

Cite this: *Analyst*, 2011, **136**, 4631

www.rsc.org/analyst

Graphene and graphene-based nanomaterials: the promising materials for bright future of electroanalytical chemistry†

Xiao-mei Chen,^{ab} Geng-huang Wu,^a Ya-qi Jiang,^a Yi-ru Wang^a and Xi Chen^{*a}

Received 29th July 2011, Accepted 11th September 2011

DOI: 10.1039/c1an15661f

Similar to its popular older cousins of fullerene and carbon nanotubes (CNTs), the latest form of nanocarbon, graphene, is inspiring intensive research efforts in its own right. As an atomically thin layer of sp²-hybridized carbon, graphene possesses spectacular electronic, optical, magnetic, thermal and mechanical properties, which make it an exciting material in a variety of important applications. In this review, we present the current advances in the field of graphene electroanalytical chemistry, including the modern methods of graphene production, and graphene functionalization. Electrochemical (bio) sensing developments using graphene and graphene-based materials are summarized in more detail, and we also speculate on their future and discuss potential progress for their applications in electroanalytical chemistry.

Introduction

Graphene, a free-standing 2D crystal with one-atom thickness, has become one of the hottest topics in the fields of material

science, physics, chemistry, and nanotechnology since it was first isolated in 2004.¹ Graphene possesses a single-, bi- or few- (no more than ten)-layer thickness of sp²-hybridized carbon atoms arranged in six-membered rings in a honeycombed network² and is considered as the fundamental foundation for all fullerene allotropic dimensionalities,^{3,4} as shown in Fig. 1. In addition to its planar state, graphene can be wrapped to zero-dimensional (0D) fullerenes, rolled up to form 1D carbon nanotubes (CNTs) generally categorised into single-walled CNTs (SWCNTs) or multi-walled CNTs (MWCNTs) depending on the presence of graphene sheets, or stacked to produce 3D graphite where the stacks generally consist of more than ten graphene sheets.^{3,5}

Although graphene is considered as the basic block of carbon allotropes, it exhibits distinctly different properties, such as its

^aDepartment of Chemistry, College of Chemistry and Chemical Engineering, State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China. E-mail: xichen@xmu.edu.cn; Fax: +86 592 2184530; Tel: +86 592 2184530

^bTesting Lab for Food and Drug Safety, Xiamen Huaxia Vocational College, Xiamen, 361021, China

† This article is part of a web theme in *Analyst* and *Analytical Methods* on Future Electroanalytical Developments, highlighting important developments and novel applications. Also in this theme is work presented at the Eirelec 2011 meeting, dedicated to Professor Malcolm Smyth on the occasion of his 60th birthday.



Xiao-mei Chen

Xiaomei Chen was born in 1981 in Fujian Province, China. She received her BS and PhD degrees in Xiamen University in 2005 and 2011, respectively. Her scientific interests focus on carbon and metal nanomaterials for electrochemical, electrochemiluminescence and bio-analytical applications.



Geng-huang Wu

Genghuang Wu is currently a MS student of the College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China. He received his BS degree from Xiamen University in 2010. His research interests involve biosensors.

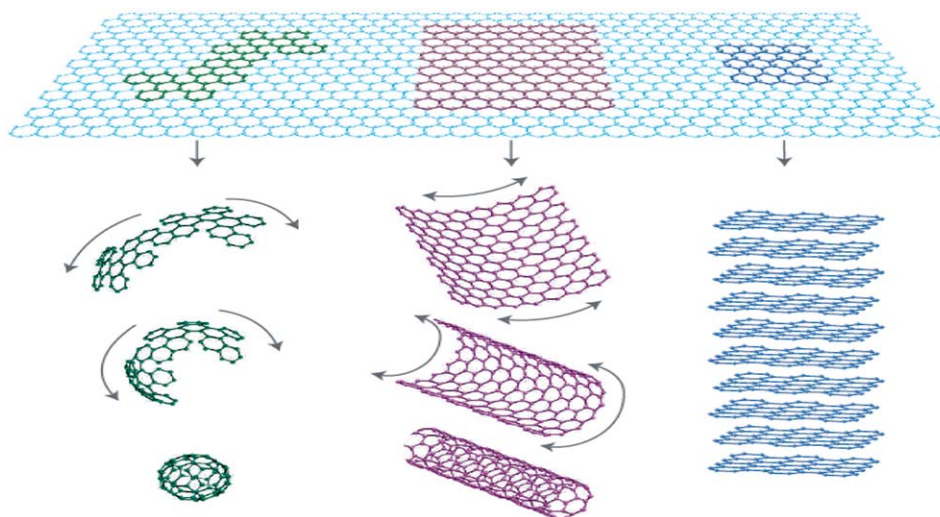


Fig. 1 The epitome of graphite forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes, or stacked into 3D graphite. (Reproduced with permission from ref. 3. Copyright 2007, Nature Publishing Group.)

unusual structural characteristics and electronic flexibility.^{6–8} It is well-known that the essential characteristic of an electrode material is its surface area, which is important in applications such as energy storage, catalytic devices, and sensors. Graphene

has a theoretical surface area of $2630 \text{ m}^2 \text{ g}^{-1}$, surpassing that of graphite ($10 \text{ m}^2 \text{ g}^{-1}$), and is two-fold larger than that of CNTs ($1315 \text{ m}^2 \text{ g}^{-1}$).^{6,9,10} The electrical conductivity of graphene has been calculated to be about 64 mS cm^{-1} , which is approximately 60-fold greater than that of SWCNTs.^{11,12} Additionally, another major advantage of graphene is the presence of oxygen-containing groups at its edges or surface. When controlled attachment of functional elements are required, such oxygen-containing groups may provide convenient attachment sites, thus specific groups can be introduced that play vital roles in electrochemical applications.^{13,14} It is worth noting that the electrochemical properties of graphene-based materials can hence be modified or tuned by chemical modification, and tailored to suit their applications. However, there is heavy debatable about whether the presence of oxides upon the graphene surface, in addition to the defect sites within graphene, may change its electronic and chemical properties beneficially or detrimentally.^{15,16}

In this review, we survey modern methods of graphene synthesis, graphene functionalization, and highlight the importance of graphene and graphene-based materials in the field of



Ya-qi Jiang

Yaqi Jiang received her BS degree in chemistry from Shanghai Jiaotong University, P. R. China, and her Master degree from Fuzhou University, she finished her doctoral course in Chemistry from Xiamen University in June this year. Since 2003, she holds the position of Associate Professor at Xiamen University. Her current research is focused on the control of surface structures and tunable properties of nanocrystallites.



Yi-ru Wang

Yiru Wang is an Associate Professor of Xiamen University in China. She received PhD degree in 1999. Her research interests cover the sample pretreatment techniques for environmental analysis, food analysis and pharmaceutical analysis.



Xi Chen

Xi Chen is a Full Professor in the Department of Chemistry at Xiamen University, China. He received his PhD (1996) degree in Analytical Chemistry from Kyoto Institute of Technology, Japan. Dr Chen's research interests cover electrochemiluminescence, bio-chemical sensors and solid-phase microextraction. He has published over 100 scientific research articles in archival scientific journals.

electroanalytical sensing. Note that there are many reviews exploring graphene applications within energy storage^{10,17,18} and other selected applications, such as fluorescence biosensors,⁵ but there is a distinct lack of reviews focusing specifically on electroanalytical chemical sensors and biosensors. This review fills this potential gap focusing solely on electroanalytical applications, and furthermore, speculating on graphene in the future and discussing potential progress for its use in electroanalytical chemistry. We hope to inspire researches into the origins of the unique properties of this emergent class of nanocarbons and to encourage their exploration in a multitude of exciting areas.

