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Graphene Oxide-Based Nanohybrids as Pesticide Biosensors: Latest Developments

Navin Kumar Mogha

Abstract

Graphene is the most significant two-dimensional nanomaterial with sp^2 hybridized carbon atoms in a honeycomb arrangement with an extremely high surface area, excellent electrical properties, high mechanical strength, and advantageous optical properties and is relatively easy to functionalize and mass produce. Various inorganic nanoparticles incorporated with graphene, such as gold, silver, and palladium nanoparticles are brought into sharp focus due to their catalytic, optical, electronic, and quantized charging/discharging properties. Graphene oxide-based nanohybrids are particularly well suited for biosensing applications and catalysis. Consequently, this area of research has grown to represent one of the largest classes within the scope of materials science and is rapidly becoming a key area in nanoscience and nanotechnology offering significant potential in the development of advanced materials in multiple and diverse applications. Here in this present chapter, synthesis, characterization of graphene oxide, and their nanohybrids are discussed thoroughly with their application in the field of pesticide biosensors. This chapter will help in a further understanding of graphene-based nanohybrids as a biosensing platform for their future applications in a sustainable environment.

Keywords: graphene oxide, pesticides, biosensors, nanohybrids, nanoparticles, chemical reduction

1. Introduction

The prevalence of harmful and toxic chemical compounds in the environment has become a serious issue in recent decades [1]. Contamination of foodstuffs, drinking water, and air with hazardous pollutants and other foreign substances are real and a direct threat to human health, whereas the accumulation of such contaminants in the human body and environment may lead to long-lasting, severe, and harmful effects after primary exposure [2]. Chemicals such as pesticides, plastic, lead, methylmercury, polychlorinated biphenyls, arsenic, toluene, rubber, and paper [3] play a key role in the economic growth of countries to fulfill their development objectives [4]. The term “pesticide” is defined as any chemical entity, which has the ability to kill the various kinds of pests including rodents, insects, fungi, weeds, etc. and henceforth categorized accordingly as rodenticides, insecticides, fungicides, and herbicides [5]. However, based on chemical composition, pesticides can be classified into five main groups as organochlorines, organophosphorus (OP), carbamates,

pyrethrin, and pyrethroids compound. The unnecessary consumption of those agrochemicals has undesirable effects on the ecosystem, including a decreased population of beneficial insects as well as risks to vulnerable species and bird habitats. Pesticide pollution is becoming one of the most severe challenges of common public health around the globe because of their particular application in the agriculture sector to assure crop yield and productivity [6]. In some cases, acute poisoning may occur because of inappropriate handling that ultimately causes adverse health effects because of long-term and low-level exposures. The widespread diffusion of such toxic chemicals adversely affects a great part of the population. A large number of people, categorized by different patterns, ages, and degrees of exposure, are at increased risk to the adverse effects of these chemicals. Workers who are involved in the manufacturing and application of pesticides are at a considerable risk of exposure, which typically occurs among specific users in public health. In the agricultural sector, farmers may get direct exposure to pesticides during spraying across the agricultural fields [7, 8]. In the general population, individuals may be at a risk of pesticide exposure on a daily basis in food and drinking water or to pesticide drift in domestic areas adjacent to spraying areas [9]. Given their hazardous effect on human health and the environment, the prime concern should be of their rapid and reliable detection by a convenient method. Although various laboratory-based analytical methods such as colorimetry, capillary electrophoresis (CE), thin-layer chromatography (TLC), gas-liquid chromatography (GLC), high-performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), and enzyme-linked immunosorbent assays (ELISA) have been employed so far, but these suffer from one and the other drawback such as the use of expensive instrumentation, time-consuming process, and requirement of trained personnel [5]. Therefore, there is a dire need to develop sensitive, rapid, economically feasible, and easy-to-use methods for the detection of these compounds in the environment. Such efficient detection methods could be developed using biosensors that are used in a variety of applications for prompt and accurate detection of different analytes such as biomolecules and chemical compounds [10]. Various nanomaterials are generally categorized into nanoparticles, nanotubes, and nanocomposites, which can be generally employed for the diagnosis, degradation, and adsorption of chemical pesticides. Carbon nanomaterials or nanoparticles (NPs) have specific characteristics, including a high surface-to-volume ratio, good electrical conductivity, catalytic action, and beneficial biocompatibility and can be simply modified with functional groups, which has made them be often used in pesticide biosensors to boost analytical efficiency [11].

It is well known that graphite and diamond are its most common allotropic form of carbon found in nature. Graphite, which is found as a natural mineral, consists of sp^2 hybridized carbon atomic layers that are stacked collectively through weak attraction forces such as van der Waals forces. Single-layer out of these carbon atomic layers are packed in a two-dimensional honeycomb structure called as “graphene” termed coined by Boehm et al. [12]. It remains almost impossible to isolate graphene monolayer for several decades before Geim and Novoselov [13] who reported a scotch tape method or micromechanical cleavage method for the isolation of graphene monolayer from silicon oxide substrate. Discovery of graphene monolayer awarded Geim and Novoselov the Nobel Prize in Physics “for groundbreaking experiments regarding the two-dimensional material graphene”.

Graphene, which consists of a one-atom-thick planar sheet comprising an sp^2 -bonded carbon structure with exceptionally high crystal and electronic quality, is a novel material that has emerged as a rapidly rising star in the field of material science [14, 15].

Research-based on graphene oxide (GO) and graphene is an established interdisciplinary field associated with different disciplines such as physics, chemistry, material sciences, and nanotechnology with still a lot of emerging ideas to be developed. The result of working experience on other carbon allotropes leads to rapid discoveries of exceptional electronic, optical, and mechanical properties of graphene. In particular, its extraordinary charge carrier mobilities, thermal, and electrical conductivity, collective with high transparency and mechanical strength make graphene a suitable material for biosensing applications.

These exceptional physicochemical properties indicate its potential for delivering new tactics and critical developments in electrochemical sciences. For instance, a large number of analytic molecules can be attached to the large surface of electrically conductive graphene sheets leading to the development of the highly sensitive miniaturized device. Direct electron transfer between graphene and redox species creates new prospects for sensing applications. Consequently, graphene has lately fascinated the attention of the scientific community worldwide.

