Graphene Based Electrochemical Sensors and Biosensors: A Review

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Abstract

Graphene, emerging as a true 2-dimensional material, has received increasing attention due to its unique physicochemical properties (high surface area, excellent conductivity, high mechanical strength, and ease of functionalization and mass production). This article selectively reviews recent advances in graphene-based electrochemical sensors and biosensors. In particular, graphene for direct electrochemistry of enzyme, its electrocatalytic activity toward small biomolecules (hydrogen peroxide, NADH, dopamine, etc.), and graphene-based enzyme biosensors have been summarized in more detail; Graphene-based DNA sensing and environmental analysis have been discussed. Future perspectives in this rapidly developing field are also discussed.

Keywords: Graphene, Carbon nanotubes, Direct electrochemistry, Enzyme, Biosensors, Glucose, DNA

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1. Introduction

Graphene has attracted strong scientific and technological interest in recent years [1–6]. It has shown great promise in many applications, such as electronics [7], energy storage and conversion (supercapacitors [8], batteries [9, 10], fuel cells [11–15], solar cells [16, 17]), and bioscience/biotechnologies [18–23] because of its unique physicochemical properties: high surface area (theoretically 2630 m^2/g for single-layer graphene) [1, 5], excellent thermal conductivity [24] and electric conductivity [1, 25], and strong mechanical strength [26].

Many methods have been developed to produce graphene [3, 5]. In 2004, Geim and coworkers [27] first reported graphene sheets prepared by mechanical exfoliation (repeated peeling) of highly oriented pyrolytic graphite. This method, which is called scotch-tape method [4, 5], is still widely used in many laboratories to obtain pristine perfect-structured graphene layer(s) for basic scientific research and for making proof-of-concept devices. However, it is not suitable for mass production. The other method for producing defect-free/defect-less graphene is the mild exfoliation of graphite [28–31], but the yield so far is very low [28]. Graphene has also been prepared by thermal decomposition of SiC wafer under ultrahigh vacuum (UHV) conditions [32–35] or by CVD growth on metal substrates (ruthenium [36], Ni [37, 38], and Cu [39]) or by substrate-free CVD [40]. This is a potential mass-production method with the aim of producing graphene for electronics applications [7, 41]. Another mass-production method is chemical [42–45] or thermal reduction [46] of graphite oxide (GO). It is also considered to be the most economical way to produce graphene [4, 5]. Most of graphene used in electrochemistry are produced with the last method of GO reduction. Graphene from GO reduction, which is also called functionalized graphene sheets or chemically reduced graphene oxide, usually has abundant structural defects [5, 46] and functional groups [42] which are advantageous for electrochemical applications [47–50]. Therefore, this review will focus on this kind of graphene.

Carbon might be the most widely-used material in electroanalysis and electrocatalysis [47, 50–60]. For example, carbon nanotubes have shown excellent performance in biosensors [50–55, 61], biofuel cells [62], and polymer electrolyte membrane (PEM) fuel cells [57–59, 63–65]. Graphene-based electrodes have shown superior performance in terms of electrocatalytic activity [66, 67] and macroscopic scale conductivity [67] than carbon nanotubes-based ones. These indicate that the opportunities in electrochemistry encountered by carbon nanotubes might be available for graphene [68]. Graphene is the basic building block for graphitic materials of all other dimensionalities (0D fullerenes, 1D nanotubes, and 3D graphite) [1]; Functionalized graphene produced through reduction of graphene oxide displays a wrinkled structure due to the presence of lattice defects and this is different than the rippled structure observed in pristine graphene (Figure 1). Studying graphene is expected to provide a fundamental insight into all carbon materials. In comparison with carbon nanotubes, graphene exhibits potential advantages of low cost, high surface area, ease of processing and safety [69]. Graphene, due to its high purity (transition metals, Fe, Ni,

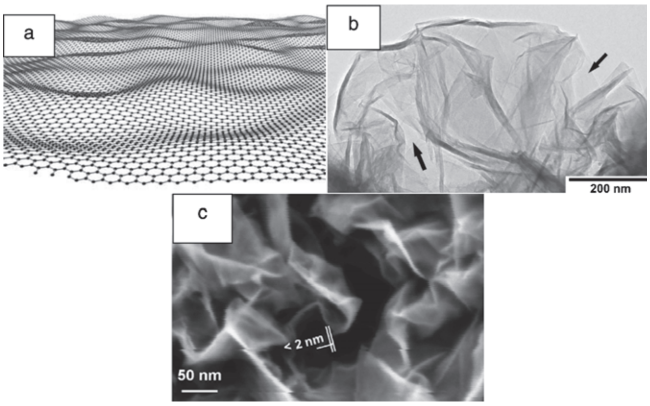

Fig. 1. (a) Structural model of pristine graphene [71], (b) TEM image of graphene [72], and (c) SEM image of graphene (from [42] with permission). Graphene in (b) and (c) are produced from chemical reduction of graphene oxide.

etc. are absent in graphene from GO reduction, not like carbon nanotubes [70]), provides a good platform to study the electrocatalytic effects of carbon materials. Graphene is expected to gradually compete with carbon nanotubes in many applications [69]. In this article, we will selectively review recent advances of graphene-based electrodes for electrochemical sensors and biosensors. Graphene exhibits excellent electron transfer promoting ability for some enzymes and excellent catalytic behavior toward small biomolecules such as H_2O_2, NADH, which makes graphene extremely attractive for enzyme-based biosensors, e.g. glucose biosensors and ethanol biosensors. Finally, the future research on graphene will be discussed.