Graphene production

The fabrication process by which graphene is synthesized defines its properties and as a result of its applications,^{19,20} and therefore graphene fabrication is currently a hot research topic. It should be noted that there is no single method of graphene synthesis that yields graphene exhibiting the optimum properties for all potential applications; therefore, many routes for the synthesis of graphene have been reported.^{1,21–46} The vast array of current synthesis methodologies of graphene can be divided into two main categories: physical methods^{1,21–29} and chemical methods,^{30–46} as shown in Table 1.

The physical methods include: (i) The historically first successful method to produce both single- and few-layer graphene based on micromechanical exfoliation of highly oriented pyrolytic graphite (HOPG) with scotch-tape.¹ Although this method has produced the highest quality samples in the range of 10 μm , it is neither high throughput nor high yield. (ii) Chemical vapor deposition (CVD) of graphene.^{21–24} The CVD processes generally utilize transition metal surfaces for the growth of graphene and use hydrocarbon gases as graphene precursors at the deposition temperature of about 1000 $^{\circ}\text{C}$. This method produces amounts of graphene nanomaterials suitable for mainstream

electrochemistry, where bulk quantities are required. (iii) Epitaxial growth of graphene layers on silicon carbide (SiC).^{25–27} It is a very promising method for the synthesis of uniform, wafer-size graphene layers. However, the conditions for graphene growth by this approach should contain high temperature, high vacuum and single-crystal substrates, which limit its usage in large-scale practical applications. (iv) Arc discharge method for graphene.^{28,29} This method for graphene has merits of good crystallinity and high thermal stability due to an *in situ* defect-elimination or healing effect of the high plasma temperature and the etching effect of H_2 on undesirable amorphous carbon.

The chemical methods include: (i) Chemical oxidation of graphite to graphene oxide (GO), and subsequent chemical reduction of GO to graphene (using *e.g.*, hydrazine,^{30,31} reducing sugar³² as a reducing agent). This approach has been evaluated as one of the most efficient methods for low-cost, large-scale production of graphene. (ii) Intercalation of small molecules between the graphene sheets within the graphite and consequent ultrasound separation of the layers.^{33–36} Since this method keeps the basic structure of graphite and has fewer defects, it provides enormous potential for obtaining high quality graphene with high electrical conductivity. (iii) Unzipping CNTs for graphene nanoribbons (GNRs).^{37–41} CNTs have the identical crystal structure with graphene, and they can be viewed as a tubular structure by rolling and zipping single-layer or few-layer graphene narrow stripes. This characteristic indicates that CNTs may serve as an abundant resource to synthesize GNRs if this tubular structure can be successfully unzipped. Some interesting unzipping methods such as oxidative treatment of CNTs,³⁷ plasma etching,^{38,39} triggered by a scanning tunneling microscopy (STM) tip,⁴⁰ and cut CNTs induced by transition metal nanoparticles (NPs) (*e.g.* NiNPs or CoNPs),⁴¹ have been developed to effectively unzip CNTs to form GNRs. For instance, Dai's group reported a facile method to produce GNRs.³⁸ This method involves the deposition of MWCNTs on a silicon substrate,

Table 1 Comparisons on different aspects of methods for graphene synthesis

Synthesis methods	Precursors	Layer characters	Advantages	Disadvantages	Ref.
Micromechanical exfoliation	Graphite	Single and multiple layers; dimension <i>ca.</i> 10 μm	Simplicity; high quality; low cost	Time-consuming; low yields	1
Chemical vapor deposition	Hydrocarbon gases	Single and multiple layers; dimension <i>ca.</i> 100 μm	High quality; uniform; large-scale production	High temperature (1000 $^{\circ}\text{C}$); high cost; complicated process; low yields	21–24
Epitaxial growth on silicon carbide	SiC wafer	Single and multiple layers; dimension <i>ca.</i> 50 μm	Uniform; high quality	High cost; low yields; high temperature; high vacuum; single-crystal substrate	25–27
Arc discharge	Graphite	Single and multiple layers; dimension hundreds of nm <i>ca.</i> 10 μm	Low cost; easy doping; good crystallinity; high thermal stability	Non-uniform; impure	28,29
Chemical reduction of GO	Graphite	Single and multiple layers; dimension tens of nm to <i>ca.</i> 100 μm	High yields; low cost; large-scale production	Low quality	30–32
Intercalation of small molecules within graphite	Graphite	Single and multiple layers; dimension in tens of μm	Simplicity; benign; large-scale production; low cost	Time-consuming; impure	33–36
Unzipping CNTs	CNTs	Single and multiple layers; dimension in several μm	Low cost; large-scale production; high quality (plasma etching)	Time-consuming; complicated process	37–41
Electrochemical method	Graphite	Single and multiple dimension; hundreds of nm to <i>ca.</i> 10 μm	Low cost; high quality	Low yields	42,43
Total organic synthesis	PAHs	Single layer, dimension less than 20 nm	High quality precisely defined structures	High cost; limited size range; complicated process	44–46

covering them with poly(methyl methacrylate) (PMMA), and consequently etching them by plasma. Depending on the etching time, the MWCNTs are opened and etched to create single- or double-layer GNRs (Fig. 2). (iv) Electrochemical method for graphene.^{42,43} Electrochemistry is an effective tool to modify electronic states *via* adjusting the external power source to change the Fermi energy level of the material surface. Thus, electrochemical reduction could provide an extremely rapid and mild green chemical process for producing graphene. Dong's group⁴² and Xia's group⁴³ independently reported the first example of electrochemical reduction of GO. (v) Total organic synthesis of graphene.^{44–46} It is a bottom-up method for preparing graphene. Considering that graphene is composed of many interconnected polycyclic aromatic hydrocarbons (PAHs, very small two-dimensional graphene segments), organic synthesis successfully provides an effective route for the controllable synthesis of graphene with different sizes.

As mentioned above, various methods to fabricate graphene have been demonstrated in detail. It should be stressed that careful characterization of produced graphene nanomaterials should be performed since small deviations from the method (or starting material properties) might lead to significant differences in the produced nanomaterial and consequently in any electrochemical response.

Graphene functionalization

Parallel with the advancement of nanomaterial science and nanotechnology, appropriate combination of different nanoscale materials with different morphologies or components may lead to the development of multifunctional nano-assembled systems. The large 2D aromatic surface of graphene makes it an ideal substrate for the synthesis and design of multicomponent nanomaterials. Based on the reports, the studies focused on graphene modification and functionalization can be separated

into four categories: functionalization with polymers,^{47–68} NPs,^{69–100} atomic dopants^{101–105} and biomolecules.^{106–112} In this section, we will mainly highlight some recent achievements on these aspects.

Graphene/polymer composites have attracted a great deal of interest because of their wide applications in high-strength and conductive materials. *In situ* synthesis has been widely applied for introducing polymers to graphene-based composites. This method allows us to precisely control the structure of the polymer since the polymer can be designed and synthesized without the disturbance of graphene or its precursor. Various polymers including insulating polymers (*e.g.* poly(vinyl alcohol) (PVA),^{47–51} poly(diallyldimethylammonium chloride) (PDDA),⁵² poly(sodium 4-styrenesulfonate) (PSSNa),⁵³ poly(acrylic acid) (PAA),⁵⁴ chitosan,^{55–57} Nafion^{58–60}) and conducting polymers (*e.g.* polyaniline (PANI),^{61–64} polypyrrole (PPy),⁶⁵ poly(3,4-ethylenedioxythiophene) (PEDOT),⁶⁶ poly(1-methoxy-4-(2-ethylhexyloxy-2,5-phenylene-vinylene)) (MEH-PPV)⁶⁷ and poly(phenylene ethynylene) (PPE)),⁶⁸ have been incorporated into graphene to form composites. For instance, GO/PANI composites can be prepared by the *in situ* polymerization of aniline in GO dispersion.^{61–64} After reduction with hydrazine, the corresponding composites with graphene can be obtained. It should be noted that the polymerization must be carried out in an acidic medium (pH = 1) for producing high-quality PANi. However, over-acidification of the solution will cause congestion of GO. Thus, the pH value of the reaction system must be adjusted carefully.

