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Recent advances on synthesis and application of graphene as novel sensing materials in analytical chemistry

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Abstract

The emergence of graphene (GR) has recently opened up an exciting new field in the science and technology of two-dimensional (2D) nanomaterials with continuously growing academic and technological impetus. GR exhibits unique electronic, optical, magnetic, thermal, and mechanical properties arising from its strictly 2D structure and, thus, has many important technical applications. In the last 2 years, GR, as novel sensing material has attracted tremendous attention and research interest. To further improve electrochemical property, large numbers of GR-based hybride materials have been well designed, synthesized, and investigated for sensing application. The hybridization can be an effective strategy to enhance functionality of the materials, and the integration of nanomaterials on GR potentially paves a new way to enhance their electronic, chemical, and electrochemical properties. As a result, the GR composites often offer better analytical characteristics than GR materials alone. However, the immobilizations of GR-based material and enzyme are important to enhance electrochemical properties and use of the biosensor. Classical coating method results in poor stability due to loss of the enzyme/antibody. To resolve the problem, we developed a green and controllable strategy to fabricate well-dispersed GR-metal nanocomposite modified functional conducting polymer film containing carbonyl groups with electrochemical deposition. Horseradish peroxidase was finally connected covalently to the film with 1-ethyl-3-(3-dimethylaminepropyl) carbodiimide (EDC)/N-hydroxysuccinimide (NHS) as activator. The as-prepared GR/gold nanocomposite offers remarkable catalysis performance to the redox of hydrogen peroxide on the electrode surface. In this review, from the viewpoint of chemistry and materials, we will cover recent significant advances in hybrids, design, and synthesis of GR-based film, as well as immobilization of enzyme/antibody on the electrode, and analytical application together with discussion on the major challenges and opportunities for future GR research.

Keywords: composites; graphene; sensor.

Introduction

Graphene (GR), a two-dimensional (2D) carbon atom monolayer, has attracted increasing attention since its discovery in 2004, mainly due to unique electronic, mechanical, physical, and chemical properties (Miller et al. 2009). At present, GR has been employed as blocks for new materials for many applications, such as solar cell (Yin et al. 2010), lithium ion battery (Lian et al. 2010), cell culture (Agarwal et al. 2010), and sensing materials (Li et al. 2009b). Recently, the use of GR for sensors received much attention (Pumera et al. 2010). However, some investigations demonstrated that single, few, and multilayer GR are not of significant advantages over graphite microparticles in electroanalysis (Goh and Pumera 2010). This is due to Van der Waals and *p-p* stacking interactions among individual GR sheets resulting in their tendency to aggregate, which will partly reduce its electrochemical properties and result in poor analytical characteristics. By incorporation of nanoparticles into GR sheets, in addition to the good distribution of nanoparticles, the aggregation problem of GR nanosheets could be minimized or prevented. Therefore, GR-metal nanocomposite has become a hot research topic in materials science because the hybridization can be an effective strategy to enhance the functionality of materials, and the integration of nanomaterials on GR sheets potentially paves a new way to enhance their electronic, chemical, and electrochemical properties (Xu et al. 2008, Xiong et al. 2010, Chen et al. 2011d). Among these, noble metals such as Au, Ag, Pt, and Pd are mostly used for fabricating GR-based composite film as sensing materials. The introduction of noble metal nanoparticles into GR nanosheets remarkably improves the electron conductivity and always results in an increasing sensitivity. However, some studies showed that the analytical characteristics of the sensor also depend on the properties of GR-based materials, including stripping degree of oxygen in GR sheet, layer numbers of GR sheets, dispersivity, morphology, and particle size of the components. Moreover, methods for the film preparation and immobilization of enzyme/antibody on the electrode surface are also important factors to enhance sensitivity and stability of the sensor. To further improve analytical characteristics, many researchers focused on the GR-based hybrids, design and synthesis of GR-based sensing film, and immobilization of enzyme/antibody on the electrode, and more than 200 papers have been published on the international journals in the last 5 years. In general, GR has increasingly become one of the most important tools in the fabrication of various sensors. In the paper, we reviewed recent advances on GR as sensing material in analytical chemistry.

Graphene-based hybrids

Many materials have been reported to employ for the preparation of GR-based nanocomposites. These mainly include

metal, metallic oxide, semiconductor quantum dots (QDs), conducting polymer, and others. Noble metals have been widely applied to make various GR/metal composites such as Au, Pt, Pd, Ag, and their alloys due to special electrochemical properties. Commonly, the introduction of noble metal nanoparticles into GR nanosheets can remarkably improve the sensitivity and electrochemical response time of the sensor. For example, Wang and coworkers reported a new nanolabel using chitosan (CS)-protected GR nanosheets as core and multi-nanogold particles as shell (shown in Figure 1). The nanogold-enwrapped GR nanocomposites could be conveniently used for the label of secondary antibodies in the sandwich-type immunoassay format. Compared with conventional labeled methods, the immunoassay exhibited high sensitivity and low detection limit. The highlight of this work is to improve the conductivity of the nanogold-based nanocomposites due to the presence of GR. The nanogold-enwrapped GR nanocomposites facilitate the electron transfer between the analyte and the base electrode. The convenient operation and ultrasensitivity of the developed methodology provides a promising potential in clinical diagnosis (Zhong et al. 2010). Because many metal oxides have some special properties in optical, electronics, and materials, GR/metal oxide composites can often offer some new functions and are used in various sensors. Among the metal oxide nanoparticles, decorating GR, intensive attention should be paid to SnO_2 nanoparticles because of their unique properties such as high optical transparency, electrical conductivity, and chemical sensitivity. To date, there have been a few reports about the preparation of SnO_2/GR composites with application in sensing. Lv group reported a facile strategy to synthesize GR sheets decorated with SnO_2 nanocrystals through a hydrothermal-assisted oxidation-reduction reaction route. The key to this method is the *in situ* formation of SnO_2 nanocrystals and GR sheets simultaneously, which can decrease the serious stacking of GR nanosheets and prevent the agglomeration of SnO_2 nanoparticles. Moreover, they developed a new application domain for GR-based composite; SnO_2/GR composite was found to be a highly efficient material for cataluminescence sensor to propanal. Because of its excellent analytical performance, the fabricated cataluminescence sensor device is potentially applicable for the *in situ* detection of propanal in monitoring the environment (Song et al. 2011). Semiconductor QDs, which are quasi zero dimensional materials, have gained a great deal of research interest in the past decade due to their exciting size- and shape-dependent properties. Much effort has been made to synthesize QD materials with band gaps that can be easily tuned by changing their size and shape (Goldman et al. 2004). These materials are highly luminescent with narrow emission line widths, which have enormous potential applications, including use in biolabeling (Algar and Krull 2010) and nanosensor (Zhang and Johnson 2009). Recently, we first developed an ultrasensitive hydrogen peroxide biosensor, in which the biosensor was fabricated by coating GR-gold nanocomposite (GR-AuNP), CdTe-CdS core-shell QDs (CdTe-CdS), gold nanoparticles (AuNPs), and horseradish peroxidase (HRP) in sequence on the surface of gold electrodes (GE) (shown in Figure 2). As providing electrocatalytic synergy of GR-AuNP, CdTe-CdS, and AuNPs toward hydrogen peroxide was achieved, the biosensor displayed a high sensitivity, detection limit (S/N=3) of 3.2×10^{-11} M, wide calibration range from 1×10^{-10} M to 1.2×10^{-8} M, and long-term stability of 20 weeks. High sensitivity of the biosensor (HRP/AuNPs/CdTe-CdS/GR-AuNP/GE) should be attributed to its unique surface architecture. First, the CdTe-CdS, located at the middle of the surface architecture, acts as an electron transfer channel between GR-AuNP and AuNPs. As the CdTe-CdS offers an ultrafast charge carrier and charge transfer, the relay of electron transfer is very efficient and rapid. Moreover, the particular alignment of conduction and valence band of the CdTe-CdS favors electron transfer between CdTe-CdS and AuNPs or GR-AuNP. Second, AuNPs, located outside of the

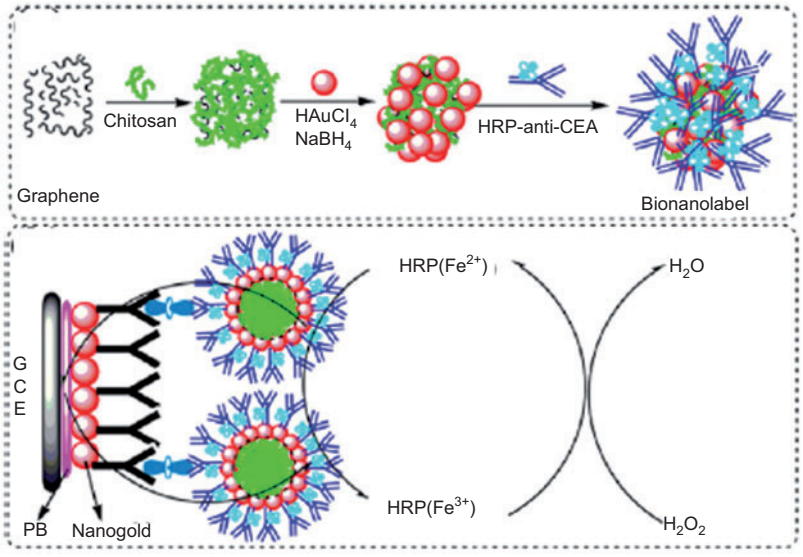

Figure 1 Fabricated process of GR/Au composited-based sensor.