2. Basic Electrochemistry of Graphene

For the potential application of a certain kind of carbon material in electrochemistry, the basic electrochemical behaviors should be first studied to determine several important parameters of carbon electrodes [47, 73, 74]: electrochemical potential window, electron transfer rate, redox potentials, etc.

Based on Zhou et al.'s report [75], graphene exhibits a wide electrochemical potential window of ca. 2.5 V in 0.1 M PBS (pH 7.0) [75], which is comparable to that of graphite, glassy carbon (GC), and even boron-doped diamond electrodes [47, 74, 75], and the charge-transfer resistance on graphene as determined from AC impedance spectra is much lower than that graphite and GC electrodes [75].

The electron transfer behavior studies of graphene using cyclic voltammetry (CV) of redox couples, such as $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{3+/2+}$, are reported, which exhibit well-defined redox peaks [76–78]. Both anodic and cathodic peak currents in the CVs are linear with the square root of the scan rate, which suggest that the redox processes on graphene-based electrodes are predominantly diffusion-controlled [77]. The peak-to-peak potential separations (ΔE_p) in CVs for most one-electron-transfer redox couples are quite low, very close to the ideal value of 59 mV, for example, 61.5–73 mV (10 mV/s) for $[Fe(CN)_6]^{3-/4-}$ [76, 78–80] and 60–65 mV (100 mV/s) for $[Ru(NH_3)_6]^{3+/2+}$ [78], much smaller than that on GC [47]. The peak-to-peak potential separation is related to the electron transfer (ET) coefficient [81], and a low ΔE_p value indicates a fast ET for a single-electron electrochemical reaction [79] on graphene.

In order to study the electrochemical response/activity of graphene toward different kinds of redox systems, Tang et al. [78] systematically studied three representative redox couples: $[Ru(NH_3)_6]^{3+/2+}$, $[Fe(CN)_6]^{3-/4-}$, and $Fe^{3+/2+}$. As is known, $[Ru(NH_3)_6]^{3+/2+}$ is a nearly ideal outer-sphere redox system that is insensitive to most surface defects or impurities on electrodes and can serve as a useful benchmark in comparing electron transfer of various carbon electrodes; $[Fe(CN)_6]^{3-/4-}$ is "surface-sensitive" but not "oxide-sensitive"; and $Fe^{3+/2+}$ is both "surface-sensitive" and "oxide-sensitive" [47]. The apparent electron-transfer rate constants (k^0) calculated from cyclic voltammograms on graphene and GC electrodes are 0.18 cm/s and 0.055 cm/s for $[Ru(NH_3)_6]^{3+/2+}$, respectively [78]. This indicates that the unique electronic structure of graphene, especially the high density of the electronic states over a wide energy range endows graphene with fast electron transfer [47]. The k^0 for $[Fe(CN)_6]^{3-/4-}$ on graphene and GC were calculated to be 0.49 cm/s and 0.029 cm/s, respectively, and the electron-transfer rates for $Fe^{3+/2+}$ at graphene electrode are several orders of magnitude higher than that at GC electrodes [78]. These indicate that the electronic structure and the surface physicochemistry of graphene are beneficial for electron transfer [47, 78, 82].

3. Direct Electrochemistry of Enzymes

The direct electrochemistry of enzyme refers to the direct electron communication between the electrode and the active center of the enzyme without the participation of mediators or other reagents [83–85], which is very significant in the development of biosensors, biofuel cells and biomedical devices [84, 86–88]. However, the realization of direct electrochemistry of redox enzymes on common electrodes is very difficult because the active centers of most redox enzymes are located deeply in a hydrophobic cavity of the molecule [20, 86, 89]. Carbon nanotubes and metal nanoparticles have exhibited excellent performance in enhancing the direct electron transfer between enzymes and electrodes, and are widely used now [50, 55, 90, 91]. Due to its extraordinary electron transport property (as shown in Section 2) and high specific surface area [1], functionalized graphene is expected to promote the electron transfer between electrode substrates and enzymes [20].

