

Review

Nanocomposite Materials Based on Electrochemically Synthesized Graphene Polymers: Molecular Architecture Strategies for Sensor Applications

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Abstract: The use of graphene and its derivatives in the development of electrochemical sensors has been growing in recent decades. Part of this success is due to the excellent characteristics of such materials, such as good electrical and mechanical properties and a large specific surface area. The formation of composites and nanocomposites with these two materials leads to better sensing performance compared to pure graphene and conductive polymers. The increased large specific surface area of the nanocomposites and the synergistic effect between graphene and conducting polymers is responsible for this interesting result. The most widely used methodologies for the synthesis of these materials are still based on chemical routes. However, electrochemical routes have emerged and are gaining space, affording advantages such as low cost and the promising possibility of modulation of the structural characteristics of composites. As a result, application in sensor devices can lead to increased sensitivity and decreased analysis cost. Thus, this review presents the main aspects for the construction of nanomaterials based on graphene oxide and conducting polymers, as well as the recent efforts made to apply this methodology in the development of sensors and biosensors.

Keywords: electropolymerization; nanomaterials; nanotechnology; graphene-oxide; conductive-polymer; electrochemical sensors



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1. Introduction

Since its first appearance in the literature in 2004, the scientific and technological transformation driven by graphene has been remarkable in recent years [1–3]. This success has been due to the impressive and extraordinary properties presented by this carbon material with a sp^2 single layer of hexagonally arranged carbon atoms [4,5]. Its impressive theoretical surface area can be highlighted, in comparison, to carbon nanotubes (CNTs), for which the inner area of the tube is not readily accessible for reactions or modifications. In addition, graphene also has impressive electron mobility along its π -conjugated network, drawing attention to applications in electronic devices [3–7].

In addition to its exceptions and exciting properties, modifications to the structure of graphene have been made to expand the possibilities for applications [4,8–10]. For applications in electronic devices, high-quality graphene is not applicable due to the absence of a band gap [11,12]. Modifications to its structure are needed to decrease its conductive ability to transform it into a semiconductor [11–13]. Another concern for technological applications is that graphene is not reactive. Graphene has a relative chemical inertia due to its π -conjugated network. In this regard, significant efforts have been made, and a variety

of graphene-based species have been synthesized and investigated, such as graphene quantum dots (QDGs), graphene doped with heteroatoms (N-doped graphene, S-doped graphene, etc.), graphene nanopallots, graphene oxide and others [14,15].

With the functionalization of graphene sheets, a new horizon of possibilities has opened up, allowing the incorporation of graphene in different systems to improve the properties and characteristics of different materials. Thus, a new field has been formed: (nano)composite materials based on graphene [7]. Graphene-based composites include the use of inorganic materials, organic crystals, organometallic structures (MOFs), biomaterials and polymers [16]. These materials are extensively exploited in applications such as batteries [17], supercapacitors [18], fuel cells [19], photovoltaics [20], sensing platforms [21], and others.

In particular, graphene oxide (GO) has received constant attention. As previously mentioned, GO has emerged as a viable alternative to incorporate and apply graphene in different systems and materials [1,2]. Obtaining GO is simple and low cost compared to graphene, making it possible to produce it industrially. Its structure consists of a single layer of sp^2 and sp^3 atoms with oxygenated functional groups distributed over the basal plane (mainly hydroxyl and hydroxy) and the edges of the GO sheets (mainly carboxy, carbonyl, phenol, lactone and quinone) (Figure 1) [22]. The ease of handling and low cost of synthesis of graphene oxide comes at the cost of a drastic decrease in the electronic conductivity of GO compared to high-quality graphene. However, an increase in the conductivity of GO can be obtained by reducing the functional groups oxygenated by chemical (rGO) and electrochemical (rGO or ERGO) processes after incorporating GO into the desired system [23].