Graphene is a useful substrate for immobilizing NPs to exhibit its high conductivity, large specific area and excellent thermal stability. Hydrophobic and static interactions are the main driving forces of adsorbing NPs on graphene surfaces. Most of the graphene/NP composites reported in the literatures consist of metals (*e.g.* Au,^{69–71} Ag,⁷² Pt,^{73–75} Pd,^{76–78} Fe,⁷⁹ Cu,⁸⁰ Sn,⁸¹ and bimetallic⁸²), oxides (*e.g.* Fe₂O₃,⁸³ Fe₃O₄,⁸⁴ Al₂O₃,⁸⁵ SnO₂,⁸⁶

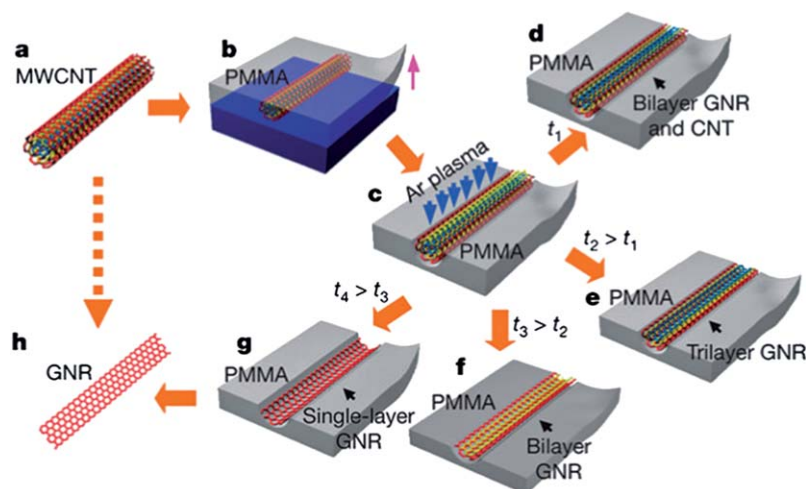


Fig. 2 Etching MWCNTs in order to prepare GNRs. (a) Pristine MWCNTs used as the starting raw material. (b) MWCNTs deposited on a Si substrate and then coated with a PMMA film. (c) PMMA-MWCNTs film peeled from a Si substrate, turned over and exposed to an Ar plasma. (d–g) Several possible products generated after etching for different durations: GNRs with CNT cores obtained after etching for a short time t_1 (d); tri-, bi- and single-layer GNRs produced after etching for times t_2 , t_3 , and t_4 , respectively ($t_4 > t_3 > t_2 > t_1$) (e–g); PMMA removed to release the GNRs (h). (Reproduced with permission from ref. 38. Copyright 2009, Nature Publishing Group.)

NiO,⁸⁷ SiO₂,^{88,89} MnO₂,⁹⁰ TiO₂,⁹¹ ZnO,⁹² Cu₂O⁹³ and Co₃O₄⁹⁴), quantum dots (e.g. CdS,⁹⁵ CdSe,⁹⁶ ZnS⁹⁷) and CNTs.^{98–100} *In situ* growth and solution mixing are the two main methods for fabricating graphene/NPs hybrids. Usually, metal NPs are synthesized following a bottom-up approach, in which metal ions are reduced to give metal NPs. The oxygenated groups on the surfaces of both GO and graphene facilitate the nucleation of metal NPs. In this sense, graphene acts as a stabilizer of metal NPs. Moreover, in many cases, capping agents are added into the synthesis systems to control the sizes and shapes of the NPs. Our group reported a facile approach to prepare ultrafine PdNPs monodispersed on GO surfaces (Fig. 3).⁷⁷ Due to the difference between the reduction potential of PdCl₄²⁻ and the oxidation potential of GO, PdNPs can spontaneously deposit on the GO surface by mixing their aqueous solutions together. As a result of the surfactant-free formation process, the clean surface of the composite can express high electrocatalytic ability in formic acid and ethanol oxidation compared to commercial Pd/C catalyst.

Doping graphene with an atomic species, such as nitrogen, is another route towards graphene functionalization.^{101–105} For example, Dai and co-workers reported the synthesis of N-doped graphene through the thermal annealing of exfoliated GO in an NH₃ atmosphere.¹⁰¹ Interestingly, the incorporation of nitrogen into the structure of graphene produces n-type electrical behavior. This result is significant because it indicates that the incorporated nitrogen atoms introduce excess electron density into the graphene. Additionally, the groups of both Wei¹⁰² and Qu¹⁰³ report the synthesis of N-doped graphene using CVD. Specifically, these groups synthesized their N-doped graphene by passing a mixture of CH₄ and NH₃ over a Cu or Ni catalyst bed. These N-graphene materials also exhibit unique properties: for

instance, Král's and Cooper's groups discover the functionalized nanopores in N-graphene monolayers and show that they could serve as ionic sieves of high selectivity and transparency.^{104,105}

In graphene-based functional biosystems, due to the varied surface functional groups, biomolecules (e.g. DNA,^{106,107} proteins,^{108–110} peptides¹¹¹ and cellulose¹¹²) can strongly modify the graphene surface through physical adsorption or chemical bonding. For instance, Patil *et al.* report that ssDNA molecules have been adsorbed on both sides of graphene sheets by π - π stacking through a self-assembly process under strong ultrasonication.¹⁰⁶ In another example, graphene tethering with DNA includes the formation of AuNPs decorated with graphene biosystems.¹⁰⁷ Thiolated ssDNA is first adsorbed onto GO sheets. Then, the resultant thiol-DNA-GO sheet is used as a 2D bionanointerface for the assembly of AuNPs. Zhang *et al.* report an enzyme immobilization matrix based on GO, horseradish peroxidase (HRP) and lysozyme.¹⁰⁸ It has been found that HRP and lysozyme can be spontaneously immobilized on GO because the individual GO sheet is enriched with oxygen-containing groups, which makes it possible to immobilize enzymes without any surface modifications or coupling reagents.