Shan et al. [20] and Kang et al. [92] reported the direct electrochemistry of glucose oxidase (GOD) on graphene. Shan et al. [20] employed the chemically reduced graphene oxide (CR-GO) and Kang et al. [92] employed thermally split graphene oxide [46], both of which exhibit similar excellent direct electrochemistry of GOD. Figure 2 shows cyclic voltammograms (CV) of graphene, graphite-GOD, and graphene-GOD modified GC electrodes in PBS solution [20]. A pair of well-defined redox peaks was only observed at the graphene-GOD modified electrode, which is characteristic of reversible electron transfer process of redox active center (flavin adenine dinucleotide, FAD) in GOD, indicating that a direct electron transfer of GOD on graphene electrode has been successfully achieved. The formal potential ($E^{\circ\prime}$) calculated by averaging the cathodic and anodic peak potentials was estimated to be ca. -0.43 V (all the electrode potentials are vs. Ag/AgCl, except specially stated), close to the standard electrode potential of FAD/FADH$_2$ [92, 93]. The redox peaks of GOD have ca. 69 mV peak-to-peak separation and ca. 1 ratio of cathodic to anodic current intensity [20], and peak current densities are in the linear relationship with scan rates [20, 92]. These indicate that the redox process of GOD on graphene electrode is a reversible and surface-confined process [92]. The electron-transfer-rate constant (k_s) of the GOD on graphene electrode is 2.83 ± 0.18 s^{-1}, much higher than most of the values reported on carbon nanotubes [94–96], indicating that functionalized graphene provides fast electron transfer between the redox center of the enzyme and the surface of electrode [92]. Graphene electrodes exhibit a high enzyme loading (1.12×10^{-9} mol/cm^2) due to its high surface area [92]. This is advantageous for increasing the sensitivity of graphene-based biosensors. The direct electron transfer of GOD on graphene is stable, for example, no obvious changes in 15 cycles on the cyclic voltammetric responses of the GOD–graphene–chitosan modified electrode in N$_2$-saturated PBS (pH 7.4) and the response retention of above 95% after 1 week storage [92].

The excellent performance of graphene toward the direct electrochemistry of GOD indicates that graphene is a potential promising material for enzyme electrodes.

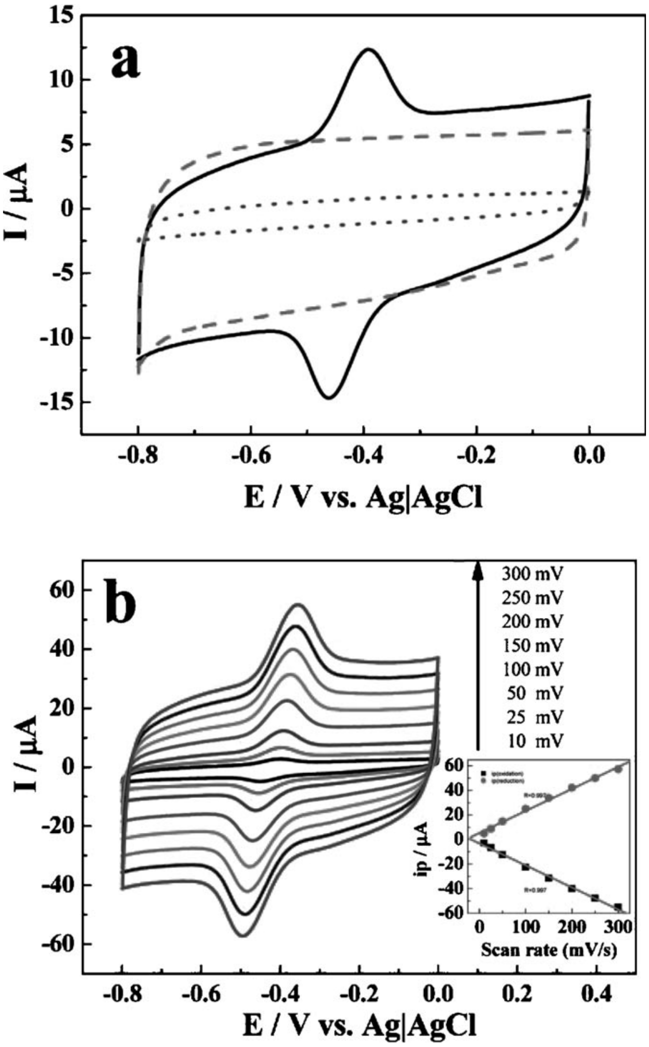

Fig. 2. (a) Cyclic voltammograms (50 mV/s) of graphene (dashed), graphite-GOD (dotted), and graphene-GOD (solid) modified electrodes in N$_2$-saturated 0.05 M PBS solution (pH 7.4). (b) Cyclic voltammograms at various scan rates on graphene-GOD modified electrodes (Inset: plot of peak current (i_p) vs. scan rate) (from [20] with permission).