1.1 Graphene and graphene oxide

GO is considered as a precursor for obtaining graphene via chemical or thermal reduction methods. It consists of single-layer graphite oxide, having various oxygen-containing groups, whose structure has been proposed through several models over the years [16–20]. Oxygen functional groups have been identified as typically in the form of hydroxyl, epoxy groups and carboxy, carbonyl, phenol, lactone, quinone on the basal plane, and at the sheet edges, respectively [21–23]. However, due to ambiguity pertaining to the nature and distribution of the oxygen-containing functional groups (Figure 1) [24, 25], its nonstoichiometric atomic composition, and the absence of adequately sensitive analytical techniques for GO characterization, its precise structure cannot be fully elucidated. The difference between GO and pristine graphene is as a result oxygenated groups present in GO which affect its electronic, mechanical, and electrochemical properties. Hence, they account for the differences between GO and pristine graphene [26]. The covalent oxygenated functional groups in GO give rise to remarkable structure defects, which are associated

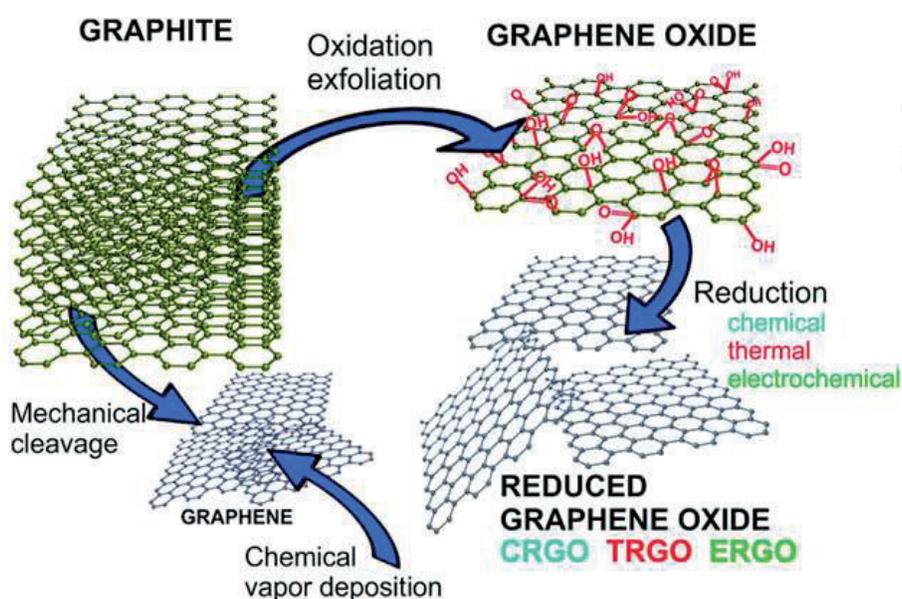


Figure 1. A schematic illustration of methods for the preparation of graphene, GO, and rGO by means of mechanical cleavage, exfoliation, CVD, and reduction methods including chemical, thermal, and electrochemical methods from graphite. Reprinted with permission from Ref. [25], Published by Elsevier.

with some loss in its electrical conductivity [27], limiting the direct application of GO in electrically active materials and devices. In contrast, these functional groups can also be proved advantageous for exploiting GO in numerous other applications. The presence of polar oxygen-containing moieties gives GO a hydrophilic character making it dispersible in many solvents particularly in water [24, 28, 29]. Subsequent stable GO suspension can be used for preparing thin conducting films using spin coating, drop-casting, or spraying methods [23] for further to be used as electrodes.

Furthermore, well-known chemistry strategies can be used for the functionalization of GO using oxygen-containing groups as a site for chemical modification, which subsequently can be exploited for immobilization of various electroactive species via covalent or noncovalent bonds different application in sensing or catalysis. Thus, the physicochemical properties of GO can be tuned very easily by engineering its chemical composition [21, 30, 31].

Hydroxyl, epoxy, and carboxyl groups present in GO are covalently bonded to the carbon atom with sp^3 hybridization are termed as oxidized region, disrupting the extended sp^2 conjugated network of honeycomb lattice in graphene, which can be viewed as an unoxidized region [32, 33]. sp^3 hybridized carbon clusters with oxygen-containing groups are uniformly but randomly distributed either above or below the GO plane [34]. Various microscopic and spectroscopic techniques have been employed for an in-depth analysis of the structure of GO. For instance, atomic force microscopy (AFM) provides the apparent thickness of the single-layer GO sheet beside the number of layers present [33, 35–37].

In contrast, conductive AFM demonstrates electrical defects found in GO [38]. Lately, one of the significant breakthroughs in determining the structure of GO, high-resolution transmission electron microscopy (HRTEM) has been employed for direct imaging of lattice atoms and topological defects present in single layer of GO [39–41]. Erickson et al. [39] identified specific atomic scale topographies of the GO monolayers, consisting of three major portions *viz.* holes, graphitic regions, and high-contrast disordered regions having approximate area percentages of 2, 16, and 82%, respectively.

According to the author, excessive oxidation and sheet exfoliation lead to the release of CO and CO₂ consequently forming holes in GO. They also proposed that graphitic regions are a result of incomplete oxidation of basal plane having the preserved honeycomb structure of graphene, whereas the disordered region is rich in oxygen functionalities, such as hydroxyl, epoxides, and carbonyls with no order between them.

The chemical composition of GO and its oxygenated functionalities have been recognized through various spectroscopic techniques, which include solid-state nuclear magnetic resonance (SSNMR) [42–44], X-ray absorption near-edge spectroscopy (XANES) [45–49], Raman spectroscopy [45–49], X-ray photoelectron spectroscopy (XPS) [49] and Fourier transform infrared spectroscopy (FT-IR) [47, 50, 51]. Three main peaks around 60, 70, and 130 ppm are assigned to carbon atoms bonding to the epoxy group, hydroxyl group, and graphitic sp^2 carbon, respectively [44], can be seen in a typical solid-state ¹³C magic-angle spinning NMR spectra of GO. Furthermore, three small additional peaks were also found at about 101, 167, and 191 ppm tentatively attributed to lactol, the ester carbonyl, and the ketone groups, correspondingly. XANES is another powerful tool for GO characterization, which provides information related to the degree of bond hybridization in mixed sp^2/sp^3 -bonded carbon, the specific bonding arrangements of functional atoms, and graphitic crystal structure's degree of alignment inside GO [49].

Besides, Raman and FTIR spectroscopy data support the presence of oxygenated species in GO and its degree of oxidation. Raman spectrum of a GO displays two characteristic bands namely a D-band at $\sim 1340\text{ cm}^{-1}$ and G-band at $\sim 1580\text{ cm}^{-1}$ [52].