Graphene for electroanalytical applications

As discussed above, graphene can be used not only as a 2D carbon support to anchor various functional materials, but also as a functional component of its composite. Thus, graphene-based composites may combine the advantageous electrical, mechanical, optical and thermal properties of graphene with the abundant functions of the other components. As a result, they can provide new opportunities for the sustainable progress of

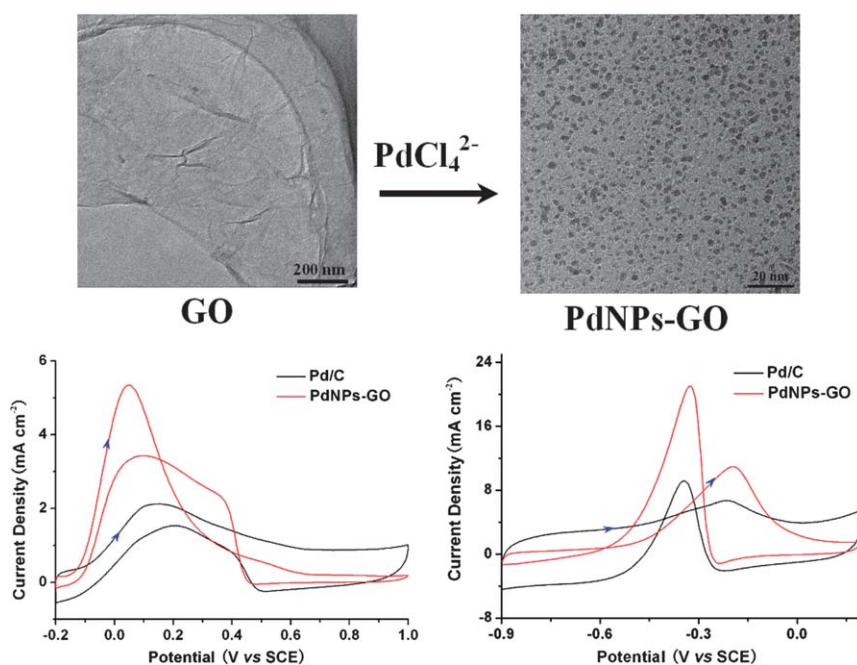


Fig. 3 Ultrafine PdNPs monodispersed on GO surfaces were successfully prepared by the redox reaction between PdCl₄²⁻ and GO. The as-made catalyst is readily 'clean' due to the surfactant-free formation process, which makes them express high electrocatalytic ability in formic acid and ethanol oxidation compared to commercial Pd/C catalyst. (Reproduced with permission from ref. 77. Copyright 2011, American Chemical Society.)

analytical sciences. The introduction of nanomaterials into analytical chemistry implants their novel functions into analytical sensing systems, resulting in many novel analytical techniques being tested and some highly sensitive and selective systems fabricated. In this section, some recent trends on graphene-based electroanalytical applications with an emphasis on chemical sensing and biosensing are briefly summarized.

The ultrahigh surface area and specific electronic features of graphene means that any molecular disruption on graphene can be easily detected, and graphene-based sensors can be expected to be highly sensitive for detecting individual molecules on and off its surface. The availability of 2D graphene will open up possibilities for designing and preparing graphene-based electrodes for a wide range of electrochemical sensors.^{19,113–140} Papakonstantinou and co-workers¹⁹ are the first researchers to apply graphene-based nanomaterials for electrochemical sensing. They grow graphene films on silica substrates using a catalyst-free method. These graphene films demonstrate fast electron-transfer kinetics for the ferro/ferricyanide couple and very good performance for the simultaneous determination of dopamine, ascorbic acid, and uric acid. Similar to the work of Papakonstantinou, Li and co-workers¹¹³ use graphene-based nanomaterials for the sensitive detection of dopamine in the presence of ascorbic acid. They demonstrate well-resolved peaks of dopamine and ascorbic acid on graphene while, on GCEs, these peaks overlap. However, the ‘graphene’ in this work is prepared by a method similar to the work of Papakonstantinou. Recently, Dong and co-workers studied the electrochemical properties of graphene in great detail.^{114,115} They report a one-step, microwave-assisted route for rapidly synthesizing a PtNPs ensemble on graphene hybrid nanosheets (PNEGHNs) with controllable PtNPs densities.¹¹⁵ The electrochemical behavior of different kinds of important electroactive compounds (*e.g.*, probe molecule (potassium ferricyanide), hydrogen peroxide (H₂O₂), neurotransmitters (DA), acetaminophen (APAP) and trinitrotoluene (TNT)) on PNEGHNs/GCE and graphene/GCE reveal that PNEGHNs/GCE shows more favorable electron-transfer kinetics and much enhanced electrochemical activities relative to graphene/GCE. Besides the above target analytes, graphene has been utilized for the sensing of individual gas molecules (*e.g.* NO₂,¹¹⁶ H₂O,^{117,118} CO^{119,120} and NH₃^{121,122}) adsorbing onto the graphene surfaces. For example, Schedin *et al.* demonstrate that the adsorbed molecules, such as NO₂, H₂O, CO and NH₃, can change the local carrier concentration in mechanically exfoliated graphene one by one electron, which leads to step-like changes in resistance; thus, micrometre-size gas sensors made from graphene are capable of detecting individual events when a gas molecule, such as NO₂, attaches to or detaches from the graphene surface.¹¹⁷ Moreover, graphene-based materials have also been developed for the environmental electrochemical analysis of some toxic substances (*e.g.* Pb²⁺, Cd²⁺ and hydrazine).^{123–125} For instance, Wang and colleagues demonstrate that the Nafion-graphene composite film electrode does not only exhibit improved sensitivity for metal ion (Pb²⁺ and Cd²⁺) detection, but also alleviates the interferences due to the synergistic effect of graphene and Nafion.¹²⁴ The linear calibration curves range from 0.5 to 50 μg L⁻¹ for Pb²⁺ and 1.5 to 30 μg L⁻¹ for Cd²⁺, respectively. The detection limits (S/N = 3) are estimated to be around 0.02 μg L⁻¹ for Pb²⁺ and Cd²⁺.

Biosensing involves the monitoring of substances that are usually apparent within biological systems.^{141–146} It is a vital utility within areas of biochemical and biophysical science. As we have shown above, graphene-based materials show improved selectivity and sensitivity, offer quicker response times, and display wider dynamic ranges, as well as exhibiting lower detection limits in chemical sensing applications. It is not surprising that graphene can continue this trend in electrochemical biosensing applications. Immunosensors are important analytical tools based on the detection of the binding event between antibody and antigen. Zhong and co-workers have developed a highly sensitive electrochemical immunosensor designed to quantify carcinoembryonic antigens (CEAs) as a tumour marker using nanogold-enwrapped graphene nanocomposites (NGGNs) that are taken as trace labels in clinical immunoassays.¹⁴¹ The device consists of a GCE coated in Prussian blue (PB), on whose surface the NGGNs are electrochemically deposited, and then further modified with the specific analyte-capturing molecule, anti-CEA antibodies. Their results indicate that the method using the anti-CEA-NGGN-PB-GCE as detection antibodies shows high signal amplification and exhibits a dynamic working range of 0.05–350 ng mL⁻¹, with a low limit of detection at 0.01 ng mL⁻¹. Lin and co-workers reported another interesting approach for the sensitive detection of a cancer biomarker, α -fetoprotein (AFP), using an electrochemical immunosensor based on a dual amplification mechanism.¹⁴² In their system, multienzyme antibody functionalized carbon nanospheres (CNs) and functionalized graphene are used as the sensor platform. Compared to the immunosensor without graphene modification and CNs labeling, the developed immunosensor shows a 7-fold increase in the detection signal. The present immunosensor could respond to 0.02 ng mL⁻¹ AFP with a linear calibration range from 0.05 to 6 ng mL⁻¹.

As a noble material, graphene and graphene-based material have extensively been applied to detect various substrates by electrochemical approaches. In order to enable the reader to better understand the significant developments of graphene in electroanalytical applications, the details are summarized in Table 2.

Future work and prospects

The emergence of graphene is opening new horizons for the investigation of materials sciences; however, research towards the applications of graphene-based materials in electrochemistry is still in its infancy, and there are several hurdles that need to be overcome.