4. Graphene-Based Electrodes for Small Biomolecules

4.1. Hydrogen Peroxide (H$_2$O$_2$)

Hydrogen peroxide is a general enzymatic product of oxidases and a substrate of peroxidases, which is important in biological processes and biosensor development [75]. Hydrogen peroxide is also an essential mediator in food, pharmaceutical, clinical, industrial, and environmental analyses [75]; therefore, it is of great importance to detect H$_2$O$_2$. The key point in developing electrodes for detecting H$_2$O$_2$ is to decrease the oxidation/reduction overpotentials. Kinds of carbon materials, such as carbon nanotubes [50, 55, 97, 98], have been developed in constructing biosensors for detecting H$_2$O$_2$. Graphene has shown promise in this aspect [77, 99].

Zhou et al. [75] studied the electrochemical behavior of hydrogen peroxide on graphene (chemically reduced graphene oxides, CR-GO) modified electrode, which shows a remarkable increase in electron transfer rate compared with graphite/GC and bare GC electrodes [75]. As shown in cyclic voltammograms (CVs) in Figure 3, the onset potentials of H$_2$O$_2$ oxidation/reduction on CR-GO/GC (a1), graphite/GC (b1), and GC electrodes (c1) are 0.20/0.10 V, 0.80/-0.35 V, and 0.70/-0.25 V, respectively, indicating superior electrocatalytic activity of graphene toward H$_2$O$_2$. The linear relationship of H$_2$O$_2$ at -0.2 V on CR-GO/GC electrode is 0.05–1500 μM, wider than the previously reported results for carbon nanotubes [75]. These can be attributed to the high density of edge-plane-like defective sites on graphene, which might provide many active sites for electron transfer to biological species [48, 100, 101]. Such significantly enhanced performance on graphene-based electrodes for detecting H$_2$O$_2$ may lead to high-selectivity/-sensitivity electrochemical sensors.

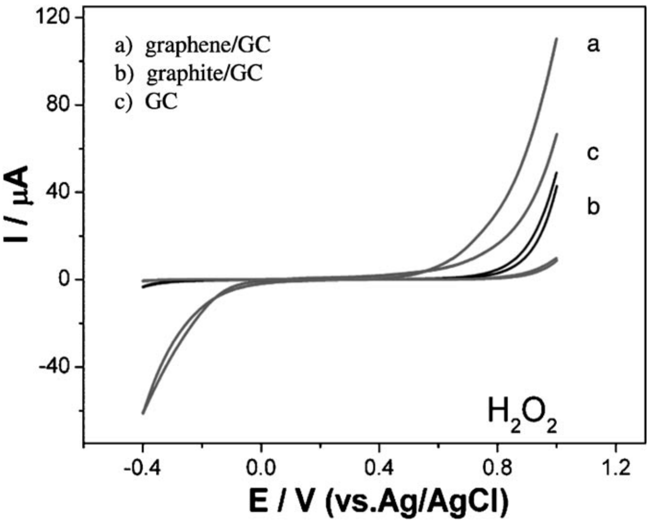

Fig. 3. Background-subtracted CVs (50 mV/s) on graphene/GC (a), graphite/GC (b), and GC electrodes (c) in 4 mM H_2O_2 + 0.1 M PBS (pH 7.0) (from [75] with permission).

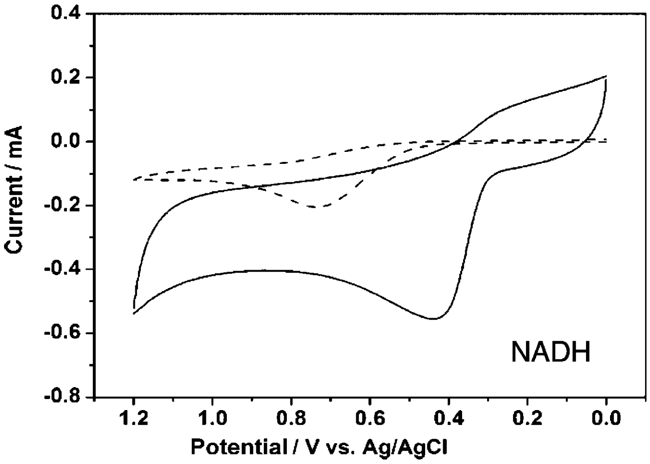

Fig. 4. Cyclic voltammograms (100 mV/s, negative currents for oxidation) in 0.1 M pH 6.8 PBS containing 1 mM NADH at bare GC (dashed line) and graphene/GC electrodes (solid line) (from [78] with permission).

4.2. NADH

β-nicotinamide adenine dinucleotide (NAD$^+$) and its reduced form (NADH) are a cofactor of many dehydrogenases [55], which has received considerable interest in developing amperometric biosensors, biofuel cells, and bioelectronic devices associated with NAD$^+$/NADH-dependent dehydrogenases [98, 102]. The oxidation of the NADH serves as the anodic signal and regenerates the NAD$^+$ cofactor, which is of great significance in biosensing important substrates such as lactate, alcohol or glucose [50]. Problems inherent to such anodic detection are the large overvoltage for NADH oxidation and surface fouling associated with the accumulation of reaction products [50]. Graphene shows promise in addressing these problems.