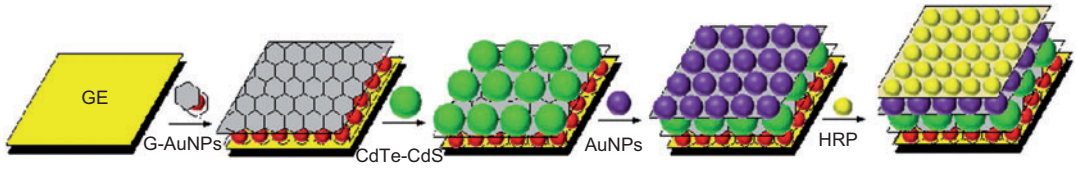

Figure 2 Preparation procedure of GR-AuNPs/CdTe-CdS/AuNPs/HRP sensor.

surface architecture, were used to immobilize the HRP and facilitate electron transfer between the HRP and CdTe-CdS. During oxidation in the redox reaction carried out on the surface of the modified electrode, the AuNPs act as the "donor" of the electron and rapidly pushes the electron toward the CdTe-CdS. Consequently, the CdTe-CdS acts as the "acceptor" of the electron and pulls the electron toward the CdTe-CdS. The push and pull activities will accelerate the electron transfer between the AuNPs and CdTe-CdS, as well as the hole transfer in the CdTe-CdS. Third, GR-AuNP, located inside the surface architecture, will enhance the electron transport between GR-AuNP and CdTe-CdS and suppresses the recombination of the electron-hole pair in the CdTe-CdS due to the large specific electronic conjugate system. During oxidation in the redox reaction carried out on the surface of the modified electrode, the GR-AuNP acts as the "acceptor" of the electron and rapidly pulls the electron toward the GR-AuNP. Consequently, CdTe-CdS acts as the "donor" of the electron and pushes the electron toward the GR-AuNP. The push and pull activities will accelerate the electron transfer between GR-AuNP and CdTe-CdS, and the hole transfer in the CdTe-CdS. In conclusion, the combination of the above three factors brings an electrocatalytic synergy toward hydrogen peroxide (Gu et al. 2011b). To further improve the conductivity between GR sheets, some researchers attempted to introduce conductive polymer into graphene sheets (Al-Mashat et al. 2010, Wang et al. 2010a, Liu et al. 2011a, Mao et al. 2011a). For example, Laith Al-Mashat and coworkers synthesized a GR/polyaniline (PANI) nanocomposite (shown in Figure 3) for its application in the development of a hydrogen gas sensor. The result showed that the GR/PANI nanocomposite-based gas sensor sensitivity is 16.57% toward 1% of H_2 gas, which is larger than the sensitivities of the sensors based on only PANI nanofibers (9.38%) and much larger than that of only GR (0.83%) (Al-Mashat et al. 2010). Moreover, some functional reagents were also used for fabrication of GR composites. For example, Dong and coworkers designed and synthesized an ionic liquid (IL)/GR hybrid nanosheets (GNs) as an enhanced material for electrochemical determination of trinitrotoluene (TNT). The results demonstrated a one-pot wet-chemical strategy for the preparation of IL-GNs. The resulting IL-GNs were used as an advanced electrode material. This material has been proven to be an excellent electron-transfer element for the electrocatalytic reduction of TNT. The simply fabricated IL-GN-based electrochemical detection platform showed superior electrochemical performance for the determination of TNT relative to those of IL-carbon nanotubes (CNTs) and bare glassy carbon electrode (GCE). With a detection limit of 4 ppb or better (1.5 ppb), the proposed system is useful for the analysis of ultratrace TNT in real water samples (Guo et al. 2011a).

Synthesis of graphene-based sensing film

GR-metal nanocomposite has become a hot research topic in materials science because the hybridization can be an effective strategy to enhance the functionality of materials, and the integration of nanomaterials on GR sheets potentially paves a new way to enhance their electronic, chemical, and electrochemical properties. It has typically been prepared by chemical (Kou et al. 2011, Zhang et al. 2011d), thermal (Jin et al. 2010, Zhang et al. 2011e), microwave (Li et al. 2010, Kundu et al. 2011), solvothermal (Wang et al. 2009c, Zhou et al. 2011c) reduction of mixtures of graphene oxide (GO) and metallic precursors. A typical procedure was stated in the following with synthesis of GR-AuNPs: the GO was dispersed in water with ultrasonication. After the dispersed solution was sonicated for several hours until it became translucent with no visible particulate matter, $HAuCl_4$ solution was added to the solution. When the solution was heated to 100°C, tri-sodium citrate and $NaBH_4$ solution were added into the solution under stirring. After continuously stirring for 1 h at 100°C, the

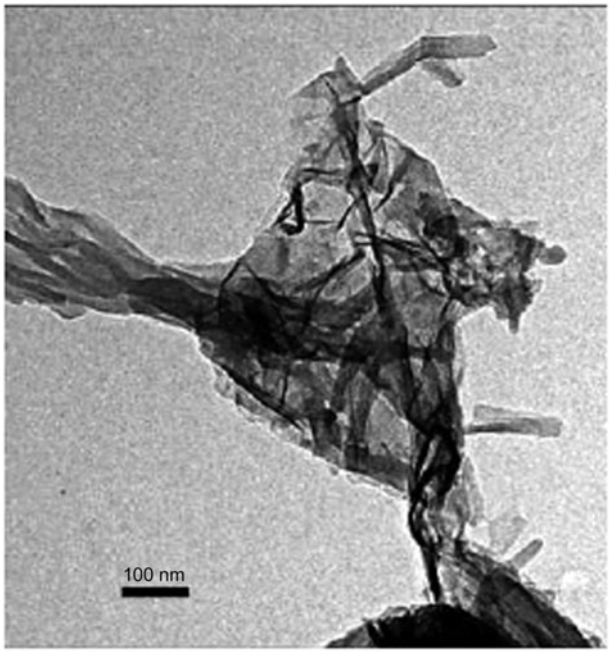

Figure 3 TEM image of a GR/PANI nanocomposite.

resulting GR-AuNP was collected by centrifugation, washed with water three times, and dried in a vacuum drier for 24 h. These methods involve highly toxic chemicals, such as hydrazine hydrate, or high temperature, microwave, and moreover, multiple steps are required that are time or labor consuming.

The electrochemical reduction of GO is attractive for GR-film synthesis due to its simple, fast, and green nature. Typically, GO was coated on the surface of the electrode, and the electrode was then immersed in a metallic precursor solution to perform one-step coelectrochemical reduction. For example, Wang and coworkers reported a facile approach to the synthesis of highly electroactive Pt nanoparticles on GR. In their study, researchers attempted two new methods for preparation of the GR/Pt nanoparticles (shown in Figure 4). After carefully discriminating the products from the morphology and dispersion of the deposited nanoparticles, the one-step electrochemical reduction for the fabrication of Pt NPs at G/GCE has been selected for methanol electrocatalysis. The resultant Pt NPs at G/GCE shows much higher catalytic activity and long-term stability toward the electrooxidation of methanol than the Pt NPs on Vulcan, demonstrating that GR is a much better catalyst support. The present approach can be extended to the preparation of other noble metals and their alloy nanoparticles on GR for electrocatalysis or electrochemical sensors (Zhou et al. 2010b). However, the method for GR synthesis lacks control over the film thickness, and more notably, the resulting GR sheets are not separated by metal particles as they are mostly located on the surface of GR films. To resolve the problem, Luo and coworkers reported a novel strategy for the synthesis of the GR-gold composite film using coelectrodeposition technique. The following is the general procedure: The synthesized graphite oxide powder was exfoliated in electrolytes by ultrasonication for 30 min to form homogeneous GO dispersions with a concentration of 1.0 mg/ml. For electrodeposition synthesis of GR/gold composite, a dispersion containing 1.0 mg/ml GO and 100 μM tetrachloroauric acid was prepared. The cyclic voltammetric reduction was performed in the deposition solutions with magnetic stirring and N_2 bubbling on electrochemical workstation using a three-electrode system: a GCE as the working electrode, Pt foil as the counter electrode, and an SCE as the reference electrode. The scan was performed between -1.5 and 0.6 V at a rate of 25 mV/s, and the loading amount of deposits was controlled by five potential cycles. After deposition, the working electrode was washed with double-distilled water. Because GR layers were spaced by layers of gold nanoparticles, the conductivity and surface area of the GR-gold composite improved compared to the pure GR film (Liu et al. 2011b). However, we observed that the redox reaction between $HAuCl_4$ and GO brings serious agglomerations of GO sheets and gold nanoparticles in the electrolyte solution (shown in Figure 5). As a result, the GR-metal composite film displays very poor dispersivity. Recently, we develop a green and highly controllable strategy to fabricate a GR-metal nanocomposite film. The strategy allows single-layer GR nanosheet and gold particles to be alternately electrodeposited on the surface of a glass carbon electrode. The investigation demonstrated that the thicknesses of GR and metal layers as well as the size and densities of metal nanoparticles can be well predetermined by controlling concentrations of GO and metallic precursor. Owing to good dispersivity, the as-prepared film shows better electrocatalysis activity toward hydroquinone (HQ) and resorcinol (RS) than that of other technologies in literatures. The method is very simple, green, and repeatable, and it can be widely applied to design a GR-metal composite film to meet the special requirement for different applications such as sensing.