First, the thickness and size have strong impacts on the properties and performance and even revealing new properties and functions of graphene, but there is still lack of a scalable production method for synthesizing high-quality graphene with controllable layer thickness and size. Therefore, the ultimate goal is to develop a low-cost, high-throughput, environmentally friendly strategy for the preparation of graphene with desirable fine structure, such as size, shape and even type and location of defects. In addition, the importance of detailed characterization of graphene-based nanomaterials prior to their employment as electrodes should be emphasized because even small variations in

Table 2 Depiction of the relative limit of detection and linear ranges of graphene based electrodes when utilized upon various analytes

Analytes	Electrode materials	Analytical parameter		Ref.
		Limit of detection	Linear range	
Lead	Graphene	0.02 $\mu\text{g L}^{-1}$	0.5–50 $\mu\text{g L}^{-1}$	124
Cadmium	Graphene	0.02 $\mu\text{g L}^{-1}$	1.5–30 $\mu\text{g L}^{-1}$	124
Hydrazine	Graphene	1 mM	1–25 mM	125
Nitric oxide	Graphene	3.6 μM	3.6–43.2 μM	126
Dopamine	Graphene	2.64 μM	4–100 μM	123
	Graphene	—	5–200 μM	127
Trinitrotoluene	GNRs/graphite microparticles	1 $\mu\text{g mL}^{-1}$	1–15 $\mu\text{g mL}^{-1}$	128
	Graphene	0.2 ng mL^{-1}	1–200 ng mL^{-1}	129
Hydrogen peroxide	Graphene/AuNPs/chitosan	0.18 mM	0.2–4.2 mM	130
	Au/graphene/HRP/chitosan	1.7 μM	0.005–5.13 mM	131
	Graphene/AuNPs/Nafion	5 μM	0.015–5.8 mM	132
Glucose	Graphene/AuNPs/GOD/chitosan	0.18 mM	2–10 mM	133
	Graphene/Nafion	—	0.2–1.4 mM	134
	N-doped graphene	10 μM	0.1–1.1 mM	135
2-(Dibutylamino) ethanol	Graphene/GOD	10 μM	0.1–10 mM	136
	GO	0.05 μM	0.6–200 μM	137
Glutathione	GO/CdTe	8.3 μM	24–214 μM	138
Ascorbic acid	Graphene	0.15 μM	0.15–34.4 μM	139
Uric acid	Graphene	0.05 μM	0.05–11.85 μM	139
Paracetamol	Graphene	0.032 μM	0.1–20 μM	140
α -Fetoprotein	Graphene/multienzyme functionalized carbon nanospheres	0.02 ng mL^{-1}	0.05–6 ng mL^{-1}	142
Prostate specific antigen	Graphene	0.08 ng mL^{-1}	0.1–100 ng mL^{-1}	143
Adenine	Graphene	0.75 μM	5–200 μM	144
IgG	Poly(diallyldimethylammonium chloride)/graphene/CdSe	0.005 pg mL^{-1}	0.02–2000 pg mL^{-1}	145
	Graphene	0.5 fg mL^{-1}	10–500 ng mL^{-1}	146

the methods of preparation lead to graphene with different electrochemical properties.

Second, due to the poor room temperature transistor behavior, the sensor response (especially for the sensing of gases) of pristine graphene is lower than that using CNTs or other nanowire-based sensors. One approach to circumvent the poor transistor behavior is to reduce the width of the graphene, creating GNRs.^{37–41} Researchers have found that the behavior of GNR transistors improves as the width of the GNR is decreased. Another method is atomic doping in graphene.^{101–105} Theoretical reports suggest that doped and defective graphene may bind gases more strongly than pristine graphene.^{147,148} This fact may explain the wide discrepancy in chemical sensitivities of doped graphene and pristine graphene (single molecule to $\mu\text{g g}^{-1}$ levels). Therefore, doping or chemically modified graphene with nitrogen and other heteroatoms is of high interest as such heteroatoms can provide electrocatalytic properties and enhance the stability of doped graphene electrodes.

Third, it is worth noting that some subtle details in graphene electrochemistry, such as the role of the structure of GO in its electrochemistry, the role of the specific oxygen-containing groups at the edges of graphene sheets, the mechanism of the oxidation/reduction of the graphene sheets themselves, and the role of surfactants, which may be beneficial or detrimental upon the electrochemical processes. Therefore, besides experimental studies, there still needs to be a great deal of work on theoretical investigations of various aspects of graphene. A good theory will help with understanding and predicting new properties associated with graphene. Rational designs combining theoretical modeling with advanced experimental techniques will significantly improve the graphene quality.

Finally, in the fabrication of electroanalytical biosensors, it is important to emphasize that graphene is a biocompatible nanomaterial, and, while serious toxicological effects are found with CNTs (mainly due to presence of metallic impurities within them), graphene is a non-toxic material.^{149–153} Moreover, graphene can provide more uniform and greater electroactive site distribution and density in order to decrease over-potentials, compared to graphite, and larger surface area (even larger than SWCNTs) for the immobilization of biomolecules. Nevertheless, it should be pointed out that cytotoxicity and the intracellular metabolic pathway of graphene and its derivatives remain almost unknown, which are highly important research areas and are crucial if we are going to use graphene in living cell studies and for *in vivo* applications.^{154–156}

Conclusions

In conclusion, although graphene is still a relatively new material, it has already made a wide and diverse impact within electroanalysis. In this review, the important advances of graphene in the last several years have been reviewed. These exciting research contributions include graphene production, graphene functionalization, and the electrochemical sensing developments using graphene and graphene-based materials. In addition, we predict a bright future for graphene as a sensing material in electrochemical (bio) sensing because of its biocompatibility, lack of metallic impurities (which are a major obstacle in electrochemical sensing research with CNTs), high conductivity and abundance of inexpensive source material. We hope that with the contribution of current literatures, more superb advantages of graphene for electroanalysis can be discovered. And with researcher

efforts, commercially available graphene-based application devices can be fabricated in the near future.

Acknowledgements

This work was financially supported by National Basic Research Program of China (2010CB732402), National Natural Science Foundation of China (Grant No. 20975085 and 21175112) and NFFTBS (No. J1030415), which are gratefully acknowledged.