The G-band is a distinctive peak of all sp^2 -hybridized carbon networks and due to first-order scattering from the doubly degenerate E_{2g} phonon modes of graphite whereas the D peak originates from structural imperfections and disorders produced by the addition of oxygenated groups on the carbon basal plane [52–54]. Hence, the intensity ratio of the D- and G-bands (I_d/I_g) points to the oxidation degree, disorders, and the size of sp^2 ring clusters in a matrix of sp^3 - and sp^2 -bonded carbon [53]. A significant decrease in I_d/I_g ratio was observed after thermal reduction, indicating a considerable regaining of conjugation in the graphitic structure after the defunctionalization of GO [45]. Functional groups can be recognized by the use of FT-IR spectroscopy and in the case of GO, it has reinforced the presence of hydroxyl (broad peak at 3050–3800 cm^{-1}), carbonyl (1750–1850 cm^{-1}), carboxyl (1650–1750 cm^{-1}), C=C (1500–1600 cm^{-1}), and ether or epoxide (1000–1280 cm^{-1}) groups [43, 47, 50].

Specific 2D structure and the presence of oxygenated functionalities are responsible for excellent properties of GO, which include electronic, optical, thermal, mechanical, and electrochemical properties along with chemical reactivity. Electronic properties like conductivity of GO sheets are dependent on its chemical and atomic structure; in particular, the degree of oxidation arises from disorders due to substantial sp^3 carbon. Generally, pristine GO films are insulating in nature with an energy gap in electron density of states, [55] as well as sheet resistance (R_s) about $10^{12} \Omega \text{ sq.}^{-1}$ or higher [56]. This inherent insulating nature of GO is strongly associated with the amount of sp^3 C–O bonding, which acts as transport barriers, leading to the lack or interruption of penetrating pathways among the sp^2 carbon clusters. However, reduction of GO, whether chemical or thermal assists the transport of carriers, [57] helps to bring R_s down to several orders of magnitude and transforming the material into a semiconductor or finally into graphene-like material [58–60]. Reduced GO has conductivity up to $\sim 1000 \text{ S/m}$, [61] and activation energy as $32 \pm 5 \text{ kcal/mol}$, estimated by the use of resistivity and temperature-programmed desorption (TPD) measurements [62]. Additionally, GO exhibits unique optical properties photoluminescence (PL) [63] occurring near-UV-to-blue visible (vis) to near-infrared (IR) wavelength range. Applications of this property have been sought in biosensing, fluorescence tags, and optoelectronic applications [64, 65].

GO also demonstrates excellent electrocatalytic properties [66–68], such as the electrocatalytic activity of GO toward oxygen reduction and certain biomolecules [66], oxidation of hydrazine by reduced GO [67]. In addition to this, GO is capable of showing high electrochemical capacitance for application in ultracapacitors [68, 69]. As compared to carbon nanotubes, reduced GO exhibit higher electrochemical capacitance and cycling durability, wherever specific capacitance for reduced GO and carbon nanotubes was found to be ~ 165 and $\sim 86 \text{ F/g}$, respectively [68].

The chemical reactivity of GO can be attributed to the presence of oxygenated functionalities and its disordered structure with defects. The reduction is the most important chemical reaction of GO, and it has been reduced by employing various approaches such as hydrazine, [70] sodium borohydride, [71] or hydroquinone, [72] in the liquid phase and the vapor phase using hydrazine/hydrogen [33, 52] or just by thermal annealing [52] or by using electrochemical techniques [73]. Chemical functionalization is another important chemical reaction involving GO, which includes the addition of other chemical groups to GO employing different chemical reactions. Oxygenated functionalities over GO surface play a very important role in its chemical reactions. Hence, it becomes an ideal approach to selectively chemical functionalize GO by utilizing reactions on these functionalities. Typically, covalent functionalization of GO can be realized using small molecules and polymers via activation, amidation, or esterification of either hydroxyls or carboxyl groups through coupling reactions [74–76]. For example, GO was made soluble in organic

solvents by rendering a coupling reaction with octadecylamine via amide formation, where carboxyl functionalities of GO were first activated by SOCl_2 [74]. Ring-opening reactions can be used to functionalize epoxy groups by nucleophilic attack at α -carbon by the amine [77]. For example, octadecylamine attachment to GO surface [57], attachment of an amine group-containing ionic liquid through ring-opening reaction with epoxy groups on GO [77] making chemically functionalized GO more soluble in water as well as other organic solvents.

Noncovalent functionalization of GO is also known in addition to covalent modifications. Noncovalent modification of GO can be accomplished by various forces and interactions including hydrogen bonding, van der Waals interaction, π - π stacking, cation- π interaction [78, 79]. Doxorubicin hydrochloride (Dox)/GO hybrid was synthesized through noncovalent interactions using π - π stacking and hydrophobic interactions between the sp^2 carbon matrix and quinone functionality of Dox as primary noncovalent interactions. Additionally, strong hydrogen bonding between hydroxyl and amine groups of Dox with hydroxyl and carboxyl groups of GO also helps in covalent modification [78].

The usefulness of GO can be estimated from this fact that along with its applications in electronics and displays, it can also act as a carbocatalyst for assisting hydration and oxidation reactions [80–82]. GO can be used as a catalyst for oxidation of alcohols and alkenes besides hydration of alkynes into aldehydes and ketones [80]. Furthermore, GO has a broad range of oxidation reaction, for example, it can oxidize olefins to diones, methylbenzene to aldehydes as well as other dehydrogenations [83].

2. Graphene oxide-based nanohybrids

GO and reduced GO (rGO) themselves have many advantageous properties, but a substantial amount of work is being done to utilize these materials in combination with other nanomaterials such as nanoparticles or polymers. Based on their morphologies, graphene oxide/nanoparticle nanohybrids can be roughly divided into two classes: first where nanoparticles are grown or decorated upon sheets of GO and second, nanoparticles are wrapped in GO sheets. Particularly in the first type, graphene/nanoparticle nanohybrid can be synthesized by combining GO or rGO with different nanoparticles such as metal nanoparticles, metal oxide nanoparticles, quantum dots, or silica nanoparticles depending upon the application desired. A unique combination of the nanoparticles and GO/rGO makes a novel synergistic nanomaterial with enhanced and diverse properties. For example, decorated metal or metal oxide nanoparticles over GO surface modify the local electronic structure and hence the charge transfer behavior of graphene [84] resulting in improved catalytic behavior of this nanocomposite. Alternatively, enhancement in sensitivity and selectivity has been observed in sensors derived from the combination of graphene material and nanoparticles having good conductivity and catalytic behavior [85, 86].