Immobilization of enzyme/antibody on the electrode

Immobilization of enzyme or antibody on the electrode is very important to improve the electrochemical properties and use of the biosensor. At present, an enzyme/antibody was immobilized on the GR-based electrode by physical adsorption. However, the method results in poor analytical characteristics in precision and repeativity due to the loss of enzyme/antibody. To overcome the problem, Liu and coworkers reported a covalent method for immobilization of enzyme on the electrode, in which a highly efficient enzyme electrode can be directly obtained using covalent attachment between carboxyl acid groups of GO sheets and amines of glucose oxidase (shown in Figure 6). The results demonstrate that the

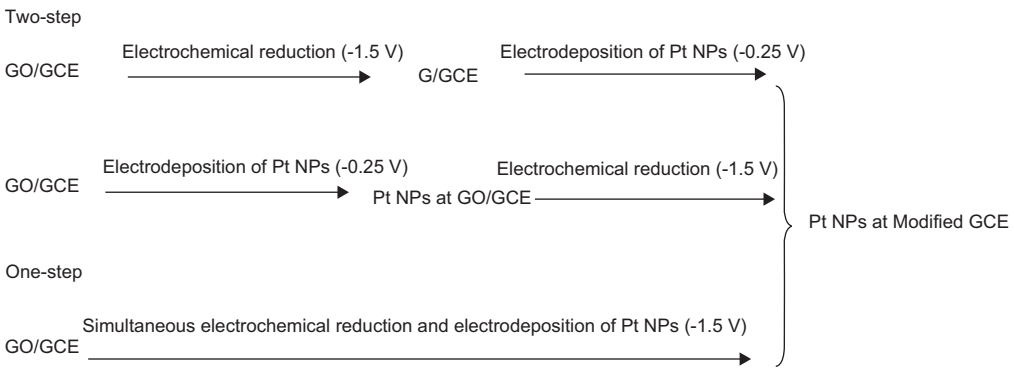

Figure 4 Synthesis of GR/Au composites with electrochemical method.

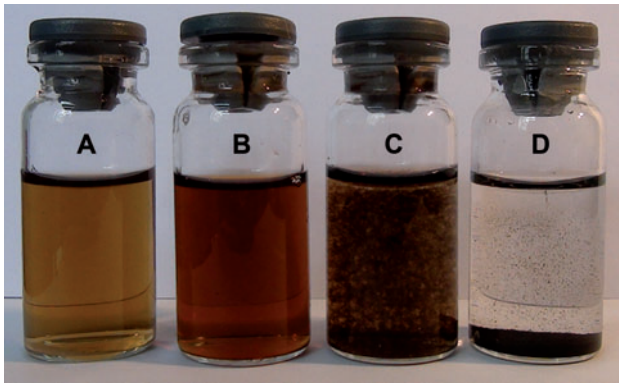

Figure 5 Dispersivity of GO in the aqueous solution after adding $HAuCl_4$ for 1 min (A), 1 h (B), 12 h (C), and 24 h (D).

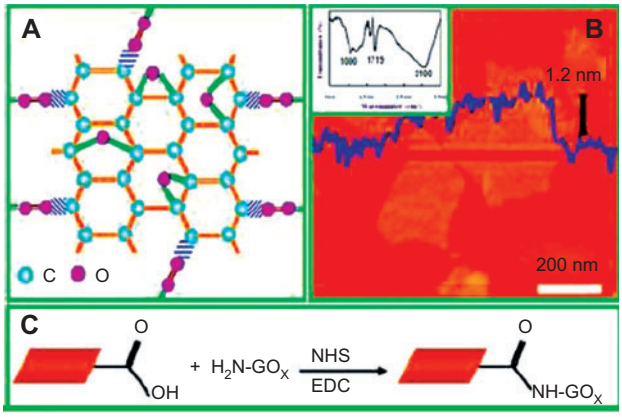

Figure 6 Schematic representation of the molecular structure of a GO sheet (A), AFM micrograph of the GO sheets (B), and schematic immobilization of GOx into GO sheets via peptide bonds between the amine groups of GOx and the carboxylic acid of GO (B, inset FTIP spectrum of GO).

covalently linked glucose oxidase (GOx)-GO enzyme electrode shows broad linearity, excellent reproducibility, and storage stability, suggesting GO to be a highly efficient biosensor electrode (Liu et al. 2010j). However, the GO-based biosensor has commonly a lower sensitivity than that of the GR-based biosensor due to its poor electron conductivity. To further improve the immobilization of the enzyme, we developed a new covalent method for immobilization of the enzyme, in which graphite oxide and chlorauric acid was electrodeposited in sequence on the surface of gold electrodes with potentiostatic electrolysis. After the above procedure was repeated for 20 cycles, 2,5-di-(2-thienyl)-1-pyrrole-1-(*p*-benzoic acid) was electropolymerized on the modified electrode by cyclic voltammetry (CV) and finally formed functional conducting polymer film containing carbonyl groups on the surface of the GR-AuNP. To prepare the hydrogen peroxide biosensor, the HRP was subsequently connected covalently to the film with DHC/NHS as activator (shown in Figure 7). Research results indicated that the GR-AuNP obtained by the electrodeposition method has excellent dispersivity, which offers remarkable catalysis performance to the redox of hydrogen peroxide on the electrode surface. Current response of the sensor increases linearly with the increasing concentration of hydrogen peroxide over the range from 2 nM to 200 nM, with a correlation coefficient (R^2) of 0.9996. The detection limit was found to be 0.67 nM (S/N=3). The sensitivity is more than that of the other sensors reported in the literatures. In addition, covalent immobilization of the enzymes results in increasing the stability and reproducibility of the sensor. The relative standard deviation is 1.2% for the determination of 5 nM hydrogen peroxide that was done 20 times. After the sensor was stored at 4°C for 3 months, its change value of the response is lower than 3%. The proposed method has been successfully applied to detect trace hydrogen peroxide in milk sample.

Application of graphene-based materials in analytical chemistry

GR and its composites as sensing materials have attracted tremendous attention and research interest. Many novel GR materials have well been designed, synthesized, and widely applied to fabricate various sensors, including chemical sensor, biosensor, immunosensor, and others (shown in Table 1). As the hybridization can be an effective strategy to enhance the functionality of materials, the integration of nanomaterials on GR potentially paves a new way to enhance their electronic, chemical, and electrochemical properties. Therefore, GR composites as novel sensing materials commonly offer better analytical characteristics than GR alone. Up to now, GR-based materials have increasingly become one of the most important tools in the fabrication of various sensors in

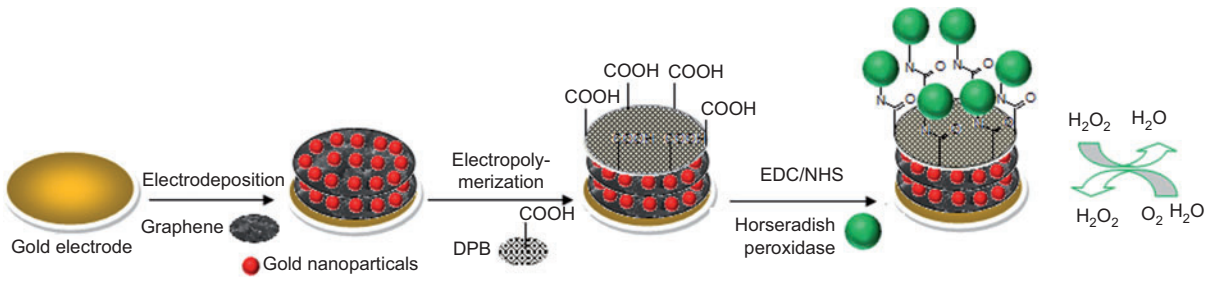

Figure 7 Procedure for preparation of the sensor.

Table 1 Application of GR and its nanocomposite as sensing material in sensors.

Sensing materials	Analyte	Detection limit	Remark	Reference
GO	Glutathione	8.3 μM	GO amplified electrogenerate chemiluminescence of QD platform and its efficient selective sensing for antioxidants, leading to an about 5-fold amplification	Wang et al. 2009a
GO	Rabbit IgG	0.67 nM	GO covalently conjugate protein molecules	Roy et al. 2011
GO/Ag	Bacteria		Combined GO sheet-mediated Ag enhancement and signal amplification of silver staining to allow the analysis and capture of bacteria	Wan et al. 2011a
GO	Humidity		GO thin film-coated quartz crystal microbalance exhibits an excellent humidity-sensing performance	Yao et al. 2011
GO	H_2O_2		GO supports efficient electrical wiring of the redox centers of heme-containing metalloproteins to the electrode. Proteins retain their structural intactness and biological activity upon forming mixtures with GO	Zuo et al. 2010
GR	Single nucleotide polymorphism of a DNA strand	82 pM	A sensitive GR platform for the detection of DNA hybridization and polymorphism. It was found that the three- and four-layer GR provided the best sensitivity	Bonanni and Pumera 2011
GR/PANI	H_2		The GR/PANI nanocomposite-based gas sensor sensitivity is 16.57% toward 1% of H_2 gas	Al-Mashat et al. 2010
GR-Prussian blue (PB)/Au	Carcino-embryonic antigen	3 pg/ml	The GR-PB/gold nanoparticles can be used not only as an electrochemical redox mediator but also as an enhancer of sensitivity	Wang et al. 2011a
GR/SnO_2	Propanal	0.3 mg/ml	The key to this method is the *in situ* formation of SnO_2 nanocrystals and GR sheets simultaneously, stacking of GR sheets, and prevention of the agglomeration of SnO_2 nanoparticles	Song et al. 2011
GR/polydiallyldimethylammonium chloride) (PDDA)/Au	Human IgG	0.05 ng/ml	PDDA-GR was successfully prepared by a simple synthetic method and decorated with Au nanoparticles. The obtained AuNPs/PDDA-GR hybrid architecture could be an ideal substrate for antibody immobilization with good stability and bioactivity	Liu et al. 2011a
GR	Bacteria and their metabolic activities	10 cfu/ml	A fast, label-free, highly sensitive, and selective GR-based biosensor was developed for detection of bacteria *Escherichia coli*	Huang et al. 2011a
GR-based conducting inks			A simple and practical inkjet printing method for fabricating electrically conductive and flexible patterns has been demonstrated using GR inks	Huang et al. 2011b
GR	Pathogenic virus		A free-standing GR film generated by simple centrifugal vacuum evaporation shows densely packed GR sheets with uniform ripple structure on the surface and displays high conductivity and rapid electron transfer property to be applied for a working electrode in electrochemical CV	Liu et al. 2011b
GR	2,4,6-TNT	1.0 μg/ml	About 20% higher accumulation ratios on few-layered GR than on graphite microparticles when we applied electrochemical preconcentration procedure. However, graphite exhibits higher sensitivity	Goh and Pumera 2011
GR/DNAzyme	Pb^{2+}	300 pM	A GR-DNAzyme-based biosensor for fluorescence "turn-on" detection of Pb^{2+} based on the remarkable difference in affinity of GO with ssDNA containing a different number of bases in length was developed. By taking advantage of the super fluorescence quenching efficiency of GO, our proposed sensor exhibits a high sensitivity	Zhao et al. 2011a
GR/PANI (GR-PANI)	4-Aminophenol (4-AP)	65 μM	GR-PANI nanocomposite was prepared and utilized as electrochemical sensing interface for 4-AP. The results indicate that the GR-PANI nanocomposite can provide a favorable microenvironment for the electrochemical reaction of 4-AP, resulting in enhanced voltammetric response	Fan et al. 2011a