References

- 1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666.
- 2 D. Li and R. B. Kaner, *Science*, 2008, **320**, 1170.
- 3 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183.
- 4 M. J. Allen, V. C. Tung and R. B. Kaner, *Chem. Rev.*, 2010, **110**, 132.
- 5 Y. Wang, Z. H. Li, J. Wang, J. H. Li and Y. H. Lin, *Trends Biotechnol.*, 2011, **29**, 205.
- 6 C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam and A. Govindaraj, *Angew. Chem., Int. Ed.*, 2009, **48**, 7752.
- 7 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos and A. A. Firsov, *Nature*, 2005, **438**, 197.
- 8 Y. B. Zhang, Y. W. Tan, H. L. Stormer and P. Kim, *Nature*, 2005, **438**, 201.
- 9 M. Pumera, *Chem. Rec.*, 2009, **9**, 211.
- 10 D. A. C. Brownson and C. E. Banks, *Analyst*, 2010, **135**, 2768.
- 11 C. Liu, S. Alwarappan, Z. Chen, X. Kong and C.-Z. Li, *Biosens. Bioelectron.*, 2010, **25**, 1829.
- 12 X. Wang, L. Zhi and K. Mullen, *Nano Lett.*, 2008, **8**, 323.
- 13 R. L. McCreery, *Electroanalytical Chemistry*, Marcel Dekker, New York, 1990.
- 14 X. Ji, C. E. Banks, A. Crossley and R. G. Compton, *ChemPhysChem*, 2006, **7**, 1337.
- 15 G. G. Wallace, J. Chen, D. Li, S. E. Moulton and J. M. Razal, *J. Mater. Chem.*, 2010, **20**, 3553.
- 16 D. Pan, S. Wang, B. Zhao, M. Wu, H. Zhang, Y. Wang and Z. Jiao, *Chem. Mater.*, 2009, **21**, 3136.
- 17 D. A. C. Brownson, D. K. Kampouris and C. E. Banks, *J. Power Sources*, 2011, **196**, 4873.
- 18 D. R. Kauffman and A. Star, *Analyst*, 2010, **135**, 2790.
- 19 S. J. Guo and S. J. Dong, *Chem. Soc. Rev.*, 2011, **40**, 2644.
- 20 M. Pumera, *Chem. Soc. Rev.*, 2010, **39**, 4146.
- 21 N. G. Shang, P. Papakonstantinou, M. McMullan, M. Chu, A. Stamboulis, A. Potenza, S. S. Dhesi and H. Marchetto, *Adv. Funct. Mater.*, 2008, **18**, 3506.
- 22 G. Nandamuri, S. Roumimov and R. Solanki, *Nanotechnology*, 2010, **21**, 145604.
- 23 X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo and R. S. Ruoff, *Science*, 2009, **324**, 1312.
- 24 A. Srivastava, C. Galande, L. Ci, L. Song, C. Rai, D. Jariwala, K. F. Kelly and P. M. Ajayan, *Chem. Mater.*, 2010, **22**, 3457.
- 25 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.
- 26 S. Shivaraman, R. A. Barton, X. Yu, J. Alden, L. Herman, M. V. S. Chandrashekar, J. Park, P. L. McEuen, J. M. Parpia, H. G. Craighead and M. G. Spencer, *Nano Lett.*, 2009, **9**, 3100.
- 27 D. Deng, X. Pan, H. Zhang, Q. Fu, D. Tan and X. Bao, *Adv. Mater.*, 2010, **22**, 2168.
- 28 Z. S. Wu, W. Ren, L. Gao, J. Zhao, Z. Chen, B. Liu, D. Tang, B. Yu, C. Jiang and H. M. Cheng, *ACS Nano*, 2009, **3**, 411.
- 29 Z. Wang, N. Li, Z. Shi and Z. Gu, *Nanotechnology*, 2010, **21**, 175602.
- 30 S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558.
- 31 D. Li, M. B. Müller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nat. Nanotechnol.*, 2008, **3**, 101.
- 32 C. Zhu, S. Guo, Y. Fang and S. Dong, *ACS Nano*, 2010, **4**, 2429.
- 33 P. K. Ang, S. Wang, Q. Bao, J. T. L. Thong and K. P. Loh, *ACS Nano*, 2009, **3**, 3587.
- 34 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 and J. N. Coleman, *J. Am. Chem. Soc.*, 2009, **131**, 3611.
- 35 M. Zhang, R. R. Parajuli, D. Mastrogianni, B. Dai, P. Lo, W. Cheung, R. Brukh, P. L. Chiu, T. Zhou, Z. Liu, E. Garfunkel and H. He, *Small*, 2010, **6**, 1100.
- 36 R. Hao, W. Qian, L. Zhang and Y. Hou, *Chem. Commun.*, 2008, 6576.
- 37 A. Hirsch, *Angew. Chem., Int. Ed.*, 2009, **48**, 6594.
- 38 L. Jiao, L. Zhang, X. Wang, G. Diankov and H. Dai, *Nature*, 2009, **458**, 877.
- 39 L. Jiao, L. Zhang, L. Ding, J. Liu and H. Dai, *Nano Res.*, 2010, **3**, 387.
- 40 M. C. Paiva, W. Xu, M. F. Proenca, R. M. Novais, E. Lagsgaard and F. Besenbacher, *Nano Lett.*, 2010, **10**, 1764.
- 41 A. L. Elias, A. R. Botello-Méndez, D. Meneses-Rodríguez, V. J. González, D. Ramírez-González, L. Ci, E. Muñoz-Sandoval, P. M. Ajayan, H. Terrones and M. Terrones, *Nano Lett.*, 2010, **10**, 366.
- 42 M. Zhou, Y. Wang, Y. Zhai, J. Zhai, W. Ren, F. Wang and S. Dong, *Chem.-Eur. J.*, 2009, **15**, 6116.
- 43 H. L. Guo, X. F. Wang, Q. Y. Qian, F. B. Wang and X. H. Xia, *ACS Nano*, 2009, **3**, 2653.
- 44 X. Y. Yang, X. Dou, A. Rouhanipour, L. J. Zhi, H. J. Rader and K. Müllen, *J. Am. Chem. Soc.*, 2008, **130**, 4216.
- 45 X. Yan, X. Cui, B. Li and L. S. Li, *Nano Lett.*, 2010, **10**, 1869.
- 46 H. Qian, F. Negri, C. Wang and Z. Wang, *J. Am. Chem. Soc.*, 2008, **130**, 17970.
- 47 X. Yang, L. Li, S. Shang and X. M. Tao, *Polymer*, 2010, **51**, 3431.
- 48 H. Chang, G. Wang, A. Yang, X. Tao, X. Liu, Y. Shen and Z. Zheng, *Adv. Funct. Mater.*, 2010, **20**, 2893.
- 49 B. Das, K. E. Prasad, U. Ramamurty and C. N. R. Rao, *Nanotechnology*, 2009, **20**, 125705.
- 50 K. W. Putz, O. C. Compton, M. J. Palmeri, S. T. Nguyen and L. C. Brinson, *Adv. Funct. Mater.*, 2010, **20**, 3322.
- 51 X. Zhao, Q. Zhang, D. Chen and P. Lu, *Macromolecules*, 2010, **43**, 2357.
- 52 T. Szabó, A. Szeri and I. Dékány, *Carbon*, 2005, **43**, 87.
- 53 H. K. Jeong, M. Jin, E. J. Ra, K. Y. Sheem, G. H. Han, S. Arepalli and Y. H. Lee, *ACS Nano*, 2010, **4**, 1162.
- 54 J. Q. Liu, L. Tao, W. R. Yang, D. Li, C. Boyer, R. Wührer, F. Braet and T. P. Davis, *Langmuir*, 2010, **26**, 10068.
- 55 X. Kang, J. Wang, H. Wu, I. A. Aksay, J. Liu and Y. Lin, *Biosens. Bioelectron.*, 2009, **25**, 901.
- 56 H. Fan, L. Wang, K. Zhao, N. Li, Z. Shi, Z. Ge and Z. Jin, *Biomacromolecules*, 2010, **11**, 2345.
- 57 X. Yang, Y. Tu, L. Li, S. Shang and X. M. Tao, *ACS Appl. Mater. Interfaces*, 2010, **2**, 1707.
- 58 J. Li, S. Guo, Y. Zhai and E. Wang, *Electrochem. Commun.*, 2009, **11**, 1085.
- 59 Y. Liu, L. Gao, J. Sun, Y. Wang and J. Zhang, *Nanotechnology*, 2009, **20**, 465605.
- 60 Y. Lian, Y. Liu, T. Jiang, J. Shu, H. Lian and M. Cao, *J. Phys. Chem. C*, 2010, **114**, 9659.
- 61 W. L. Zhang, B. J. Park and H. J. Choi, *Chem. Commun.*, 2010, **46**, 5596.
- 62 K. Zhang, L. L. Zhang, X. S. Zhao and J. Wu, *Chem. Mater.*, 2010, **22**, 1392.
- 63 H. Wang, Q. Hao, X. Yang, L. Lu and X. Wang, *Electrochem. Commun.*, 2009, **11**, 1158.
- 64 A. V. Murugan, T. Muraliganth and A. Manthiram, *Chem. Mater.*, 2009, **21**, 5004.
- 65 Z. Gu, C. Li, G. Wang, L. Zhang, X. Li, W. Wang and S. Jin, *J. Polym. Sci., Part B: Polym. Phys.*, 2010, **48**, 1329.
- 66 S. Bittolo Bon, L. Valentini and J. M. Kenny, *Chem. Phys. Lett.*, 2010, **494**, 264.
- 67 Y. B. Wang, D. Kurunthu, G. W. Scott and C. J. Bardeen, *J. Phys. Chem. C*, 2010, **114**, 4153.
- 68 H. F. Yang, Q. X. Zhang, C. S. Shan, F. H. Li, D. X. Han and L. Niu, *Langmuir*, 2010, **26**, 6708.
- 69 R. Muszynski, B. Seger and P. V. Kamat, *J. Phys. Chem. C*, 2008, **112**, 5263.