Tang et al. [78] studied the electrochemical behavior of NADH on graphene (chemically reduced graphene oxides, CR-GO) modified electrode, which shows a remarkable increase in electron transfer rate compared with graphite/GC and GC electrodes [78]. The peak potentials of NADH oxidation is shifted from 0.70 V on GC and graphite to 0.40 V on CR-GO (Figure 4) [78]. These are attributed to the high density of edge-plane-like defective sites on CR-GO, which provide many active sites for electron transfer to biological species [48, 100, 101].

Liu et al. [103] reported a further enhanced performance of graphene-based electrode toward the oxidation of NADH through increasing the dispersity of graphene via noncovalent functionalization of graphene with methylene green (MG). The oxidation of NADH on MG-graphene electrode takes place ~ 0.14 V, which is much lower than that (+ 0.40 V) for pristine graphene (i.e., without MG functionalization) [103] and carbon nanotubes based biosensors [104 – 106].

The enhanced activity of graphene modified electrodes toward NADH oxidation is further confirmed in Lin et al.'s report when compared with bare edge plane pyrolytic graphite electrode (EPPGE) which has many edge-plane-like defective sites [77]. It is known that the high density of edge-plane-like defective sites, which might provide many active sites for electron transfer to biological species, contribute to the enhanced activity of carbon materials toward oxidation/reduction of small biomolecules such as NADH [48, 100, 101]. The higher activity of functionalized graphene modified EPPGE than bare EPPGE indicates that, in addition to the high density of edge-plane-like defective sites on graphene (chemically reduced graphene oxides), there are other special properties of graphene that contribute to its high activity. The exact mechanisms still need more investigation. Pumera et al.'s report [102] on high-resolution X-ray photoelectron spectroscopy (HR-XPS) and ab initio molecular dynamics study of adsorption of NAD$^+$/NADH (Figure 5) might provide preliminary insight into this. It shows that the adsorption of NAD$^+$ molecules on the edges of graphene is attributed to the interaction with oxygen-containing groups such as carboxylic groups, while graphene edges substituted only with hydrogen are prone to passivation [102]. Therefore, the oxygen-containing groups might play one key role for the enhanced activity of graphene.

4.3. Dopamine

Dopamine (DA), an important neurotransmitter, plays a significant role in the central nervous, renal, hormonal, and cardiovascular systems [79]. Its detection has gained significant attention. Rapid, simple, and sensitive electrochemical methods have shown promising in the neurotransmission detection. However, at traditional solid electrodes, DA and its coexisting species ascorbic acid (AA) and uric acid (UA) have an overlapping voltammetric response, resulting in rather poor selectivity and sensitivity of DA.

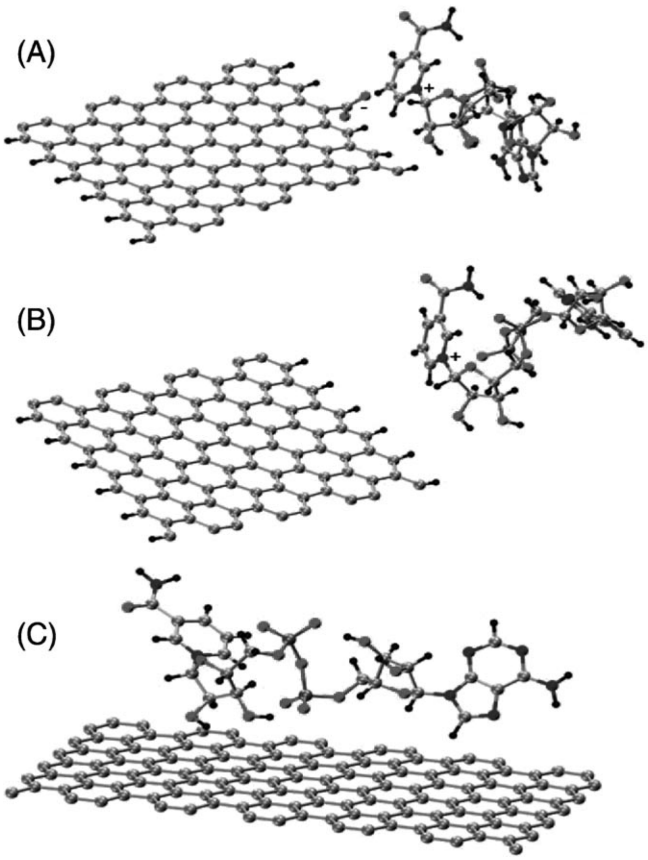

Fig. 5. Model for the adsorption of NAD^+ on a A) graphene basal plane, B) graphene edge fully terminated by hydrogen atoms, and C) graphene edge terminated by hydrogen atoms and containing one $-COO^-$ group via Car–Parrinello molecular dynamics. Gray, C; blue, N; red, O; yellow, P; black, H [102].

Thus, it is a challenge to distinguish the coexistence of DA, AA, and UA in a biological environment.