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
GR/Pt (GN-Pt)	H_2O_2	0.5 μM	A nonenzymatic H_2O_2 sensor was fabricated based on GN-Pt nanocomposite with high Pt nanoparticle loading. Electrochemical investigation indicated that the GN-Pt-modified electrode exhibited much better catalysis and higher sensitivity for H_2O_2 detection than that based on a single component	Xu et al. 2011
GR-modified EDTA (EDTA-RG)	Dopamine (DA)	0.01 μM	A new type of EDTA chemically modified GR, EDTARG, was synthesized and found that it can be used as an ideal electrode material to fabricate biosensors. A DA electrochemical biosensor with a high selectivity had been made by applying EDTA-RG/Nafion film onto a glass carbon electrode	Hou et al. 2010
GR/Nafion	Pb^{2+} and Cd	0.02 μg/l	The composite film combining the advantages of GR and the cationic exchange capacity of Nafion enhanced the sensitivity for metal ion assays compared with that of Nafion-coated electrodes	Li et al. 2009a
GR/multiwalled carbon nanotubes (MWCNTs)/Pt	H_2		The investigation of the hydrogen-sensing properties of Pt nanoparticles dispersed on hybrid carbon nanostructures consisting of GR nanoplatelets (GNPs) interspersed with MWCNTs and the effect of hydrogen concentration, temperature, and morphology suggests that Nafion-solubilized Pt/f-GNPs:f-MWCNTs (1:1) gives the best hydrogen-sensing response	Kaniyoor and Ramaprabhu 2011
GR	H_2		Epitaxial GR deposited by chemical vapor deposition on SiC was coated with platinum to detect hydrogen gas. I–V comparisons showed that platinum acted as a dopant and increased the conductance of GR. Gas testing results showed that exposure to hydrogen decreased the resistance of the GR/Pt, and three activation energies were observed depending on the temperature range. Real-time measurement of the sensor suggests that it has robust and repeatable response to hydrogen	Chu et al. 2011
GR/Pt	H_2		The nanocomposite was prepared via layer-by-layer deposition. This technique can be easily automated and scaled up for the deposition of large quantities of sensor materials. It is shown that this material is electrocatalytically active and can be used to detect hydrogen	Lange et al. 2011
GR	Bacteria		Low-cost, versatile, and robust reduced graphene sheets (RGS)-doped impedimetric immunosensors combined with controllable electrodeposition was fabricated for sulphate-reducing bacteria (SRB) detection. The proposed sensor for SRB detection shows good fabrication reproducibility and measurement precision	Wan et al. 2011b
GR/ionic liquid (IL-GNs)	TNT	4 ng/ml	This material has been proven to be an excellent electron-transfer element for the electro-catalytic reduction of TNT. The simply fabricated IL-GN-based electrochemical detection platform showed superior electrochemical performance for the determination of TNT relative to those of IL-CNTs and bare GCE	Guo et al. 2011a
GR/Nafion/Pd	Glucose	1 μM	The present work demonstrates that a nonenzymatic glucose sensor can be designed with PdNPs *in situ* formed within Nafion-GR film assembled on GC electrode. The PdNPs are confined in the Nafion-GR film. The sensor shows high electrocatalytic ability to glucose oxidation in alkaline solution and exhibits good linear dependence and selectivity to glucose concentration change	Lu et al. 2011a
GR/aptamer	Immunoglobulin E	4.7 nM	The aptamer-modified graphene field-effect transistor (GR-FET) electrically detected IgE protein, whereas other proteins were not detected; these findings indicate that nonspecific binding of nontarget proteins was successfully suppressed. The dissociation constant was estimated to be 47 nM on the basis of the IgE concentration dependence. These results clearly show that GR-FETs are promising devices for use as label-free biological sensors that can electrically detect biomolecules	Ohno et al. 2010

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
GR/cobalt hexacyanoferrate nanoparticles (CoNP)	Prostate-specific antigen	0.01 ng/ml	CoNP was prepared, and in combination with GS, the electroactivity of CoNP was greatly improved due to the synergistic effect. Molecule 1-pyrenebutanoic acid, succinimidyl ester (PBSE) was selected and adsorbed onto GS through *p-p* stacking, which was then used for the conjugation of anti-PSA antibody. The GS-CoNP-PBSE composite film displayed high electroactivity and good stability	Li et al. 2011a
GR/DNAzyme	Cu^{2+}	2.0 nM	Owing to the catalytic activity of Cu(II)-dependent DNAzymes and the binding activity of fluorophore, the novel GR-quenched DNAzymes catalytic beacon not only provided a convenient protocol but also improved the sensitivity in comparison with the reported DNAzyme-based catalytic beacon	Liu et al. 2011c
GR	DNA	10^{-13} M	The results of XPS, Raman spectroscopy, and EIS confirmed that the probe DNA was successfully anchored and then hybridized with target DNA on the surface of reduced graphene oxide (rGO). Compared with the bare GCE, the presence of rGO favors anchoring to both ssDNA and dsDNA, which provides the stable response of impedance	Wang et al. 2011b
Cationic polyelectrolyte-functionalized IL-decorated GR sheets (PFIL-GS)	H_2O_2	1.0 μM	Upon injecting H_2O_2 into the reaction cell, optical surface plasmon resonance (SPR) signals and electrochemical current responses were simultaneously monitored in real time. This simultaneous detection method can provide dual information to improve the reliability of the test results, which may offer a new outlook of sensor preparations	Mao et al. 2011a
GR/Pt-Au or Au	Glucose	1.0 μM	The addition of nanocrystalline (Pt-Au) or (Au) metal nanoparticles act as spacers and eliminates the restacking of f-GR, which has resulted in the increase in the electroactive surface area of the electrode, thereby decreasing the overpotential in the detection of H_2O_2 and enhances glucose-sensing performance	Baby et al. 2010
GR/DNAzyme/metal ion	Pb^{2+}		The extremely high sensitivity of this sensor allows it to readily detect Pb^{2+} at room temperature. GO is highly amenable for large-scale fabrication, providing a cost-effective approach to metal ion detection. The planar structure of GR allows it to adsorb multiple kinds of DNA probes	Wen et al. 2011
Ag/GO	H_2O_2	1.9 μM	A new method for effective immobilization of Ag nanoparticle (AgNP)-decorated GO (AgNP/GO) composites onto thiolated single-stranded DNA-decorated Au electrode (AuE) surface was developed. The novel immobilization method is based on the coordination interactions and p-p stacking interactions between DNA bases and AgNP/GO composites	Lu et al. 2011b
GO nanoribbons (NRs)	Ascorbic acid (AA), DA, and uric acid (UA)	0.06 μM for AA, 0.08 μM for DA, and 0.15 μM for UA	A unique microwave-assisted unzipping process has been reported for the synthesis of graphene oxide nanoribbons (GONRs). The reaction time of this microwave process was very short compared with that reported in the literature. The power-dependent GONR structures created from the unzipping of MWCNTs were characterized and used for the detection of AA, DA, and UA	Sun et al. 2011a
GR/DNAzyme	Cu^{2+}	0.365 nM	Owing to the intrinsic advantage of 2D GR and the catalytic activity of Cu^{2+}-dependent DNAzyme, the novel catalytic beacon not only provided convenient protocol but also effectively increased the sensitivity in environmental monitoring	Liu et al. 2011d
GR/PB/CS	DNA	0.0158 nM	GR, used as the carbon paste material for the electrode instead of graphite, can greatly improve the sensitivity of the biosensor. The presence of a PB layer on the surface of the GPE showed good electrochemical properties; the CS film protected the stability of the PB film significantly. The established DNA biosensor with high selectivity can discriminate completely complementary target sequence, three-base-mismatched sequence and noncomplementary target sequence	Bo et al. 2011a