- 70 G. Goncalves, P. A. A. P. Marques, C. M. Granadeiro, H. I. S. Nogueira, M. K. Singh and J. Grácio, *Chem. Mater.*, 2009, **21**, 4796.
- 71 J. Liu, S. Fu, B. Yuan, Y. Li and Z. Deng, *J. Am. Chem. Soc.*, 2010, **132**, 7279.
- 72 J. Shen, M. Shi, N. Li, B. Yan, H. Ma, Y. Hu and M. Ye, *Nano Res.*, 2010, **3**, 339.
- 73 C. Zhu, S. Guo, Y. Zhai and S. Dong, *Langmuir*, 2010, **26**, 7614.
- 74 Y. Shao, S. Zhang, C. Wang, Z. Nie, J. Liu, Y. Wang and Y. Lin, *J. Power Sources*, 2010, **195**, 4600.
- 75 S. J. Guo, S. J. Dong and E. K. Wang, *ACS Nano*, 2009, **4**, 547.
- 76 G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth and R. Mühlaupt, *J. Am. Chem. Soc.*, 2009, **131**, 8262.
- 77 X. M. Chen, G. H. Wu, J. M. Chen, X. Chen, Z. X. Xie and X. R. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 3693.
- 78 Z. Tang, S. Shen, J. Zhuang and X. Wang, *Angew. Chem., Int. Ed.*, 2010, **49**, 4603.
- 79 Y. H. Zou, H. B. Liu, L. Yang and Z. Z. Chen, *J. Magn. Magn. Mater.*, 2006, **302**, 343.
- 80 X. Bin, J. Chen, H. Cao, L. Chen and J. Yuan, *J. Phys. Chem. Solids*, 2009, **70**, 1.
- 81 G. Wang, B. Wang, X. Wang, J. Park, S. Dou, H. Ahn and K. Kim, *J. Mater. Chem.*, 2009, **19**, 8378.
- 82 H. M. A. Hassan, V. Abdelsayed, A. E. R. S. Khder, K. M. Abouzeid, J. Terner, M. S. El-Shall, S. I. Al-Resayes and A. A. El-Azhary, *J. Mater. Chem.*, 2009, **19**, 3832.
- 83 K. Morishige and T. Hamada, *Langmuir*, 2005, **21**, 6277.
- 84 M. Zhang, D. Lei, X. Yin, L. Chen, Q. Li, Y. Wang and T. Wang, *J. Mater. Chem.*, 2010, **20**, 5538.
- 85 Y. Fan, L. Wang, J. Li, J. Li, S. Sun, F. Chen, L. Chen and W. Jiang, *Carbon*, 2010, **48**, 1743.
- 86 S. M. Paek, E. Yoo and I. Honma, *Nano Lett.*, 2008, **9**, 72.
- 87 D. H. Wang, R. Kou, D. Choi, Z. G. Yang, Z. M. Nie, J. Li, L. V. Saraf, D. H. Hu, J. G. Zhang, G. L. Graff, J. Liu, M. A. Pope and I. A. Aksay, *ACS Nano*, 2010, **4**, 1587.
- 88 H. Zhang, X. Lv, Y. Li, Y. Wang and J. Li, *ACS Nano*, 2010, **4**, 380.
- 89 H. B. Yao, L. H. Wu, C. H. Cui, H. Y. Fang and S. H. Yu, *J. Mater. Chem.*, 2010, **20**, 5190.
- 90 J. Yan, Z. Fan, T. Wei, W. Qian, M. Zhang and F. Wei, *Carbon*, 2010, **48**, 3825.
- 91 K. K. Manga, Y. Zhou, Y. Yan and K. P. Loh, *Adv. Funct. Mater.*, 2009, **19**, 3638.
- 92 W. T. Zheng, Y. M. Ho, H. W. Tian, M. Wen, J. L. Qi and Y. A. Li, *J. Phys. Chem. C*, 2009, **113**, 9164.
- 93 C. Xu, X. Wang, L. Yang and Y. Wu, *J. Solid State Chem.*, 2009, **182**, 2486.
- 94 S. Yang, X. Feng, L. Wang, K. Tang, J. Maier and K. Müllen, *Angew. Chem., Int. Ed.*, 2010, **49**, 4795.
- 95 H. Chang, X. Lv, H. Zhang and J. Li, *Electrochem. Commun.*, 2010, **12**, 483.
- 96 Y. Lin, K. Zhang, W. Chen, Y. Liu, Z. Geng, J. Zeng, N. Pan, L. Yan, X. Wang and J. G. Hou, *ACS Nano*, 2010, **4**, 3033.
- 97 C. Nethravathi, T. Nisha, N. Ravishankar, C. Shivakumara and M. Rajamathi, *Carbon*, 2009, **47**, 2054.
- 98 D. Cai, M. Song and C. Xu, *Adv. Mater.*, 2008, **20**, 1706.
- 99 D. Yu and L. Dai, *J. Phys. Chem. Lett.*, 2010, **1**, 467.
- 100 T. K. Hong, D. W. Lee, H. J. Choi, H. S. Shin and B. S. Kim, *ACS Nano*, 2010, **4**, 3861.
- 101 X. Li, H. Wang, J. T. Robinson, H. Sanchez, G. Diankov and H. Dai, *J. Am. Chem. Soc.*, 2009, **131**, 15939.
- 102 D. Wei, Y. Liu, Y. Wang, H. Zhang, L. Huang and G. Yu, *Nano Lett.*, 2009, **9**, 1752.
- 103 L. Qu, Y. Liu, J. B. Baek and L. Dai, *ACS Nano*, 2010, **4**, 1321.
- 104 D. E. Jiang, V. R. Cooper and S. Dai, *Nano Lett.*, 2009, **9**, 4019.
- 105 K. Sint, B. Y. Wang and P. Král, *J. Am. Chem. Soc.*, 2008, **130**, 16448.
- 106 A. J. Patil, J. L. Vickery, T. B. Scott and S. Mann, *Adv. Mater.*, 2009, **21**, 3159.
- 107 J. B. Liu, Y. L. Lin, Y. M. Li, J. H. Li and Z. X. Deng, *J. Mater. Chem.*, 2010, **20**, 900.
- 108 J. L. Zhang, F. Zhang, H. J. Yang, X. L. Huang, H. Liu, J. Y. Zhang and S. W. Guo, *Langmuir*, 2010, **26**, 6083.
- 109 P. Laaksonen, M. Kainlahti, T. Laaksonen, A. Shchepetov, H. Jiang, J. Ahopelto and M. B. Linder, *Angew. Chem., Int. Ed.*, 2010, **49**, 4946.
- 110 J. B. Liu, S. H. Fu, B. Yuan, Y. L. Li and Z. X. Deng, *J. Am. Chem. Soc.*, 2010, **132**, 7279.
- 111 T. H. Han, W. J. Lee, D. H. Lee, J. E. Kim, E. Y. Choi and S. O. Kim, *Adv. Mater.*, 2010, **22**, 2060.
- 112 Q. Yang, X. J. Pan, F. Huang and K. C. Li, *J. Phys. Chem. C*, 2010, **114**, 3811.