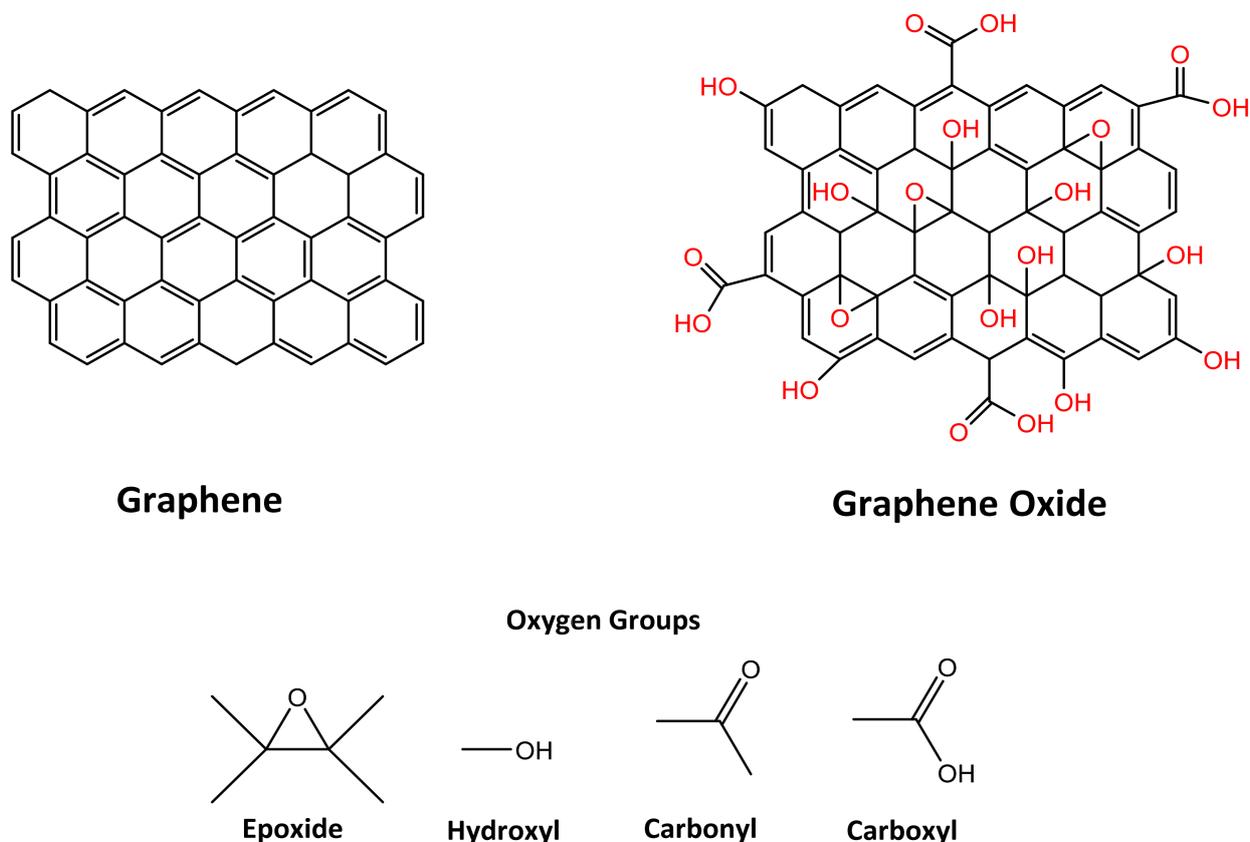


Figure 1. Graphene and graphene oxide structures and graphene oxide oxygenated groups.

The graphene-composite material synthesis step is a fundamental part of modulating the properties and characteristics that allow the material to achieve maximum efficiency. Among the various synthesis strategies, electrochemical syntheses have interesting and

remarkable characteristics, mainly for the construction of thin films intended for applications in optical electronic devices, data and energy storage and as sensors [6,24,25]. Low-cost syntheses, with few preparation steps, added to the possibility of control over the electrosynthesized material, make electrochemical methods attractive alternatives for the construction of reduced graphene oxide-based materials [25].