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
GR/tyrosinase	Organophosphorus	0.2, 0.8 and 3 ng/ml for chlorpyrifos, profenofos, and malathion	The tyrosinase could be successfully immobilized on the electrode by the electrostatic interaction between cysteamine and enzyme. Besides integrating the unique properties of GR and platinum nanoparticles, the prepared biosensor showed high sensitivity to o-quinone reduction and was further successfully applied to determine organophosphorus pesticides based on the inhibition of tyrosinase activity to catalyze catechol (CC)	Liu et al. 2011e
GR/aptasensor	Cancer cells		The constructed GR surface does not show cytotoxicity under our experimental conditions. When AS1411 form GR-quadruplex and has high binding affinity and specificity to the overexpressed nucleolin on the cancer cell surface compared with normal cells, our designed electrochemical aptasensor has the ability to differentiate cancer cells and normal ones	Feng et al. 2011a
GO	DA		The multiple noncovalent interactions between GO and DA resulted in effective self-assembly of DA on the surface of GO and significant fluorescence quenching, allowing to develop a simple label-free photoinduced charge transfer (PCT)-based NIR fluorescence biosensor for selective and sensitive detection of DA in biological fluids	Chen et al. 2011e
GO/peptide	Metalloproteinase		This is the first study to confirm the feasibility of the GO-peptide-based fluorescence sensors in the detection of MMP2 in real biosystems and to reveal the level of MMP2 secreted by HeLa cells quantitatively. Moreover, the fluorescence sensor may have great potential for monitoring MMP2 levels of cancer patients, and the present strategy may be used to develop the GO-peptide based fluorescence sensors for the detection of other proteases and even the screening of protease inhibitors	Feng et al. 2011b
GR/Au^{3+}	*p*-nitro-phenol	1.25 ng/ml	The highlights of this study are to combine the catalytic properties of gold nanocatalysts with recycling of p-aminophenol (PAP) to p-quinone imine (PQI), and avoid the use of two working electrodes or multiple enzymes	Liu et al. 2011f
GR	Paracetamol	0.32 nM	Owing to the unique properties of GR, including subtle electronic characteristics, good π-π interaction, and strong adsorptive ability, the GR-modified GCE obviously promotes the sensitivity of the determination of paracetamol with a low detection limit	Kang et al. 2010
GR/Nafion	Caffeine	0.12 μM	Owing to the unique properties of GR, including subtle electronic characteristics and strong adsorptive ability, and the enrichment effect of Nafion, the Nafion-GR/GCE obviously promotes the sensitivity of the determination of caffeine with a low detection limit.	Sun et al. 2011b
GR/oligomer	Lectin, *E. coli*		Integration of GO can almost completely quench the fluorescence of (4,7-bis(9,9-bis(2-(2-(2-(2,3,4,5,6-pentahydroxyhexanal)-ethoxy)ethyl)fluorenyl)benzothiadiazole (FBT) as a result of π-π interaction between GO and FBT. Such interactions can be inhibited by specific protein-carbohydrate interaction between FBT and concanavalin A (ConA), and the quenched fl prescence of GO/FBT is greatly recovered in the presence of ConA	Wang et al. 2011c
GR/Al_2O_3	Ethanol		The as-prepared nanocomposite displays high chemiluminescence (CL) sensitivity and high selectivity to the ethanol gas, which provides a facile, green, and low-cost route for the preparation of ethanol nanoscopic-sensing devices with applications in safe protection, food fermentation, medical processes, and traffic safety. The method can be easily expanded to the fabrication of other GR-based functional nanocomposites	Jiang et al. 2011a

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
GR/DNA	Hemin	50 nM	A label-free DNA rGO-based fluorescent sensor for detection of hemin is introduced. rGO can effectively quench the fluorescence of acridine orange (AO) and form the AO-rGO, but the complex is easily destroyed and the fluorescence intensity of AO increases significantly by a GR-quadruplex structure aptamer	Shi et al. 2011
GR/Ag	H_2O_2	31.3 μM	The detection of H_2O_2 without using an enzyme in the electrode modified by AgNP/rGO hybrids has also been demonstrated, and it is revealed that the AgNPs show excellent notable catalytic activity for the reduction of H_2O_2. Our present findings provide us a low-cost approach to the production of stable aqueous dispersions of rGO and nanoparticle/rGO hybrids on a large scale for applications	Liu et al. 2011g
GR/PANI	DNA	3.25×10^{-13} M	The results indicate that the GR and PANI can provide favorable environment and promote the direct electron transfer at the electrode surface. The ssDNA/PANI GR/GCE showed high selectivity and sensitivity toward complementary DNA sequence	Bo et al. 2011b
GR/poly(sodium styrenesulfonate) (PSS)	Hydrazine	1.0 μM	The morphology of PSS-GR was characterized by SEM, and the electrocatalysis ability to hydrazine was also studied by CV and aperometric analysis	Wang et al. 2010a
GR	H_2O_2	1.7×10^{-6} M	The as-prepared GR was combined with CS, Au, and HRP to construct a H_2O_2 biosensor. Cyclic voltammograms showed that the biosensor realized the direct electron transfer between HRP and the electrode and exhibited the typical catalytic reduction of H_2O_2	Zhou et al. 2010a
GR/Nafion/methylene/Au	Carcinoembryonic antigen	0.17 ng/ml	This methodology has several attractive advantages, such as lack of need for redox agent in working cell, high stability of AuNP monolayer formed, easy adsorptive immobilization of antibody on AuNPs monolayer, efficient activity retention of loading immunoreactants as well as the simplicity of use and cost effectiveness	Li et al. 2011b
GR	CC and HQ	1×10^{-6}~ 5×10^{-5} M	A well-defined peak and the significant increase of peak current were observed at the GR/GCE, which clearly demonstrated that GR could be used as an efficient promoter to enhance the kinetics of the electrochemical process of HQ and CC. The well-distinguished two anodic peaks of HQ and CC at the GR/GCE showed that the simultaneous determination of them was possible	Du et al. 2011a
GR/QDs	Choline and acetylcholine	8.8 μM for choline and 4.7 μM for acetylcholine	The reduction process efficiently restored the backbone structure of GR, enhanced the electronic conjugation in GR sheets, and produced new graphitic domains with smaller size, which led to high electronic conductivity and strong adsorption of O_2 on electrochemically reduced graphene oxide (ERGO). Thus, ERGO could greatly enhance the ECL emission of QDs when using O_2 as the coreactant. The amplified ECL of QDs/ERGO could be used to construct sensitive biosensors based on the consumption of dissolved O_2 in enzymatic reaction	Deng et al. 2011
GR	CO, O_2, NO_2, and H_2O		GR shows weak sensitivity to the CO and H_2O molecules, while the electronic properties of PG are sensitive to the adsorption of O_2 and NO_2 molecules. Compared with PG, SiG has a higher chemical reactivity toward the gas molecules due to the doping of Si atom and shows the higher adsorption energy with CO, O_2, NO_2, and H_2O	Zou et al. 2011
GR/polyoxometalate (PRG-POM)	HQ, CC, and RS	40 nM for CT, 50 nM for HQ and 90 nM for RS	The electrochemical performance of such PRG-POMs has been demonstrated to be much higher than that of PRG, CNTs, and bare GCE, which was attributed to the high electrochemical conductivity and the enhanced catalytic activity of the PRG-POMs	Cao et al. 2011a

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
GR	Glucose	5 μM	Experimental results suggested that the displacement-based QCM glucose sensor could exhibit high sensitivity, good reproducibility and selectivity. The highlight of this study is to replace the detection of small molecules from the determination of macromolecule	Tang et al. 2011a
GR/Au	Methyl parathion (MP)	0.6 ng/ml	The as-prepared composite matrix, combining the advantages of GR nanosheets together with AuNPs, greatly facilitated the preconcentration of MP onto the surface with the stripping current response greatly enhanced. The resulting biosensor showed both good reproducibility and ideal stability	Gong et al. 2011
GR/mesoporous silica/Au	DNA	6.6 pM	The as-prepared GSGHs could be used as an advanced building block to construct new functional interface with tunable thickness, which could be used as sensitive electrochemical-sensing platform for the detection of DNA hybridization and SNPs. Most importantly, we demonstrated the use of triplex DNA system for amplifying the detection of DNA on the integrated functional interface *via* combining the strand-displacement DNA polymerization reaction	Du et al. 2011b
GR/polyethylene terephthalate	Prostate		The flexible cancer sensor based on layer-by-layer self-assembled GR reported in this letter demonstrates features including ultrahigh sensitivity and low cost due to GR material properties in nature, self-assembly technique, and polyethylene terephthalate substrate. According to the conductance change of self-assembled GR, the label free and labeled GR sensors are capable of detecting very low concentrations of prostate-specific antigen	Zhang and Cui 2011
GR-AuNP/CdTe-CdS/Au(AuNP)	Glucose	3×10^{-12} M	CdTe-CdS core-shell QD was utilized as ultrafast electron transfer relay for improving electron transfer between the electrode and aqueous phase. The relay creates a promising electrocatalytic synergy of GR-AuNP, CdTe-CdS, and AuNP toward glucose sensing. Moreover, AuNP-CS film offers a favorable microenvironment to keep the bioactivity of GOx	Gu et al. 2011a
GR/Ag	H_2O_2	7.1 μM	The noncovalent functionalization of GO by aniline leads to a GO dispersion that can be very stable for several months without the observation of any floating or precipitated particles.	Liu et al. 2011h
GR/cetyltrimethylammonium bromide (GR-CTMAB)	Caffeine	91 nM	The developed sensor shows an excellent electrocatalytic activity toward the oxidation of caffeine. The CTAB-GR/GCE obviously improves the sensitivity of the electrode toward caffeine and has a low detection limit. The results were attributed to the specific characteristics of GR	Sun et al. 2011c
GR/cyclodextrin (CD-GR)	MP	0.05 ng/ml	The introduction of CD in the GR matrix significantly reduced the aggregation of GR and effectively maintained its effective surface area. The large delocalized π-electron system of GR could form strong π-π stacking interaction with the aromatic ring in the MP, facilitating the strong binding of MP on its surface	Wu et al. 2011
GO	Glucose	0–28 mM	The covalently linked GOx-GO enzyme electrode shows broad linearity, good sensitivity, excellent reproducibility, and storage stability, suggesting GO to be a highly efficient biosensor electrode. The direct utilization of the functional groups of GO sheets opens up possibilities for the direct preparation of novel practical enzyme electrodes from GO for a wide range of applications, such as electrochemistry, biology, and biofuel cells	Liu et al. 2010a
GR	Ethanol	20 μM	The electrochemical activity of GR/GC electrode was investigated with electroactive molecules, which show a remarkable increase in the rate of electron transfer compared with graphite/GC and bare GC electrodes. Furthermore, on the basis of well electrocatalytic activity at the GR/GC electrode toward NADH, ADH was immobilized on the GR/GC electrode to show faster and selective response with wider linear range and lower detection limit	Guo et al. 2011b