Shang et al. [79] reported multilayer graphene nanoflake films (MGNFs) based electrode (for detecting DA) which was synthesized through catalyst-free microwave plasma enhanced chemical vapor deposition. The MGNFs exhibited well resolved simultaneous discrimination of AA, DA, and UA, and the detection limit of DA is 0.17 μM. The superior biosensing performance is mainly due to edge plane sites/defects that occur at the end of the vertical graphene nanoflakes, and their ability to act essentially as nanoconnectors that electrically transport the electrons to the underneath substrate [79].

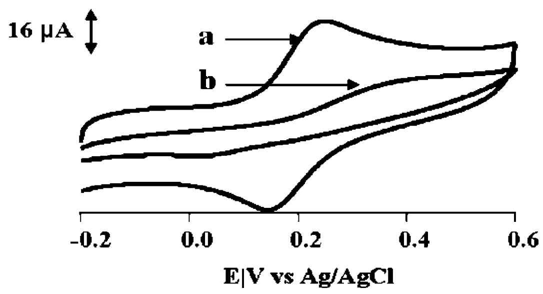

Fig. 6. Cyclic voltammograms of (a) graphene and (b) SWCNT in 2.5 mM DA (from [67] with permission).

Alwarappan et al. [67] reported that graphene exhibited a better sensing performance toward dopamine than SWCNTs (Figure 6) and can effectively distinguish AA, DA, and ST (serotonin). This is attributed to the presence of more sp^2-like planes and various edge defects present on the surface of graphene [67].

Wang et al. [66] reported that graphene exhibited high selectivity for sensing dopamine with a with a linear range of 5 μM – 200 μM, and a better performance than multiwalled carbon nanotubes. They attributed it to the high conductivity, high surface area and $\pi - \pi$ stacking interaction between dopamine and graphene surface [66].

5. Graphene-Based Electrochemical Sensors

The excellent electrochemical behaviors of graphene indicate graphene is a promising electrode material in electroanalysis [47, 50]. Several electrochemical sensors based on graphene and graphene composites for bioanalysis and environmental analysis have been developed [20, 75, 92].

5.1. Graphene-Based Enzyme Biosensors

On the basis of the high electrocatalytic activity of graphene toward H_2O_2 and the excellent performance for direct electrochemistry of GOD, graphene could be an excellent electrode material for oxidase biosensors. Several graphene-based glucose biosensors have been reported [20, 21, 75, 92, 99, 107].

Shan et al. [20] reported the first graphene-based glucose biosensor with graphene/polyethylenimine-functionalized ionic liquid nanocomposites modified electrode which exhibits wide linear glucose response (2 to 14 mM, $R = 0.994$), good reproducibility (relative standard deviation of the current response to 6 mM glucose at -0.5 V was 3.2% for 10 successive measurements), and high stability (response current $+4.9\%$ after 1 week) [20].

Zhou et al. [75] reported a glucose biosensor based on chemically reduced graphene oxide (CR-GO). Graphene(CR-GO)-based biosensor exhibits substantially enhanced amperometric signals for sensing glucose: wide linear range (0.01 – 10 mM), high sensitivity (20.21 μA mM cm^{-2}) and low detection limit of 2.00 μM ($S/N = 3$). The linear range for glucose detection is wider than that on other carbon materials-based electrodes, such as carbon nanotubes [108] and carbon nanofibers [109]. The detection limit for glucose at the GOD/CR-GO/GC electrode (2.00 μM at -0.20 V) is lower than that of some reported carbon materials-based biosensors, such as carbon nanotubes paste [110], carbon nanotubes nanoelectrode [111], carbon nanofiber [109], exfoliated graphite nanoplatelets [107], and highly ordered mesoporous carbon [112]. The response at the GOD/CR-GO/GC electrode to glucose is very fast (9 ± 1 s to steady-state response) and highly stable (91% signal retention for 5 h), which makes GOD/CR-GO/GC electrode a potential fast and highly stable biosensor to continuously measure the plasma glucose level for the diagnosis of diabetes.

Kang et al. [92] employed biocompatible chitosan to disperse graphene and construct glucose biosensors. It was found that chitosan helped to form a well-dispersed graphene suspension and immobilize the enzyme molecules, and the graphene-based enzyme sensor exhibited excellent sensitivity (37.93 μA mM^{-1} cm^{-2}) and long-term stability for measuring glucose.

Graphene/metal nanoparticles (NP) based biosensors have also been developed. Shan et al. [113] reports a graphene/AuNPs/chitosan composites film based biosensor which exhibited good electrocatalytical activity toward H_2O_2 and O_2. Wu et al. [99] reports GOD/graphene/PtNPs/chitosan based glucose biosensor with a detection limit of 0.6 μM glucose. These enhanced performance were attributed to the large surface area and good electrical conductivity of graphene, and the synergistic effect of graphene and metal nanoparticles [99, 113].