Graphene-polymer (nano)composites have been the focus of attention and intense studies [7,25,26]. This interest mainly arises from the synergistic effect generated by filling a polymer matrix with graphene, which results in a 3D material with improved mechanical, thermal, electrical and optical properties for the polymer [27]. For example, aimed at the use of a graphene-polymer couple in electrochemical sensors, the improvement in a material produced by the introduction of graphene into its structure may lead to increased sensitivity to the molecule of interest, since there is an improvement in the electronic communication of the material [25,28]. In addition, the incorporation of graphene can also act to improve a material's robustness due to increased mechanical and thermal stability [29]. In fact, the graphene-polymer set demonstrates exceptional skills for the construction and application of wearable sensors since they have high biocompatibility and remarkable flexibility [30].

Despite the diverse and interesting advantages, at present, there is still no review work addressing the focus of electrochemical strategies to synthesize graphene-polymer (nano)materials for sensing applications. In view of this, the present review aims to highlight the main characteristics of electrochemical techniques for the electrosynthesis of graphene oxide-based materials, perform an overview of the details to be considered during the electrodeposition of graphene oxide, and present the main highlights in the field of sensors based on graphene-based materials in the past 5 years, pointing out their advantages, possibilities, challenges and presenting a future perspective on the subject.

2. Electrochemical Synthesis

2.1. Main Aspects

The synthesis of materials on conductive substrates via electrochemical methods has been shown to be a consolidated field in recent decades [31–36]. For applications in electronic devices, electrosynthesis is attractive because the sensitive material, at the end of the synthesis process, is deposited onto the desired substrate surface. This avoids the loss of material and reduces steps such as filtration, washing, purification and others, and just involves the final deposition of the material onto the target substrate. For electrochemical sensors and capacitors, step-shortening results in a better cost/benefit ratio for the built device [37–39]. For example, in comparison with other coating techniques, such as dip, spin and spray coating, several steps of processing can result in low reproducibility and material waste [40]. On the other hand, electrochemical techniques offer ample control over the deposited material, allowing the construction of nanometric films as well as a high reproducibility of the response due to the control over deposition and low material waste.

Electrodeposition and electrosynthesis, more specifically, can be performed by applying potentials (potentiometric methods) or by applying current (galvanostatic methods) (Figure 2) [41–43]. These techniques can be easily modulated and are can be used to deposit various materials in solution in a controlled manner using different deposition potentials. There is also the possibility of mixing these techniques in the same electrosynthesis, further expanding the horizon for the possible applications of these techniques. Another advantage is the possibility of observing the progress of electrosynthesis in real time using graphs provided as voltammograms and chronoamperograms, which, in turn, is not possible in chemical syntheses.

2.2. Electrodeposition of Graphene Oxide

As highlighted above, the use of electrochemical deposition techniques has the advantage of real-time monitoring of the progress of electrosynthesis [6]. Through these methods, it is possible to check the increase or decrease in the current values, check the time necessary for saturation or obtain a desired amount of material. By using voltammetry, there is still

the possibility of visualizing oxidation and reduction peaks for oxygenated groups present in graphene oxide sheets [44–46].

Regardless of the electrochemical technique intended to be used for the construction of a sensor, some details must be taken into account to obtain a suitable electrodeposition. Figure 3 schematically draws attention to some important points to be considered prior to the electrodeposition of graphene oxide sheets, and, consequently, of a graphene-material composite.