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
GO/oligo-electrolyte	Heparin	0.046 U/ml	Efficient fluorescence quenching of TFP by GO occurs due to the electrostatic and π-π interactions, featuring a quenching constant of 0.61 mg/l. Although TFP itself is unable to effectively differentiate Hep from its analogs, integration of GO into the TFP assay can substantially reduce the background signal, ultimately allowing for light-up visual detection of Hep. This improvement stems from the interaction-mediated fluorescence quenching of TFP by GO in the presence of analytes, which favors high fluorescence for Hep relative to that for ChS and HA	Cai et al. 2011
GR	CO_2		The GR sensor shows significant conductance changes when exposed to various concentrations of CO_2 in air. The response time of the sensor is less than 10 s, suggesting that the device shows fast response to CO_2 gas. Because of the weak interaction between CO_2 and GR, the device response is rapid and reproducible	Yoon et al. 2011
GR/Au	β-NADH	1.2 μM	We used the natural polymer CS to assist the stabilization of GR in aqueous solution and immobilize the electronegative Au nanoparticles through electrostatic attraction. The synergy of Au with GR for catalytic oxidation of NADH made the overpotential ca. 220 mV less positive than that on the bare electrode and remarkably increased the oxidation current	Chang et al. 2011
Cyclodextrin/GR (CD-GNs)	Carbendazim	2 nM	The high sensitivity and improved detection limit of the CD-GNs/GCE are promising for the determination of trace amounts of carbendazim in water sample. Furthermore, this simple sensing platform in principle can be extended to the detection of other benzimidazole fungicide, which can form host-guest complexes	Guo et al. 2011c
GR/Pt	Cholesterol	10.2 μM	Cholesterol oxidase and cholesterol esterase were immobilized on the Pt nanoparticles-decorated GR for the development of an amperometric cholesterol biosensor. The biosensor linearly responds to cholesterol and cholesterol ester for a wide linear range and is highly sensitive. This sensor can detect cholesterol ester at the submicromolar level	Dey and Raj 2010
GR/IL (ER-GNO/IL)	Glucose	1.0 μM	With the high density of edge-plane-like defective sites on ER-GNO, the developed ER-GNO/ the ionic liquid doped screen-printed electrode (IL-SPE) possessed very excellent electrocatalytic activity toward biomolecules NADH and H_2O_2. The substantial decrease in the overpotential of H_2O_2 reduction at the ER-GNO/ILSPE promotes the glucose oxidase (GOD) and ER-GNO-constructed bioelectrode to amperometric biosensor for glucose sensing	Ping et al. 2011
GR/3-aminopropyltriethoxysilane (GO/APTES)	Glucose		The reduced GO adsorbed on glassy carbon electrode was modified with GOx by covalent bonding *via* a polymer generated by electrografting *N*-succinimidyl acrylate. The direct electron transfer between the electrode and GOx molecules was realized. The bioactivity of GOx maintains very well on the electrode.	Wang et al. 2009b
TiO_2/GR/IL	H_2O_2	0.3 μM	Chit-[bmim]PF_6-TiO_2-GR nanocomposite film showed a suitable biocompatible microenvironment for Hb. The catalytic properties proved that the Hb has been kept in its natural structure and can retain its biological activity	Sun et al. 2011d
GR/Au	H_2O_2	50 nM	Au/GR-NH_2 composite film retained the activity of the immobilized Cat and facilitated the direct electron exchange between Cat and electrode. The H_2O_2 biosensor based on the fast direct electron transfer of the Cat immobilized in Au/GR-NH_2 matrix exhibited the characteristics such as wide linear detection range, acceptable reproducibility, high sensitivity, long-term stability, and much lower detection limit	Huang et al. 2011c

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
GR/polyvinylpyrrolidone	H_2O_2		Because of their good electronic properties and biocompatibility, GR-based composites achieved the direct electron transfer of redox enzyme and maintained its bioactivity well	Shan et al. 2009
GR	Glucose	10 μM	This study has not only established a general route for fabricating GR-based hybrid *via* assembling enzymes/proteins on GR but also expanded the scope of GR applications to the field of bioelectroanalytical chemistry, which may open up a new challenge and approach to explore the electrochemical features of GR or its hybrid materials for the potential utilizations	Wu et al. 2010a
GR	H_2O_2	0.11 μM	HRP has immobilized stably on the GC electrode by Nafion/GR film, and the direct electrochemistry of HRP was realized. Furthermore, the HRP in the film is not denatured and retains the bioelectrocatalytic activity for the reduction of H_2O_2 even at the very low H_2O_2 level. Those results demonstrate that the Nafion/GR film could provide a favorable microenvironment for the enzyme and promote the direct electron transfer at the electrode surface	Li et al. 2011d
GR	NADH	1.9 μM	The electrochemical detection of NADH is of considerable interest because it is required as a cofactor in a large number of dehydrogenase-based biosensors. However, the presence of oxygenated functionalities on the electrode often causes fouling due to the adsorption of the oxidized form, NAD^+. Here, we report an electroanalytical NADH sensor based on DMF-exfoliated GR. The latter is shown to have a very low oxygen content, facilitating the exceptionally stable and sensitive detection of this important analyte	Keeley et al. 2011
GR/DNA/Au (AuNPs)	Glucose	0.3 μM	The oxidization of glucose-producing H_2O_2 reduces $[AuC_4]^-$ into Au(0), and then, Au(0) self-assembled with the SH and NH_2 groups of the DNA chain. A novel method of glucose detection was constructed based on the CV response of AuNPs deposited with different concentrations of glucose. The biosensor showed a low determination limit and high sensitivity	Zheng et al. 2011
GR	DNA	1 pM	We have developed a novel strategy for controllable self-assembly of GO using DNA hybridization, which was confirmed thoroughly by AFM, TEM, XRD, and spectra measurements	Tang et al. 2011b
Single wall nanotube/GR	H_2O_2	2 pM	With the synergistic amplifying action produced from hemin/GR-quadruplex system and HRP, the proposed aptasensor exhibited extraordinary electrochemical biocatalysis toward H_2O_2, which largely increased the sensitivity of proposed aptasensor	Yuan et al. 2011
TiO_2/GR (TiO_2-GR)	Paracetamol	2.1×10^{-7} M	The results indicate that the Nafion/TiO_2-GR nanocomposite can provide a favorable interface and microenvironment for the electrochemical reaction of paracetamol. The composite film-modified electrode was successfully employed for the voltammetric determination of paracetamol with low detection limit, wide linear range, and good selectivity	Fan et al. 2011b
GR	AA	7×10^{-8} M	Compared with the bare electrode, the oxidation current of AA increased greatly, and the oxidation peak potential shifted negatively by 110 mV (vs. Ag/AgCl). GR was a good candidate of advanced electrode materials and could be combined with other functional materials to fabricate the sensing interface for more applications in the fields of electroanalysis	Li et al. 2011d

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
GR	O_2, H_2O_2		Chemically converted GR (CCG) sheets are an effective substrate for immobilizing hemin molecules through *p-p* interaction. The introduction of CCG strongly increased the electrochemical stability and electrocatalytic activity of hemin-modified electrode for the reduction reactions of oxygen and hydrogen peroxide. Considering the low cost of CCG and the facile process of synthesis, CCG-hemin composite is a cheap catalyst with high catalyzation performance on oxygen reduction reaction (ORR). It is also an attractive material for fabricating O_2 or H_2O_2 sensor with high sensitivity and durability	Chen et al. 2011a
GR/IL/Nafion	Acrylamide and its metabolite		Based on the changes of guanine signal, DNA damage was directly detected at PGE/GR-IL-Nafion/$(HRP/DNA)_3$. Moreover, our results also indicated that glycidamide could induce more serious DNA damage than AA, which provided further evidence for the mainly carcinogenic activity of glycidamide. More importantly, this method for directly detecting DNA damage, as a simple and quick means, shows great promise for genotoxicity screening of new chemical pollutants and drugs *in vitro*	Qiu et al. 2011
Polypyrrole (PPyox)/GR	DA	0.1 μM	The good electronic conductivity and electrocatalytic activity of immobilized GR combined with the selective feature of PPyox exhibited superior sensitivity and selectivity toward the oxidation of DA in the presence of AA. Furthermore, PPyox could be used as a template to immobilize GR, which made the sensor exhibit good reproducibility and excellent stability.	Zhuang et al. 2011
GR/Fe_3O_4/ferrocene (FC)	Cancer biomarker	2.0 pg/ml	Owing to a great amount of DA molecules anchored onto Fe_3O_4 and the available amino groups on DA, a large number of FC could be easily conjugated onto Fe_3O_4; The large specific surface area of GS increased Ab1 loading, and its good conductivity enhanced the detection sensitivity of FC. The resulting immunosensor possesses high sensitivity, good selectivity and reproducibility. We anticipate that the proposed immunosensor can be applied for the detection of different cancer biomarkers	Li et al. 2011e
Go/Nafion	Colchicine	1.5×10^{-8} M	The composite of GO and Nafion can significantly enhance the oxidation peak current, and the modified electrode exhibited an excellent immunity from epinephrine, DA, and AA interference. Based on this, a simple and sensitive electrochemical method was proposed for detecting colchicine in medicinal tablets	Wang et al. 2011d
GR/MWNT	*p*-nitro-phenol (p-NP)	0.6 μM	The electrochemical oxidation of p-NP at the GR-modified electrode was examined by CV and differential pulse voltammetry and compared to MWNT-modified electrode. It has been shown that the oxidation of p-NP gives rise to an anodic peak at +0.9 V in phosphate buffer pH 7 with a similar behavior at both GR and MWNT electrodes	Arvinte et al. 2011
GO/PB	H_2O_2	1.22×10^{-7} M	The electrochemical and electrocatalytic behaviors of a novel hybrid film modified the electrode, which was successfully prepared by electropolymerizing PB onto the GO-modified glassy carbon electrode. The GO/PB-modified electrode showed higher PB deposition and larger peak current compared to the bare GC electrode. The GO/PB film-modified electrode exhibited high electrocatalytic activities toward the reduction of H_2O_2	Zhang et al. 2011a
Au/GR/DNAzymes	L-histidine	0.1 pM	A sensitive aptasensor for detection of L-histidine based on the switching structure of aptamer and Au nanoparticle-GR nanosheet composite was reported for the first time. The fabricated biosensor shows an expanded linear range, excellent sensitivity and selectivity against other amino acids	Liang et al. 2011