Similarly, in graphene oxide/polymer nanohybrids, surface functionalities present on GO surface groups can assist the combination of GO with polymers or synthesis of the polymer by different polymerization techniques [87, 88]. A typical modification strategy includes covalent bonding, that is, “Grafting to” and “Grafting from” approaches, whereas noncovalent modification includes π - π stacking, electrostatic interaction, and hydrogen bonding [89–91]. Similarly, fabrication strategies of graphene oxide/polymer nanohybrids synthesis include in situ polymerization, melt compounding, latex blending, solution mixing, and electro polymerization [92, 93].

3. Synthetic methodologies for graphene oxide/nanoparticle nanohybrids

Graphene oxide/nanoparticle nanohybrids in which GO/rGO sheets are decorated with nanoparticles having dimensions ranging from few nanometers to a couple of hundred nanometers [94] can be attained by attaching different types of nanoparticles to the surface of GO sheets either by in situ method or by ex situ method. In situ method comprises growing nanoparticles on the surface of GO; however, in the case of ex situ method, pre-synthesized nanoparticles are immobilized over the surface of GO. The presence of defects and oxygenated functionalities makes GO an encouraging templates for the attachment, nucleation, and growth numerous metal (e.g., Au [87, 95], Ag [96], Pt [97], etc.) and metal oxide nanoparticles (e.g., Fe₃O₄ [98], TiO₂ [99], ZnO [100], SnO₂ [101], Cu₂O [102, 103], MnO₂ [104], NiO [105, 106], La₂O₃, [107, 108], etc.). Subsequent graphene oxide/nanoparticle nanohybrid offers several unique and beneficial properties for various applications depending on individual characteristics showed by nanoparticles immobilized upon GO.

The following section includes the different methods for the preparation of graphene oxide/nanoparticles nanocomposites, for example, chemical reduction, hydrothermal route, and electrochemical method or ex situ synthesis, while primarily focusing on individual characteristics and advantages of each technique correlated to the properties of resulting graphene oxide/nanoparticle nanohybrids.

3.1 Chemical reduction method

Graphene oxide/metal nanoparticle nanohybrids are mostly synthesized by chemical reduction of their metal salt precursors such as HAuCl₄, AgNO₃, and K₂PtCl₄ utilizing reducing agents such as sodium citrate, ethylene glycol or polyethylene glycol, and sodium borohydride [96, 109], positively charged metallic salts get nucleated on negatively charged functional groups of GO which results in the growth of metal nanoparticles on its surface, while reducing GO to rGO, preserving the excellent electrical properties of rGO. Moreover, the density of metal nanoparticles can also be controlled by tuning the density of oxygenated functionalities on GO.

Chemical reduction technique is the most basic method for the preparation of Graphene oxide/noble metal nanoparticle nanohybrids. In particular, gold (AuNP) and silver nanoparticles (AgNPs) are among the most comprehensively studied nanomaterials with a wide range of biomedical applications such as diagnostics, imaging, drug delivery [110]. High biocompatibility and surface plasmon resonance are some of the very unique properties of noble nanoparticles making them of particular interest. These properties can be tuned to desired values according to the shape and size of the nanoparticles [111]. Furthermore, graphene oxide/noble metal nanoparticle nanohybrids are able to show SERS in addition to enhanced catalytic activity [112]. Reduced graphene oxide/AuNPs are the most common and utilized nanocomposites, which can be prepared by mixing HAuCl₄ with GO and sodium citrate, followed by reduction using NaBH₄ to form AuNPs while reducing GO to rGO [113, 114]. Similarly, instead of using HAuCl₄, AgNO₃ is used for reduced graphene oxide/AgNPs composite synthesis [112, 114]. In a similar way, reduced graphene oxide/platinum nanoparticle or reduced graphene oxide/palladium nanoparticle nanohybrids are formed by mixing graphene oxide with chloroplatinic acid (H₂PtCl₆) or tetrachloropalladic acid (H₂PdCl₄), followed by reduction with ethylene glycol or any other reducing agent.

3.2 Hydrothermal methods

Another very common method for synthesizing inorganic nanoparticles is the hydrothermal method. This method gives nanoparticles with high crystallinity and narrow size distribution over graphene oxide. Moreover, there is no need for post-annealing or calcination for reduced graphene oxide/metal nanoparticle nanohybrids. In general, the growth of nanocrystals is induced by high temperature and pressure, which is also responsible for the conversion of GO to rGO during the process. However, in most cases reducing agents are also added to make sure a complete reduction of GO [115].

The most common nanohybrids synthesized by the hydrothermal method are reduced graphene oxide/ metal oxide nanoparticle nanohybrids which include ZnO [116], TiO₂ [117], Fe₃O₄ [118], SnO₂ [119], etc.

Reduced graphene oxide/metal oxide nanoparticle hybrids illustrate their specific properties such as higher capacitance, which depends upon nanoparticle size, shape, and crystallinity; also, it helps in the suppression of restacking and agglomeration in graphene oxide sheets. Furthermore, these nanocomposites also exhibit enhancement in electron conductivity, high surface area as compared to GO or graphene, also shortened route for ion transfer, which in all responsible for their higher electrochemical activity. For instance, reduced graphene oxide/SnO₂ nanosphere nanohybrid exhibited significantly enhanced formaldehyde sensing performance compared to the pristine SnO₂ nanospheres [119]. Alternatively, reduced graphene oxide/magnetic nanoparticle nanohybrid has been prepared using FeCl₃ as an iron source and ethylene glycol as a reducing agent [120]. Resulting nanohybrid displayed outstanding electrical conductivity as well as magnetic properties. Similarly, chalcogenide quantum dots, for example, CdS [121], ZnS [122], Cu₂S [123], and MoS₂ [124], etc. have been successfully immobilized on graphene oxide exploiting hydrothermal methods.

