Geim, *Nano Lett.*, 2011, **11**, 2396–2399.
- 5 A. A. Balandin, Nat. Mater., 2011, 11, 569-581.
- 6 R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. Peters and A. K. Geim, *Science*, 2008, 320, 1308.
- 7 C. Lee, X. Wei, J. W. Kysar and J. Hone, *Science*, 2008, **321**, 385–388.
- 8 J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. Zande, J. M. Parpia, H. G. Craighead and P. L. McEuen, *Nano Lett.*, 2008, 8, 2458–2462.
- 9 H. Bi, F. Huang, J. Liang, X. Xie and M. Jiang, *Adv. Mater.*, 2011, **23**, 3202–3206.
- 10 G. Xiong, C. Meng, R. G. Reifenberger, P. P. Irazoqui and T. S. Fisher, *Electroanalysis*, 2014, 26, 30–51.
- Z. Yang, Z. Yao, G. Li, G. Fang, H. Nie, Z. Liu, X. Zhou, X. Chen and S. Huang, ACS Nano, 2012, 6, 205–211.
- 12 X. Li, J. Yu, S. Wageh, A. A. Al-Ghamdi and J. Xie, *Small*, 2016, **12**, 6640–6696.
- 13 X. Xie, L. Qu, C. Zhou, Y. Li, J. Zhu, H. Bai, G. Shi and L. Dai, *ACS Nano*, 2010, 4, 6050–6054.
- 14 Y. Dong, W. Tian, S. Ren, R. Dai, Y. Chi and G. Chen, ACS Appl. Mater. Interfaces, 2014, 6, 1646–1651.
- 15 Y. Shao, J. Wang, H. Wu, J. Liu, Y. Lin and I. A. Aksay, *Electroanalysis*, 2010, **22**, 1027–1036.
- 16 Y. Dong, G. Li, N. Zhou, R. Wang, Y. Chi and G. Chen, Anal. Chem., 2012, 84, 8378–8382.
- 17 Z. Zou, L. Fu, X. Song, Y. Zhang and Z. Liu, *Nano Lett.*, 2014, 14, 3832–3839.
- 18 Y. Xue, B. Wu, Y. Guo, L. Huang, L. Jiang, J. Chen, D. Geng, Z. Li, W. Hu and G. Yu, *Nano Res.*, 2011, 4, 1208– 1214.
- 19 E. Sutter, P. Albrecht and P. Sutter, *Appl. Phys. Lett.*, 2009, 95, 133109.
- 20 P. W. Sutter, J. I. Flege and E. A. Sutter, *Nat. Mater.*, 2008, 7, 406–411.
- 21 M. E. Ramón, A. Gupta, C. Corbet, D. A. Ferrer, H. C. P. Movva, G. Carpenter, L. Colombo, G. Bourianoff, M. Doczy, D. Akinwande, E. Tutuc and S. K. Banerjee, *ACS Nano*, 2011, 5, 7198–7204.
- 22 E. V. Rut'kov, A. V. Kuz'michev and N. R. Gall', *Phys. Solid State*, 2011, **53**, 1092–1098.
- 23 F. Müller, S. Grandthyll, C. Zeitz, K. Jacobs, S. Hüfner, S. Gsell and M. Schreck, *Phys. Rev. B: Condens. Matter.*, 2011, 84, 075472.
- 24 T. Oznuluer, E. Pince, E. O. Polat, O. Balci, O. Salihoglu and C. Kocabas, *Appl. Phys. Lett.*, 2011, **98**, 183101.
- 25 K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi and B. H. Hong, *Nature*, 2009, 457, 706–710.

- 26 T. Nasir, B. J. Kim, K. W. Kim, S. H. Lee, H. K. Lim, D. K. Lee, B. J. Jeong, H. C. Kim, H. K. Yu and J. Y. Choi, *Nanoscale*, 2018, **10**, 21865–21870.
- 27 W. A. De Heer, C. Berger, M. Ruan, M. Sprinkle, X. Li, Y. Hu, B. Zhang, J. Hankinson and E. Conrad, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 16900–16905.
- 28 N. Mishra, J. Boeckl, N. Motta and F. Iacopi, *Phys. Status Solidi A*, 2016, **213**, 2277–2289.
- 29 D. Badami, Carbon, 1965, 3, 53-57.
- 30 B. Gupta, M. Notarianni, N. Mishra, M. Shafiei, F. Iacopi and N. Mott, *Carbon*, 2014, **68**, 563–572.
- J. Chen, Y. Wen, Y. Guo, B. Wu, L. Huang, Y. Xue, D. Geng,
 D. Wang, G. Yu and Y. Liu, *J. Am. Chem. Soc.*, 2011, 133, 17548–17551.
- 32 H. Medina, Y. C. Lin, C. Jin, C. C. Lu, C. H. Yeh, K. P. Huang, K. Suenaga, J. Robertson and P. W. Chiu, *Adv. Funct. Mater.*, 2012, 22, 2123–2128.
- 33 H. Bi, S. Sun, F. Huang, X. Xie and M. Jiang, *J. Mater. Chem.*, 2012, **22**, 411–416.
- 34 L. Zhang, Z. Shi, Y. Wang, R. Yang, D. Shi and G. Zhang, Nano Res., 2011, 4, 315–321.

- 35 E. Ruiz-Hitzky, M. Darder, F. M. Fernandes, E. Zatile, F. J. Palomares and P. Aranda, *Adv. Mater.*, 2011, 23, 5250– 5255.
- 36 M. M. Richter, Chem. Rev., 2004, 104, 3003-3036.
- 37 W. Miao, Chem. Rev., 2008, 108, 2506-2553.
- 38 X. Wang, C. Zhi, L. Li, H. Zeng, C. Li, M. Mitome, D. Golberg and Y. Bando, *Adv. Mater.*, 2011, 23, 4072–4076.
- 39 Y. Dong, L. Wan, J. Cai, Q. Fang, Y. Chi and G. Chen, *Sci. Rep.*, 2015, 5, 10037.
- 40 C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng,
 Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First and
 W. A. de Heer, *J. Phys. Chem. B*, 2004, **108**, 19912–19916.
- 41 M. Wieligor, Y. Wang and T. W. Zerda, J. Phys.: Condens. Matter, 2005, 17, 2387.
- 42 A. Morozan, B. Jousselme and S. Palacin, *Energy Environ.* Sci., 2011, 4, 1238–1254.
- 43 M. Shao, A. Peles and K. Shoemaker, *Nano Lett.*, 2011, 11, 3714–3719.
- 44 Y. Zu and A. J. Bard, Anal. Chem., 2001, 73, 3960-3964.
- 45 X. Lin, L. Zheng, G. Gao, Y. Chi and G. Chen, *Anal. Chem.*, 2012, **84**, 7700–7707.