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
GR/congo red-molecular imprinted polymers (GSCR-mips)	DA		Owing to the unique mechanical properties and extremely large area of GSCR, the resulting GSCR-MIP composite possesses fast desorption and adsorption dynamics, high selectivity compared with other analogs, and good sensitivity toward template molecules. The GSCR-MIP-modified electrodes can specially recognize DA	Mao et al. 2011b
GO	CC		A GO-based DNA biosensor was developed for CC monitoring. The unique property of GO leads to a significantly enhanced voltammetric response of DNA sensor without enhancing the background current. Owing to the interaction between DNA and CC, while CC was degraded, the inhibition of pollutant to DNA signal was restored, demonstrating that the GO-based DNA biosensor provides an effective assessment approach to the genotoxic pollutant control	Wei et al. 2011
GR/Au-palladium (ERGO-AuPdNPs)	Glucose	6.9 μM	The synthesized ERGO-AuPdNPs composite shows a homogeneous dispersion of the Au-Pd alloy NPs in the wrinkled ERGO scaffold, with good biocompatibility, fast electron transfer kinetics, large electroactive surface area, high sensitivity and stability against O_2 reduction	Yang et al. 2011
Nafion/TiO_2-GR	L-tryptophane (Trp) and L-tyrsine (Tyr)	0.7 μM and 2.3 μM	Using this electrochemical sensor, the amino acids can be detected with high sensitivity and low detection limit. The excellent analytical performance can be attributed to the good biocompatibility and high conductivity of TiO_2 nanoparticles, which effectively regulate the surface chemistry and electrochemical properties of the GR substrate	Fan et al. 2011c
Doping GR/layered double hydroxide films (LDHs)	DA	0.3 μM	The stable raphene-LDH/GC electrodes were prepared by GR and LDH composites. This modified electrode exhibited high electrocatalytic activities toward the oxidation of DA by significantly decreasing the oxidation overpotential and enhancing the peak current	Wang et al. 2011e
GR-CdS	Glucose	0.7 mM	Based on the decrease of the electrocatalytic response of the reduced form of GOD to dissolved oxygen, a glucose sensor has been developed, which displays satisfactory analytical performance over a linear range from 2.0 to 16 mM along with good stability because of the large surface area and fast electron transfer of GR and CdS nanocrystals. Interference from UA and AA that usually coexist with glucose in real samples has been found to be negligible	Wang et al. 2011f
GR/*p*-amino-benzoic acid (p-ABA)	DA	20 nM	The GR/p-ABA/GCE exhibited good electrocatalytic effect on the oxidation of DA and presented a high sensitivity and selectivity for DA detection without interference of excess AA.	Huang et al. 2011d
Phosphotungstic acid/GR oxide (PTA/GO)	Methyl jasmonate (MEJA)	2×10^{-7} M	Based on the electrocatalytic effect of this sensing material on the oxidation of alkylene group in MEJA, a novel electrochemical sensor for the determination of MEJA was fabricated. This sensor showed excellent linear relation and high sensitive for the determination of MEJA in the wheat spikelet samples	Gan et al. 2010
GR/PB	H_2O_2	3 μM	The PB-GR/GCE had admirable electrocatalytical performance toward both the reduction of H_2O_2 and the oxidation of hydrazine. Both of the situations can be attributed to the unique zeolite structure of PB, which allowed molecules (H_2O_2 and hydrazine) with low molecular weight and scale to penetrate into the crystal and achieve well electrocatalysis	Jiang et al. 2011b
GO	Phosphorylated p53	0.01 nM	Enhanced sensitivity is achieved by using functionalized GO as a nanocarrier to link enzyme and signal antibody at high ratio. The proposed immunosensor shows excellent performance for detection of phosphorylated protein with a wide linear range and low detection limit and acceptable stability, reproducibility, and accuracy	Du et al. 2011c

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
GR	DA		By exploring the behavior of the FGGE toward the electrochemical oxidation of AA, DA, and UA, we have developed a novel system for the selective and simultaneous determination of DA and UA. As the electrode preparation is very easy and the prepared electrode is very stable, its use in clinical analysis for the determination of DA and UA in the presence of high concentrations of AA is very promising	Mallesha et al. 2011
Ni(II)/quercetin/GR	Glucose	0.5 μM	Results demonstrated the sensor has a good ability toward the catalytic oxidation of glucose, which showed fast electron transfer kinetics and excellent electrocatalytic activity for glucose. The sensor has been envisaged to be useful for fundamental studies on GR-based electrochemistry and for practical electrochemical applications	Sun et al. 2011e
Pt/GR	Glucose	0.6 μM	Such a sensitivity is attributed to the synergy of FGS and Pt nanoparticles on the electrocatalytic activity to H_2O_2. The glucose biosensor has good responses because of the large surface area and fast electron transfer of GR and Pt nanoparticles. The biosensor also has good reproducibility and long-term stability. The interfering signals from AA and UA are negligible compared with the response to glucose	Wu et al. 2009
GR/CS	Glucose	0.02 mM	The results indicate that the GR can provide a favorable microenvironment for the enzyme and promote the direct electron transfer at the electrode surface. CS also plays an important role in forming a well-dispersed GR suspension and immobilizing the enzyme molecules.	Kang et al. 2009
Au/GR-magnetic beads (GMGP)	α-fetoprotein (AFP)	1.0 pg/ml	2D nanosheets and 3D nanoparticles are simultaneously utilized for the synthesis of the bionanocomposites and enhance the immobilized amount of biomolecules. The electrochemical immunoassay is direct, rapid, and simple without multiple labeling and separation steps; and the magneto-controlled electrochemical immunoassay method can pull the bio-GMGP from one laminar flow path to another by applying a local magnetic field gradient and selectively remove them from flowing biological fluids without any washing steps	Zhang et al. 2011b
Au-Ag-GR	AFP	0.5 pg/ml	The present study demonstrates a new approach toward advanced development of highly sensitive electrochemical immunoassay of AFP (as a model analyte) in clinical immunoassays by using Au-Ag-GNs as matrices and nanogold-enclosed titania nanoparticles as labels. Use of the hybrid nanosheets greatly improved the electrochemical properties of the immunosensing interface and enhanced the sensitivity of the immunosensor. Moreover, the signal could be further amplified by using nanogold-attached TiO_2 nanoparticle-labeled secondary antibodies	Su et al. 2011
GR	1,4-Dihydroxybenzene (HQ), 1,2-dihydroxybenzene (CC)	0.2 μM for HQ, and 0.1 μM for CC	The GR-modified electrode showed enhanced electron transfer properties and high resolution capacity to the HQ and CC isomers. Wide linear concentration ranges, low detection limits, and excellent reproducibility and stability were achieved on the EG/GCE, indicating GR as a promising sensing platform for isomer determination	Chen et al. 2011b
GR/Pd	H_2		Although only 4×4 GR film was demonstrated, the size of GR film, which can be synthesized by this approach, is not limited by the size of CVD chamber at all owing to the rolled-up Cu foil during synthesis. Raman spectrum shows 99% area of the film has a ratio of 2D band to G band larger than 2, which indicates most of the films are monolayered. Thanks to the synthesis of wafer-scale GR with uniform thickness, sensors based on the GR are expected to have an identical performance compared with other nanomaterials, such as CNTs. Hydrogen sensors were demonstrated on Pd-decorated CVD GR films. The hydrogen sensors show high sensitivity, fast response and recovery, and are usable for multiple cycles	Wu et al. 2010b

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
Nafion/GO	Caffeine	2×10^{-7} M	This study demonstrated a new caffeine voltammetric sensor, Nafion/GO/GCE, which can be applied to the detection of caffeine with excellent sensitivity and selectivity. Nafion/GO/GCE exhibited significant advantages of wide linear range and low detection limit for caffeine compared with previous works. Besides, the modified electrode presented nice reliability and stability, had a superior immunity to some interference, and offered a good possibility for extending the technique in routine analysis of caffeine.	Zhao et al. 2011b
ZnO/GR	Ethanol	1.0 μg/ml	The hybrid architectures on glass substrates exhibited good optical transmittance for visible light, while those on flexible metal foils could accommodate flexural deformation without mechanical or electrical failure under repeated bending-unbending up to 100 times. Furthermore, our gas sensors enabled ppm-level detection for ethanol vapor with very high sensitivity.	Yi et al. 2011
GR/poly(ethyleneimine)	Maltose, H_2O_2, and glucose		By combining the unique properties of GR and the versatility of layer-by-layer assembly, we expect that this work will stimulate the development of highly efficient electrochemical sensors and advanced biosensing systems.	Zeng et al. 2010
Magnetic GR	Triphosphate (ATP), and cocaine	0.1 pM for ATP and 1.5 pM for cocaine	Compared with other strategies, the method is sensitive, rapid, simple, and reusable. Significantly, the assay does not require sophisticated fabrication and is well suited for high throughput biomedical sensing and application in both clinical and biodefense areas.	Tang et al. 2011c
TiO_2/GR	Adenine and guanine	0.1 μM for adenine and 0.15 μM for guanine	This synthetic approach consists of intercalation and graft of titanium isopropoxide on GR oxide sheets and hydrothermal treatment to immobilize TiO_2 nanoparticles on the GR substrate. The as-prepared TiO_2-GR nanocomposite-modified glassy carbon electrode exhibits remarkable electrocatalytic activity toward adenine and guanine oxidation. The good adsorptivity and conductivity of TiO_2 greatly improved the electrochemical sensing performance.	Fan et al. 2011d
PDDA/graphing/AuNPs/GNs	UA	0.1 μM	The results suggested that adsorption was the best method to form AuNPs/GNs hybrid nanocomposites for electrocatalytic application from the electrochemical point of view. Consequently, negatively charged citrate-AuNPs were replaced by positively charged PDDA-AuNPs, and the obtained PDDA-AuNPs/GNs gave better electrocatalytic activity for the oxidation of UA. Under the optimizing conditions, the anodic peak current of UA at PDDA-AuNPs/GNs/GCE increased 102.1-fold in comparison to bare GCE.	Xue et al. 2011
GR/Pt	AA, DA, and UA	0.15 μM for AA, 0.03 μM for DA, and 0.05 μM	A GR/Pt-modified glassy carbon electrode was created to simultaneously characterize AA, DA, and UA levels *via* CV and differential pulse voltammetry.	Sun et al. 2011f
Silver nanowire/GR	AFP	5 pg/ml	The synthesized bionanolabel could be used for convenient detection of biomarkers with a wide linear range and low limit of detection. The highlight of this work is to design a novel nanostructure for the label of biomolecules by coupling with the highly loaded capacity and excellent conductivity of GR and silver nanowire. By controlling the target antigen or antibody, importantly, the assay can be further extended for use with other disease-relevant biomarkers and thus represents a versatile detection method.	Tang et al. 2011d