3.3 Electrochemical deposition method

The electrochemical deposition method is a very simple, low cost, fast, easy to miniaturize, highly stable, reproducible, and green technique for preparation of graphene oxide/nanoparticle composite [125]. The advantage of this technique is that the size and shape of the nanoparticles to be deposited can be precisely controlled using varying the conditions of electrochemical deposition. Electrochemical deposition methods have been established for the fabrication of a vast variety of graphene oxide/metal nanoparticle composites for noble metals like Au, [126] using cyclic voltammetry (CV), which helped in fabricating an electrode for the determination of trace amount As(III) employing square wave anodic stripping voltammetry, Ag, [127] for carrying out the oxidation of different amino acids such as glycine, alanine, leucine, aspartic and glutamic acids using cyclic voltammetry and amperometric techniques. Similarly for Pt [128], Pt nanoparticles embedded rGO on glassy carbon electrode are utilized to carry out electrooxidation of formic acid. Generally, a typical electrochemical deposition experiment is consisting of three basic steps, that is, assembly of graphene oxide sheets on the electrode, graphene oxide-coated electrode immersion in an electrolytic solution of selected metal precursors, and potential applied across electrodes. A majority of research has concentrated on using electrochemical deposition methods for synthesizing graphene oxide/metal nanoparticle composite, but there are some reports for preparation of graphene oxide/metal oxide nanoparticle composite synthesis by the same technique. For instance, Cl-doped n-type Cu₂O nanoparticles with a direct band gap of ca. 2.0 eV [128] have been deposited on rGO electrodes with a subsequent carrier concentration of up to $1 \times 10^{20} \text{ cm}^{-3}$ [129].

3.4 Graphene oxide/encapsulated nanoparticles

Flexible and 2D sheet-like structure of graphene oxide and its derivatives help in wrapping or encapsulating nanoparticles in the range from 100 nm to few micrometers.

GO and rGO sheets are most commonly used for nanoparticle encapsulation due to their hydrophilic nature and ease of fabrication. Noncovalent bonds are responsible for this type of encapsulation; for instance, modification of nanoparticle surface with a positive charge is used for electrostatic interaction with negatively charged GO [130, 131]. Encapsulation of a variety of nanomaterials, for example, polymer, inorganic nanoparticles, metal, and metal oxide nanoparticles, can be achieved by controlling the cracked size of GO and rGO, thus obtained composite offer enhanced properties and additional advantages. For example, enhancement in electrical, optical, and electrochemical properties has been observed for graphene oxide encapsulated nanoparticles, also suppression of aggregation of small nanoparticles [132, 133]. Moreover, leaching of nanoparticles is reduced in graphene oxide encapsulated nanoparticles due to the high amount of contact between GO and nanoparticles, making them more stable. Several reports have revealed the encapsulation of metal oxide nanoparticles with graphene oxide. For example, rGO encapsulated cobalt oxide nanoparticles have shown a very high reversible capacity (1000 mAh g^{-1}) over 130 cycles, much more than the normal cobalt oxide nanoparticles used for capacitors [131]. Moreover, rGO encapsulated Co_3O_4 nanofibers-based sensor exhibited an excellent sensitivity with a fast response and recovery to different concentrations of ammonia from 5 to 100 ppm at room temperature [134]. Furthermore, a nonenzymatic electrochemical sensor based on 3D porous phase graphene oxide sheets encapsulated chalcopyrite (GOS@CuFeS_2) nanocomposite is reported for the detection of methyl paraoxon [135]. Encapsulation of nonconducting silicon oxide nanoparticles within conducting rGO can be used as the “bridging-material” in a field-effect transistor-based biosensor [130, 136]. Similarly, Si nanoparticles encapsulated with rGO via electrostatic interaction using APTES has also been reported [137, 138], resulting in less destruction and aggregation of SiNPs as compared to pristine nanoparticles. It also exhibited a high reversible capacity of 902 mAh g^{-1} after 100 cycles at 300 mA g^{-1} when used as the electrode.

4. Graphene oxide-based nanohybrids as pesticide biosensors

An analytical device that utilizes a biological sensing element to detect a specific analyte molecule or family of the analytical molecule is called as biosensor. Biosensors can seek applications in diverse fields such as food safety, environmental monitoring, and biomedical field. Generally, biosensors are consisting of two basic parts: first receptor, any organic or inorganic material that interacts with analytes. The second part, a transducer, which converts a recognition event, happened between analyte and receptor, into a measurable signal. Evaluation of biosensor's performance is measured by its sensitivity to target, linear range, the limit of detection, dynamic ranges, reproducibility, precision in response, and selectivity [139]. Other parameters that are also important include the sensor's response time, ease of use, portability, storage, and operational stability. Graphene oxide/nanoparticle nanohybrids are known to be well suited for application in biosensing because of the rise of new advantageous properties due to the combination of graphene oxide and nanoparticles. Here, in this section, a detailed aspect of graphene oxide nanohybrid-based biosensors, specifically electrochemical biosensors are discussed.

Electrochemical sensors are the largest group of sensors for detecting or analyzing various molecules by directly converting biological recognition event into an electrical signal. A typical electrochemical biosensor is composed of a three-electrode system with a working electrode consisting of a biological recognition element, counter electrode, and reference electrode separated by suitable electrolytes. Based on their biological recognition process, electrochemical biosensors can be divided into two main groups: first, affinity-based sensors, and second, catalytic sensors. The basic principle of working in affinity biosensors is the measurable electric signal that arises due to the interaction of the biological component like an antibody, enzyme, nucleic acid, or a receptor and target molecules. Whereas in catalytic sensors, incorporated nanoparticles or enzymes recognize the analyte molecules and produce an electroactive species by catalysis. The electrical signal produced by the electroactive species is then correlated to the concentration of the target analyte molecule. Commonly used techniques in electrochemical biosensing include different forms of voltammetry (e.g., cyclic, linear sweep, differential, square wave, etc.) and amperometry [139].

The large surface area of graphene oxide nanohybrids is beneficial for the immobilization of biomolecules to use it as a platform for biosensing material. Furthermore, the synergistic effect of graphene oxide also enhances achievable sensitivities and measurable ranges. Most commonly biomolecule immobilized biosensors utilize enzymes, antibodies, and DNA as biomolecules.

Lately, enzyme immobilized GO nanohybrids-based biosensors have fascinated a lot for the detection of various kinds of analytes. The most common example is the determination of glucose, which has an important role in the diagnosis and therapy of diabetes. Apart from glucose oxidase based biosensors, other enzyme-based biosensors are also known with high sensitivity and selectivity, which includes biosensors based on alcohol dehydrogenase [140], microperoxidase [141], horseradish peroxidase [142], tyrosinase [143], urease [144], and acetylcholinesterase [145]. Acetylcholinesterase (AChE) is a catalytic enzyme present in the central nervous system, which catalyzes the hydrolysis of acetylcholine and choline esters. Its catalytic ability is severely affected by the presence of different types of organophosphorus and carbamate pesticides even in trace amounts. AChE can be easily immobilized on the surface of graphene oxide-based nanohybrids which offer a large surface area and abundant active sites so that they can be used for developing AChE inhibition-based biosensors [146].