- 113 Y. Wang, Y. Li, L. Tang, J. Lu and J. Li, *Electrochem. Commun.*, 2009, **11**, 889.
- 114 M. Zhou, Y. Zhai and S. Dong, *Anal. Chem.*, 2009, **81**, 5603.
- 115 S. Guo, D. Wen, Y. Zhai, S. Dong and E. Wang, *ACS Nano*, 2010, **4**, 3959.
- 116 D. R. Kauffman and A. Star, *J. Phys. Chem. C*, 2008, **112**, 4430.
- 117 F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 652.
- 118 Y. Dan, Y. Lu, N. J. Kybert, Z. Luo and A. T. C. Johnson, *Nano Lett.*, 2009, **9**, 1472.
- 119 A. Star, V. Joshi, S. Skarupo, D. Thomas and J. C. P. Gabriel, *J. Phys. Chem. B*, 2006, **110**, 21014.
- 120 D. R. Kauffman, D. Sorescu, D. Schofield, B. L. Allen, K. D. Jordan and A. Star, *Nano Lett.*, 2010, **10**, 958.
- 121 E. Bekyarova, I. Kalinina, M. E. Itkis, L. Beer, N. Cabrera and R. C. Haddon, *J. Am. Chem. Soc.*, 2007, **129**, 10700.
- 122 P. Qi, O. Vermesh, M. Grecu, A. Javey, Q. Wang, H. Dai, S. Peng and K. J. Chao, *Nano Lett.*, 2003, **3**, 347.
- 123 J. Li, S. Guo, Y. Zhai and E. Wang, *Electrochem. Commun.*, 2009, **11**, 1085.
- 124 J. Li, S. Guo, Y. Zhai and E. Wang, *Anal. Chim. Acta*, 2009, **649**, 196.
- 125 Y. Wang, Y. Wan and D. Zhang, *Electrochem. Commun.*, 2010, **12**, 187.
- 126 J. F. Wu, M. Q. Xu and G. C. Zhao, *Electrochem. Commun.*, 2010, **12**, 175.
- 127 Y. R. Kim, S. Bong, Y. J. Kang, Y. Yang, R. K. Mahajan, J. S. Kim and H. Kim, *Biosens. Bioelectron.*, 2010, **25**, 2366.
- 128 M. S. Goh and M. Pumera, *Anal. Bioanal. Chem.*, 2011, **399**, 127.
- 129 L. H. Tang, H. B. Feng, J. S. Cheng and J. H. Li, *Chem. Commun.*, 2010, **46**, 5882.
- 130 T. T. Baby, S. S. J. Aravind, T. Arockiadoss, R. B. Rakhi and S. Ramaprabhu, *Sens. Actuators, B*, 2010, **145**, 71.
- 131 K. F. Zhou, Y. H. Zhu, X. L. Yang, J. Luo, C. Z. Li and S. R. Luan, *Electrochim. Acta*, 2010, **55**, 3055.
- 132 S. Bong, Y. R. Kim, I. Kim, S. Woo, S. Uhm, J. Lee and H. Kim, *Electrochem. Commun.*, 2010, **12**, 129.
- 133 C. S. Shan, H. F. Yang, D. X. Han, Q. X. Zhang, A. Ivaska and L. Niu, *Biosens. Bioelectron.*, 2010, **25**, 1070.
- 134 M. Pumera, R. Scipioni, H. Iwai, T. Ohno, Y. Miyahara and M. Boero, *Chem.–Eur. J.*, 2009, **15**, 10851.
- 135 C. Shan, H. Yang, J. Song, D. Han, A. Ivaska and L. Niu, *Anal. Chem.*, 2009, **81**, 2378.
- 136 P. Wu, Q. Shao, Y. J. Hu, J. Jin, Y. J. Yin, H. Zhang and C. X. Cai, *Electrochim. Acta*, 2010, **55**, 8606.
- 137 X. M. Chen, G. H. Wu, J. M. Chen, Y. Q. Jiang, G. N. Chen, M. Oyama, X. Chen and X. R. Wang, *Biosens. Bioelectron.*, 2010, **26**, 872.
- 138 Y. Wang, J. Lu, L. H. Tang, H. X. Chang and J. H. Li, *Anal. Chem.*, 2009, **81**, 9710.
- 139 C. L. Sun, H. H. Lee, J. M. Yang and C. C. Wu, *Biosens. Bioelectron.*, 2011, **26**, 3450.
- 140 X. Kang, J. Wang, H. Wu, J. Liu, I. A. Aksay and Y. Lin, *Talanta*, 2010, **81**, 754.
- 141 Z. Zhong, W. Wu, D. Wang, D. Wang, J. Shan, Y. Qing and Z. Zhang, *Biosens. Bioelectron.*, 2010, **25**, 2379.
- 142 D. Du, Z. Zou, Y. Shin, J. Wang, H. Wu, M. H. Engelhard, J. Liu, I. A. Aksay and Y. Lin, *Anal. Chem.*, 2010, **82**, 2989.
- 143 M. H. Yang and S. Q. Gong, *Chem. Commun.*, 2010, **46**, 5796.
- 144 H. Yin, Y. Zhou, Q. Ma, S. Ai, P. Ju, L. Zhu and L. Lu, *Process Biochem.*, 2010, **45**, 1707.
- 145 L. L. Li, K. P. Liu, G. H. Yang, C. M. Wang, J. R. Zhang and J. J. Zhu, *Adv. Funct. Mater.*, 2011, **21**, 869.
- 146 B. Q. Liu, D. P. Tang, J. Tang, B. L. Su, Q. F. Li and G. N. Chen, *Analyst*, 2011, **136**, 2218.
- 147 Y. H. Zhang, Y. B. Chen, K. G. Zhou, C. H. Liu, J. Zeng, H. L. Zhang and Y. Peng, *Nanotechnology*, 2009, **20**, 185504.
- 148 Z. M. Ao, J. Yang, S. Li and Q. Jiang, *Chem. Phys. Lett.*, 2008, **461**, 276.

- 149 C. E. Banks, A. Crossley, C. Salter, S. J. Wilkins and R. G. Compton, *Angew. Chem., Int. Ed.*, 2006, **45**, 2533.
- 150 X. Ji, R. O. Kadara, J. Krussma, Q. Chen and C. E. Banks, *Electroanalysis*, 2010, **22**, 7.
- 151 M. Pumera, *Chem.–Eur. J.*, 2009, **15**, 4970.
- 152 A. Ambrosi and M. Pumera, *Chem.–Eur. J.*, 2010, **16**, 1786.
- 153 M. Pumera and Y. Miyahara, *Nanoscale*, 2009, **1**, 260.
- 154 Y. L. Chang, S. T. Yang, J. H. Liu, E. Y. Dong, Y. W. Wang, A. N. Cao, Y. F. Liu and H. F. Wang, *Toxicol. Lett.*, 2011, **200**, 201.
- 155 O. Akhavan and E. Ghaderi, *ACS Nano*, 2010, **4**, 5731.
- 156 K. Yang, J. M. Wan, S. Zhang, Y. J. Zhang, S. T. Lee and Z. Liu, *ACS Nano*, 2011, **5**, 516.