The excellent catalytic activity of functionalized graphene toward NADH oxidation indicates that graphene is a promising material for dehydrogenase biosensors. Zhou et al. [75] reports an ethanol biosensor based on graphene-ADH. The ADH-graphene-GC electrode exhibits faster response, wider linear range, and lower detection limit for ethanol detection compared with ADH-graphite/GC and ADH/GC electrodes. This enhanced performance can be explained by the effective transfer of substrate and products through graphene matrixes containing enzymes as well as the inherent biocompatibility of graphene [19, 75].

5.2. Graphene-Based Electrochemical DNA Biosensors

Electrochemical DNA sensors offer high sensitivity, high selectivity and low cost for the detection of selected DNA sequences or mutated genes associated with human disease, and promise to provide a simple, accurate and inexpensivie platform of patient diagnosis [114, 115]. Electrochemical DNA sensors also allow device miniaturization for samples with a very small volume [75]. Among all kinds of electrochemical DNA sensors, the one based on the direct oxidation of DNA is the simplest [74, 75, 115].

Zhou et al. [75] reported an electrochemical DNA sensor based on graphene (chemically reduced graphene oxide). As shown in Figure 7, the current signals of the four free bases of DNA (i.e., guanine (G), adenine (A), thymine (T), and cytosine (C)) on the CR-GO/GC electrode (Figure 7a, green) are all separated efficiently, indicating that CR-GO/GC can simultaneously detect four free bases, but neither graphite nor glassy carbon can. This is attributed to the antifouling properties and the high electron transfer kinetics for bases oxidation on CR-GO/GC electrode [75] which results from high density of edge-plane-like defective sites and oxygen-containing functional groups on CR-GO that provide many active sites and are beneficial for accelerating electron transfer between the electrode and species in solution [48, 100, 101]. As shown in Figure 7b and 7c, CR-GO/GC electrode is also able to efficiently separate all four DNA bases in both single-stranded DNA (ssDNA) and double-stranded DNA (ds-DNA), which are more difficult to oxidize than free bases, at physiological pH without the need of a prehydrolysis step, which allows to detect a single-nucleotide polymorphism (SNP) site for short oligomers with a particular sequence at the CR-GO/GC electrode without any hybridization or labeling processes [75]. This is attributed to the unique physicochemical properties of CR-GO (the single-sheet nature, high conductivity, large surface area, antifouling properties, high electron transfer kinetics, etc.) [75].

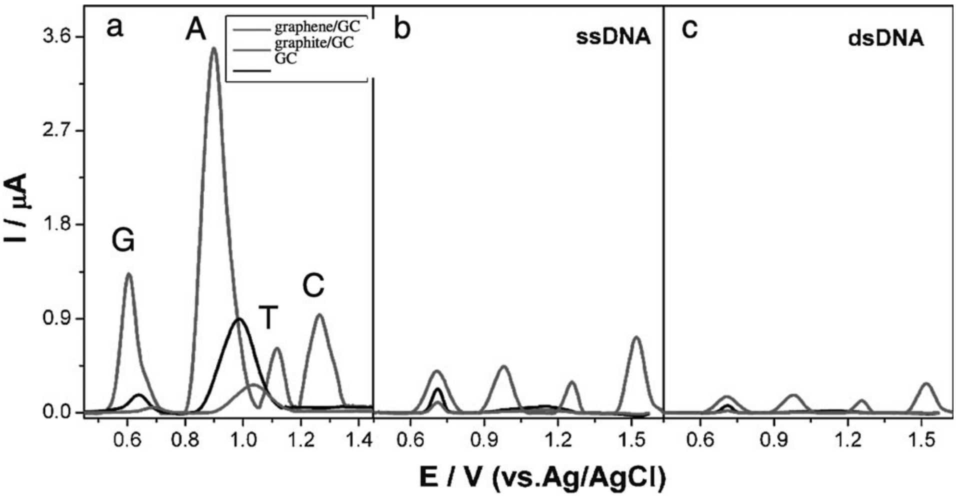

Fig. 7. Differential pulse voltammograms (DPV) for (a) a mixture of DNA free base (G, A, T, and C), (b) ssDNA, and (c) dsDNA in 0.1 M pH 7.0 PBS at graphene/GC (green), graphite/GC (red), and bare GC electrodes (black). Concentrations G, A, T, C, ssDNA or dsDNA: 10 μg mL^{-1} (from [75] with permission).