Although a lot of work has already been reported on graphene-based biosensors; however, due to novel microbes and diseases associated with them, excess use of toxicants in food and feed products, nonjudicial use of pesticide and day by day disintegrating environmental conditions urgently need tools for detection of such chemicals and biologicals, and hence, more rapid and urgent requirement for the development of biosensors arises. In the past 2 years, countless new graphene oxide nanohybrids-based biosensors are reported. For example, Yao et al. [147] reported an electrochemical biosensor based on the inhibition of AChE, using a gold nanocage/graphene oxide-chitosan nanocomposite-modified screen-printed carbon electrode for detection of chlorpyrifos (**Figure 2**). Where the biosensor showed good electrocatalytic activity for the oxidation of enzymatically produced thiocholine and detected chlorpyrifos concentrations as low as 3 ng L^{-1} .

Similarly, Bao et al. [148] developed a biosensor for malathion detection based on three-dimensional graphene-copper oxide nanoflowers nanocomposites electrode, and the group was able to obtain a wide linear relationship to malathion concentration ranging from 3 pM to 46.665 nM with a theoretical limit of detection at 0.92 pM . Moreover, Cui et al. reported a very stable electrochemical AChE biosensor for detection of dichlorvos by adsorption of AChE on chitosan, TiO_2 sol-gel,

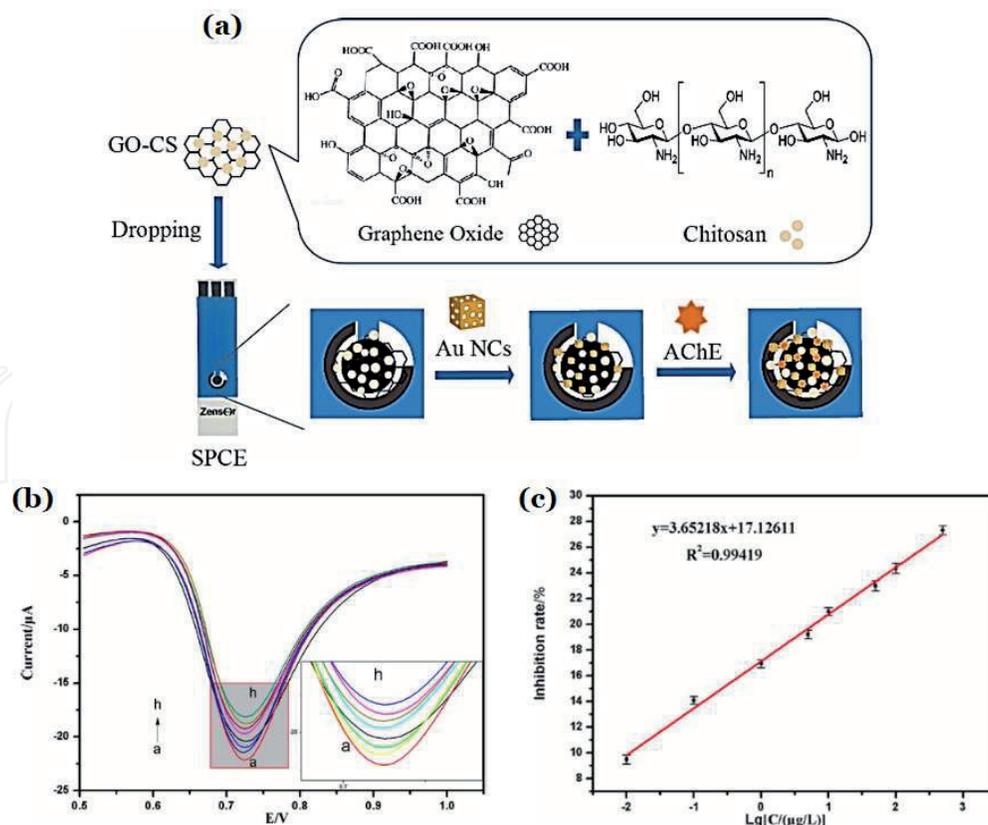


Figure 2. (a) A schematic diagram of the construction process of AChE biosensor based on screen-printed electrodes, (b) and (c) DPV behavior, and percent inhibition obtained by biosensor in the presence of chlorpyrifos. Reprinted with permission from ref. [147], published by the Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

and rGO-based many fold matrix, with the linear range varying from 0.036 μM to 22.6 μM , limit of detection of 29 nM and total time for detection about 25 min. Furthermore, electrochemical acetylcholinesterase biosensor based on the silver nanowire, graphene, TiO_2 sol-gel, chitosan, and acetylcholinesterase is fabricated by Zhang et al. [149] (**Figure 3**).

On a similar note, Zhang et al. [150] developed a highly sensitive AChE amperometric biosensor based on conjugated polymer and Ag-rGO- NH_2 nanocomposite. Group used a slightly different method for electrode fabrication where authors first electrochemically polymerized 4, 7-di (furan-2-yl) benzothiadiazole on electrode surface followed by deposition of Ag-rGO- NH_2 nanocomposite. The biosensor is found to be biocompatible with high efficiency having the linear range from 0.099 to 9.9 $\mu\text{g L}^{-1}$ 0.032 $\mu\text{g L}^{-1}$ for malathion and 0.001 $\mu\text{g L}^{-1}$ for trichlorfon. Moreover, Mogha et al. [151] developed a biosensor for the detection of Chlorpyrifos using rGO supported Zirconium Oxide immobilized AChE (**Figure 4**). The group is able to detect the Chlorpyrifos in two linear ranges first from 10^{-13} to 10^{-9} M, whereas the second linear range was observed between 10^{-9} and 10^{-4} M.

Aghaie et al. [152] developed a nonenzymatic biosensor for the detection of paraoxon ethyl. A graphene-based NiFe bimetallic phosphosulfide nanocomposite biosensor is fabricated, where square wave voltammetric is used as a detection technique. The linear range for the detection of paraoxon methyl is found to be 12.3–10,000 nmol L^{-1} and limit of detection as 3.7 nmol L^{-1} .