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
GR/Ag	H_2O_2	28 μM	The decoration of GR with Ag *via* direct adsorption of preformed, negatively charged Ag or *in situ* chemical reduction of silver salts. The detection of H_2O_2 without using enzyme in the electrode modified by Ag/GR nanocomposites has also been demonstrated, and it revealed that the Ag contained therein exhibits notable catalytic activity toward the reduction of H_2O_2	Liu et al. 2010
Anionic stacked GR nanofiber (SGNF) dopant into a polypyrrole	DNA		The electrochemical activity of the electrode was maintained upon doping with SGNFs, shown by the high selectivity exhibited toward guanine, an essential biomarker for label-free electrochemical detection of DNA hybridization	Scott et al. 2010
PdNP/CS-grafted (GR)	Glucose	0.2 μM	PdNPs/CS-GR were then synthesized by *in situ* reduction using the mixture of Pd salt and CS-GR. It was observed that PdNPs were well dispersed and densely decorated on CS-GR nanosheets. The PdNPs/CS-GR nanocomposite-modified electrode showed high electrocatalytic activity toward the oxidation of H_2O_2. With GOD as a model oxidase enzyme, we constructed a glucose biosensor through covalent immobilization of the enzyme on the PdNPs/CS-GR nanocomposites	Zeng et al. 2011
Au/GR(GNPs)/PFG	UA	2×10^{-7} M	The introduction of a small amount of PFG sheets into the GNP-PFG composite strongly increased the electrocatalytic activity and stability of the GNP-modified electrode. Furthermore, the sensing electrode based on the composite exhibited highly sensitive and stable responses to UA	Hong et al. 2010
PDDA-GR	CC and HQ	2×10^{-7} M	A modified GCE by PDDA-functionalized GR nanosheets was fabricated, and the electrochemical behaviors of CC and HQ on the modified electrode were investigated by using CV and DPV techniques. PDDA was employed to functionalize GR nanosheets and adsorbed onto the surface of GR *via* the electrostatic interaction	Wang et al. in press
GR/Nafion (RGON)	Organophosphate	1.37×10^{-7} M	Functionalization by Nafion *via* hydrophobic interactions provided a highly stable dispersivity of RGOs and mechanical integrity of the hybrid materials due to the intrinsic molecular structures and functionality of Nafion. From the perspective of electrochemical applications, RGON films exhibited Nernstian behavior, fast ET reaction, and low interfacial resistance	Choi et al. 2010
GR/CS/poly(amido-amine) dendrimer	Rutin	0.6 nM	Compared with the response of rutin at the bare GCE, the redox peak current of rutin at the fabricated electrode was significantly improved. Under the optimized conditions, a relative low detection limit was obtained	Yin et al. 2011
Cu_2O/GR	DA	10 nM	Cu_2O/GR nanocomposites were successfully prepared through a polyol process by using EG as the solvent and reducing agent. The as-prepared Cu_2O/GR was characterized by XRD, XPS, TEM, SEM, and electrochemical workstation	Zhang et al. 2011c
GR/Au	AFP	0.05 ng/ml	Experimental results indicated that the electrochemical immunoassay was rapid, sensitive, low cost and favorable for real specimens. Meanwhile, such a low LOD was suitable for the requirement of low sample volume for the practical measurements. Although the assay was focused on the detection of AFP in this paper, it could be extended for the determination of other biomarkers, thus providing a promising approach in clinical immunoassays	Chen et al. 2011c

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
PtNi/GR	Glucose	0~35 mM	Compared with PtNi alloy NPs, PtNi-GR, and PtNi-SWNT nanocomposites, PtNi-GR-modified electrode exhibits smaller electron transfer resistances and larger electrochemically active surface area, which makes it an ideal electrode material for electrocatalytic application. When used for glucose sensing, we found that the PtNi-GR nanocomposite-based nonenzymatic sensor possesses many merits in terms of high selectivity, superior resistance to poisoning, low detection limit, rapid response, excellent reproducibility and stability, which outmatches the performance of any other nonenzymatic Pt-based glucose sensor that have been reported	Cao et al. 2011b
GR-mesoporous silica-gold	Adenosine triphosphate (ATP)	0.023 nM	SMSs had high binding capacity and an environment friendly property and could easily be separated directly by earth gravity. Here, we used them as separation elements to remove the "waste" after the ATP recognition process, which could decrease the unexpected potential background produced by the unreacted duplexes remaining on the SMSs. Several amplification processes were integrated in the sensor design	Guo et al. in press
N-doped GR	Glucose	0.01 mM	The as-prepared N-doped GR exhibited excellent electrocatalytic activity for the reduction of hydrogen peroxide, fast electron transfer kinetics of glucose oxidase, and high sensitivity and selectivity for glucose biosensing. As low as 0.01 mM glucose could be detected in the presence of interferences. Moreover, as GR has an atomic structure common to many carbon materials, doping with the plasma treatment might be an alternative method to fulfill the intrinsic modification of other carbon materials such as CNTs, graphite, carbon fiber, and porous carbon, etc.	Wang et al. 2010b
Nafion/GR	Cadmium	0.005 μg/l	The nanocomposite film combining the advantages of GR and the cationic exchange capacity of Nafion enhanced the sensitivity of Cd^{2+} assay. The practical application of the Nafion-GR electrode was assessed. Furthermore, this simple sensing platform cannot only be extended to the detection of other different heavy metal ions, but be used as upgrading arrangement for bismuth film for the sensitive determination of Cd^{2+}	Li et al. 2009b
β-cycodextrin/GR sheets (β-CD/GS)	AA		The electrode modified by β-CD/GS nanocomposite exhibited more reversible electrochemical response to DA than that of the unmodified GS	Tan et al. 2010
GR functionalized carboxylic group (COOH)	Adenine and guanine	$2.5–5\times10^{-8}$ M	After optimizing the experimental parameters, guanine and adenine exhibited well-separated and well-defined oxidation peaks. Remarkable enhancement effects on the oxidation peak currents were observed with the negative shift of the oxidation peak potentials. The results were attributed to the specific characteristics of GR-COOH	Huang et al. 2011c
SiO_2/GO	H_2O_2	4×10^{-6} M	A simple method for the synthesis of well-defined SiO_2/GO nanosheets and their subsequent use as an advanced support for loading AgNPs *via* direct adsorption of preformed, negatively charged AgNPs and *in situ* chemical reduction of silver salts. The detection of H_2O_2 without using enzyme in the electrode modified by AgNP/F-SiO_2/GO nanocomposites has also been demonstrated. Furthermore, a glucose biosensor has also been constructed *via* immobilizing GOD into the nanocomposite-modified GCE. Such AgNP/F-SiO_2/GO nanocomposites may hold great promise for applications in areas including biosensor, analytical and electroanalytical chemistry	Lu et al. 2011c
Poly[*N*-(1-one-butyric acid)-benzimidazole] (PBI-BA)/GR/Au	H_2O_2		The probe is highly selective, with a rapid response time and good thermal stability. Deprotonation of the protonated imine at high temperatures noticeably increases the probe s sensitivity. Furthermore, using PBI-BA to disrupt GR aggregates can provide superior conductivity and an increased surface area for use in PBI-BA-GR/Au electrodes, improving the performance of the sensor markedly	Hua et al. 2011

(*Table 1 continued*)

Sensing materials	Analyte	Detection limit	Remark	Reference
Pd/GR	2-chlorophenol (CP)		An electrochemical sensor for CPs was constructed based on the nanocomposite. The as-prepared IL-Pd-GR nanocomposite exhibited remarkable current enhancement and good stability in the determination of CPs	Shi and Zhu 2011
1-Octadecanethiol/GR	Hg^{2+}	10 μg/ml	Compared with random absorption of receptors on GR sensors, highly ordered molecular adlayers are very attractive to modify single-layer GR whose electronic performances have been shown to be very sensitive to randomness and fluctuations from the surrounding environment	Liu et al. 2011i
Porphyrin/GR	2,4-dinitrotoluene, 2,4,6-TNT, and 1,3,5-trinitritro-toluene	0.5–2.0 ng/ml	Porphyrin functionalized GR is used to electrochemically detect ultratrace nitroaromatic explosives. The porphyrin/GR sensor shows high sensitivity, good reproducibility and selectivity, and can detect nitroaromatic explosives with an ultratrace detection	Guo et al. 2011d
GO	Coffee	3×10^{-7} M		Zhao et al. 2011b
GR-COOH	Pb^{2+} and Cd^{2+}	2×10^{-10} M		Xu et al. 2010

analytical chemistry, and more than 200 papers have been published on the important international journals.

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