5.3. Graphene-Based Electrochemical Sensors for Heavy Metal Ions

Graphene-based electrochemical sensors have been developed for environmental analysis for the detection of heavy metal ions (Pb^{2+} and Cd^{2+}) [116, 117]. Li et al. [116, 117] report that Nafion-graphene composite film based electrochemical sensors not only exhibits improved sensitivity for the metal ion (Pb^{2+} and Cd^{2+}) detections, but also alleviates the interferences due to the synergistic effect of graphene nanosheets and Nafion [116]. The stripping current signal is greatly enhanced on graphene electrodes. As shown in the differential pulse anodic stripping voltammograms (DPASV) in Figure 8, the stripping current signal is well-distinguished. The linear range for the detection of Pb^{2+} and Cd^{2+} is wide (0.5 $\mu g\,L^{-1}$ – 50 $\mu g\,L^{-1}$ and 1.5 $\mu g\,L^{-1}$ – 30 $\mu g\,L^{-1}$ for Pb^{2+} and Cd^{2+}, respectively). The detection limits ($S/N = 3$) are 0.02 $\mu g\ L^{-1}$ for both Cd^{2+} and Pb^{2+}, which are more sensitive than those of Nafion film modified bismuth electrode [118], and ordered mesoporous carbon coated GCE [119], and comparable to Nafion/CNT coated bismuth film electrode [120]. The enhanced performance is attributed to the unique properties of the graphene (nanosized graphene sheet, nano-scale thickness of these sheets and high conductivity), which endowed the capability to strongly adsorb target ions, enhanced the surface concentration, improved the sensitivity, and alleviate the fouling effect of surfactants [116, 117].

6. Concluding Remarks and Future Directions

As the building block of carbon materials of all dimensions, graphene exhibits specific electronic structure, properties, and physicochemistry. Graphene has shown excellent performance in direct electrochemistry of enzyme, electrochemical detection of small biomolecules, electroanalysis (electrochemical sensors for bioanalysis and environmental analysis). As a competitor to carbon nanotubes, graphene has exhibited superior performance in these applications. However, the development of graphene-based materials/devices is still in its infancy. The future scientific research and application development of graphene-based materials/devices for electroanalysis and electrocatalysis is worthy of discussion here.

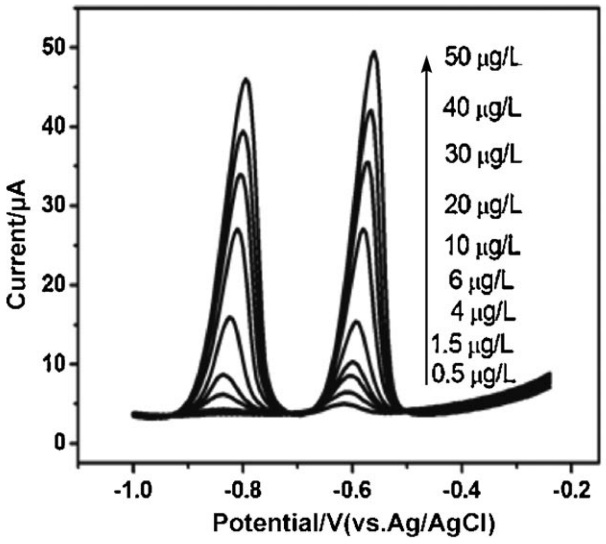

Fig. 8. Striping voltammograms for the different concentrations of Cd^{2+} and Pb^{2+} on an in situ plated Nafion-G-BFE (bismuth film electrode) in solution containing 0.4 mg L^{-1} Bi^{3+} (from [116] with permission).

Novel methods for well-controlled synthesis and processing of graphene should be developed. As stated in the Introduction, graphene has been synthesized with various strategies. However, the economical production approach with high yield is still not widely available. For electrochemical applications, the approach with chemical/thermal reduction of graphene oxide looks promising. Graphene sheets from chemical/thermal reduction of graphene oxide usually tend to re-stack during the synthesis and the processing [5]. So far, many strategies [121 – 124] have been suggested in the synthesis and processing of graphene to prevent re-stacking and to improve the dispersion of graphene in solvents. In several recent reports, graphene was produced through the electrochemical reduction of graphene oxide [21, 125 – 128], and the electrochemically reduced graphene oxide exhibit much better performance for electrochemical applications than chemically reduced one [80, 125, 128], which indicates a promising strategy in graphene synthesis and processing.

Doping graphene with heteroatoms (nitrogen, boron, etc.) should be investigated. Heteroatom doping in carbon nanotubes has shown to greatly improve the electrocatalytic activity [57, 58, 129, 130]. This strategy has been applied in graphene-based material synthesis [131 – 134] and theoretical study [135], but no reports are available on electrochemical study. Nitrogen doping usually takes place at high temperatures (600 – 1000 °C) [59], for example, with ammonia oxidation/heat-treatment, which makes graphene to re-stack more easily. So alternative doping strategy should be developed.

Better understanding of physics and chemistry at the surface of graphene and interaction of chemicals and bimolecules at the interface of graphene will play an important role in applying graphene as nanoscaffold in catalysis, chemical/biosensing, imaging and drug delivery [22, 47, 136, 137]. For example, the absorption mechanism of molecules on graphene, orientation of biomolecules on the graphene and how these interactions affect transport properties of graphene, etc. these studies will provide us further understanding of graphene and its interaction with molecules, which may lead to great advancement of graphene science and its various application such as catalysis and sensors.

In summary, graphene is an excellent electrode material for electroanalysis and electrocatalysis, and there is still much room for the scientific research and application development of graphene-based theory, materials, and devices.

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