Furthermore, a group of Hondred et al. [153] (**Figure 5**) utilized salt impregnated inkjet maskless lithography for preparation of 3D porous architected graphene for application in biosensing of paraoxon and supercapacitor. The as developed biosensor showed a wide linear range from 10 to 500 nM, low limit of

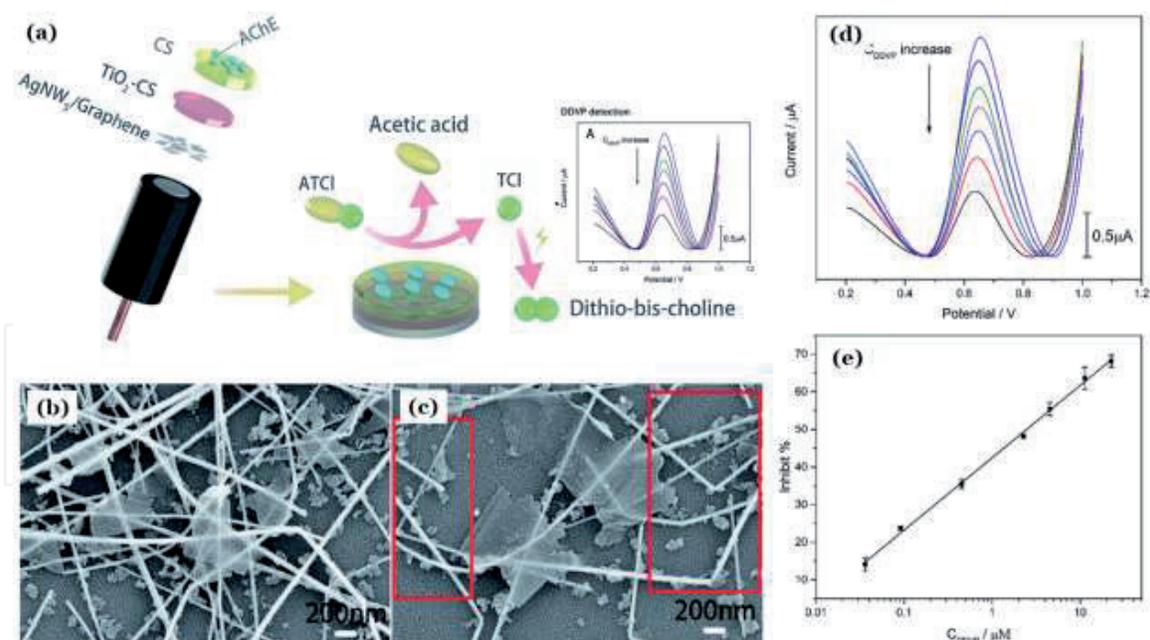


Figure 3. (a) Schematic illustration of the AChE based biosensor and its working mechanism to ATCl. (b) and (c) SEM images of Gra/AgNWs/SiO₂ nanohybrids, where large graphene sheet is enhancing the connection with AgNWs in (b) with small graphene pieces further improving the performance of biosensor (in red rectangle shown in (c)), while (d) and (e) represent the inhibition of AChE in presence of DDVP using the biosensors. Reprinted with permission from ref [149], Published by The Royal Society of Chemistry.

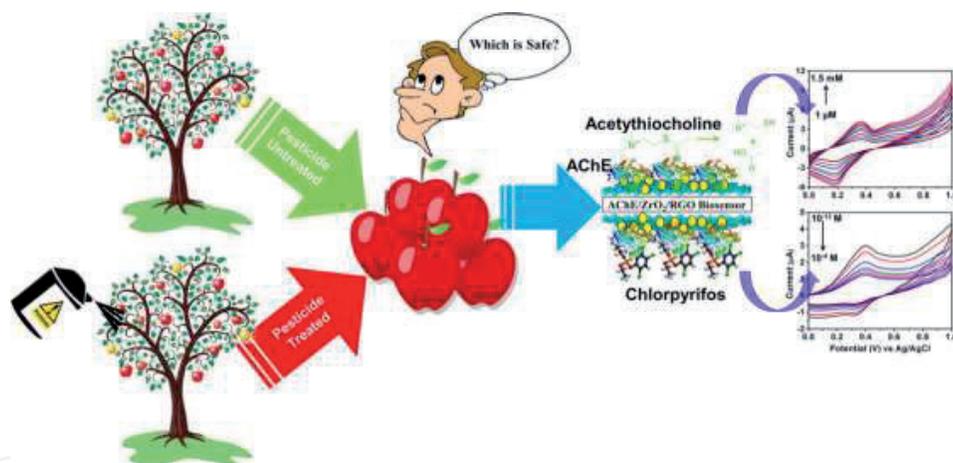


Figure 4. An illustration of rGO supported Zirconium Oxide immobilized AChE nanohybrid as a biosensing platform for chlorpyrifos detection. Reprinted with permission from Ref. [151], published by Elsevier.

detection of 0.6 nM with high sensitivity of 12.4 nA nM⁻¹; moreover as a supercapacitor, it demonstrates a high energy density of 0.25 mW h cm⁻³ at a power density of 0.3 W cm⁻³. Similarly, another AChE biosensor is developed based on a film of gold nanoparticles/three-dimensional graphene, by Dong et al. [154], for methyl parathion and malathion detection in a linear range from 1.0 × 10⁻¹⁰ to 1.0 × 10⁻⁶ g L⁻¹, having limits of detection as 2.78 × 10⁻¹¹ g L⁻¹ and 2.17 × 10⁻¹¹ g L⁻¹.

Some more examples of biosensors based on graphene oxide nanohybrids for the detection of different types of pesticides such as methyl parathion [155–158], carbofuran [155, 157, 159], chlorpyrifos [156], imidacloprid [160], phoxim with graphene/GCE [161], poly(3-methylthiophene)/nitrogen-doped graphene [162], and carboxylic chitosan /silver nanoclusters-rGO [163], paraoxon and chlorpyrifos with TiO₂-GO/UiO-66 composite [164], carbaryl with MWCNTs/GO nanoribbons [165], carbaryl and chlorpyrifos with AgNPs-CGR/NF composite [166],

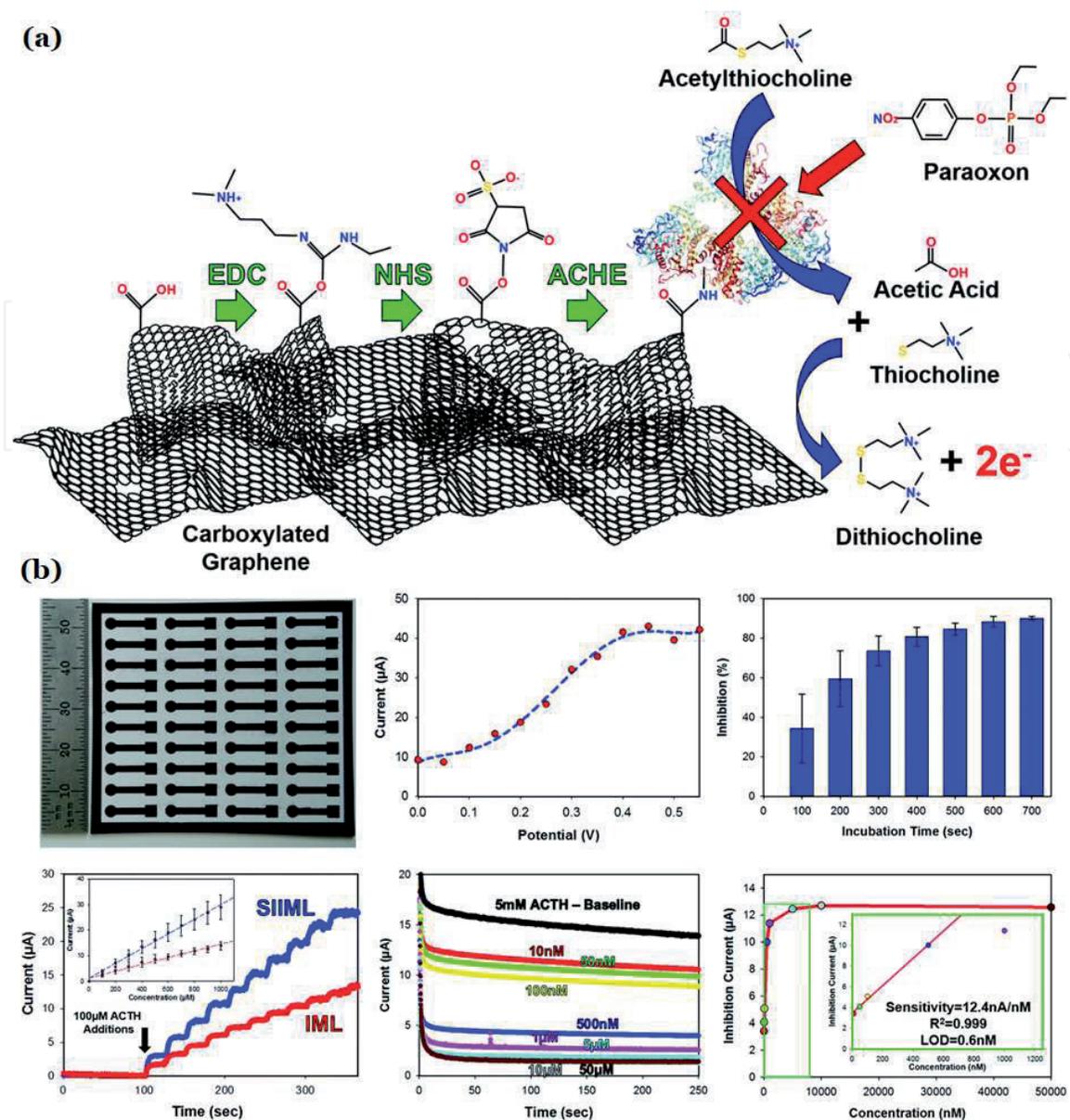


Figure 5. (a) Schematic diagram of AChE biosensor portraying the functionalization approach for pesticide detection using EDC/NHS. (b) AChE pesticides biosensor characterization with photograph, activity, sensitivity, and comparison between salt impregnated inkjet maskless lithography (SIIML) and inkjet maskless lithography (IML)-based biosensors. Reprinted with permission from Ref. [153], published by The Royal Society of Chemistry.

chlorpyrifos and carbofuran with ZnONPs-CGR/NF composite [167], carbaryl and monocrotophos with ionic liquid-functionalized graphene /gelatin [168], monocrotophos with Prussian blue nanocubes [169], malathion and carbaryl with rGO-AuNP/ β -cyclodextrin/Prussian blue-CS nanocomposites [170], fenitrothion with cerium oxide nanoparticle-decorated rGO [171], diuron with rGO-AuNPs [172], paraoxon-ethyl with rGO-AuNPs/polypyrrole [173], carbaryl with Graphene/polyaniline nanohybrid [174], carbaryl with an electrochemically induced porous GO network [175], and methyl parathion and malathion with plant esterase—Chit/AuNPs-graphene nanosheets [176].

5. Conclusion and future aspects

Graphene oxide is an attractive material that has gathered ever accumulative interest from the scientific community over the past several years. Owing to its

extraordinary properties, graphene oxide and its derivatives are already being exploited in a wide variety of applications comprising electronics, energy, biosensors, catalysis, green chemistry, etc. Though, in the last decade, the relentless search for new opportunities benefiting from graphene oxide has led to the introduction and evolution of graphene oxide-based nanohybrids, which combine matchless and beneficial properties of nanomaterials/nanotechnology with those of graphene oxide to yield valuable and synergistic effects.

In this chapter, we have discussed the brief history of graphene oxide and graphene, emphasizing the structural details of graphene oxide and excellent properties associated with it. Graphene oxide-based nanohybrids show the synergistic effect of having properties of both graphene oxide as well as other constituting material whether nanoparticle or polymer. Synthetic mythologies of graphene oxide-based nanohybrids have also been discussed here in this chapter, in particular, graphene oxide/nanoparticle nanohybrids. Finally, applications of graphene oxide-based nanohybrids were presented in the field of biosensors and catalysis. In the case of biosensors, the main emphasis was given to the largest class of biosensors, that is, electrochemical biosensors, which consist of mainly enzyme biosensors and electrochemical DNA sensors, but some cases of other electrochemical sensors were also demonstrate. Applications of these graphene oxide-based hybrids in catalysis were also discussed emphasizing their use as an organic reaction catalyst, photocatalysts for the degradation of environmentally harmful molecules.

In conclusion, we have highlighted the properties of graphene oxide-based nanohybrids wherein these nanostructures can bring excellent synergistic advantages to a wide variety of biosensing applications. While promising, the field of graphene oxide-based nanohybrids is still not completely exhausted and several intriguing issues must be resolved before its maximum potential can be achieved. Besides, we envision that the evolution of this technology will result in the use of graphene oxide-based nanohybrids in a much wider range of applications by employing high quality and large-scale fabrication of these materials to minimize the cost leading to their commercialization. We also hope that this chapter has motivated attention from various disciplines that will gain benefits from the expansion of graphene oxide-based nanohybrids development for applications in numerous other fields of interest.

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