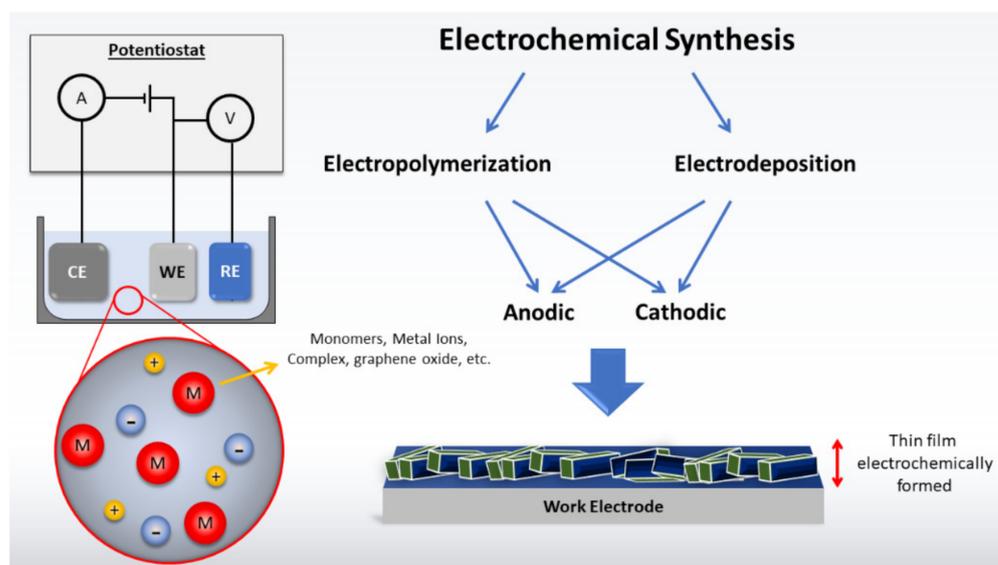


Figure 2. Schematic representation of the main components of a conventional electrochemical cell used for performing electrosynthesis. The main techniques used are highlighted, and in all of these methods, it is possible to obtain the thin film formation for the electrodeposited/electropolymerized material.

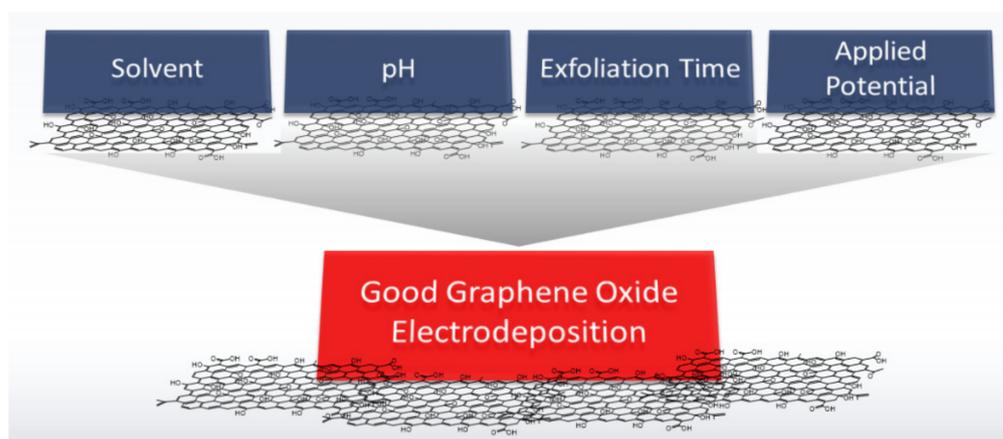


Figure 3. The main concerns that must be considered for obtaining an acceptable electrodeposition of graphene oxide on conductive substrates using electrochemical techniques.

The solvent is the first highlight. Thus, it is a necessary condition that the materials that will constitute the nanocomposite film can be solubilized or can easily form stable dispersions in an electrolytic solution. In the case of one-step routes, the solvent must necessarily meet this need for both the monomer (or nanoparticle) and graphene oxide since the two materials will share the same solution.

Electrosynthesis that makes use of environmentally friendly solvents, such as water, is preferable. In this sense, graphene oxide has a great advantage in terms of forming stable dispersions in aqueous solution due to the strong hydrogen bonding of its oxygenated groups with water molecules, mostly via hydroxyl groups (Figure 4) [5,47–49]. In addition to solubility in water, graphene oxide also has stability and easy dispersion properties in other solvents, such as ethylene glycol, dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) [49].

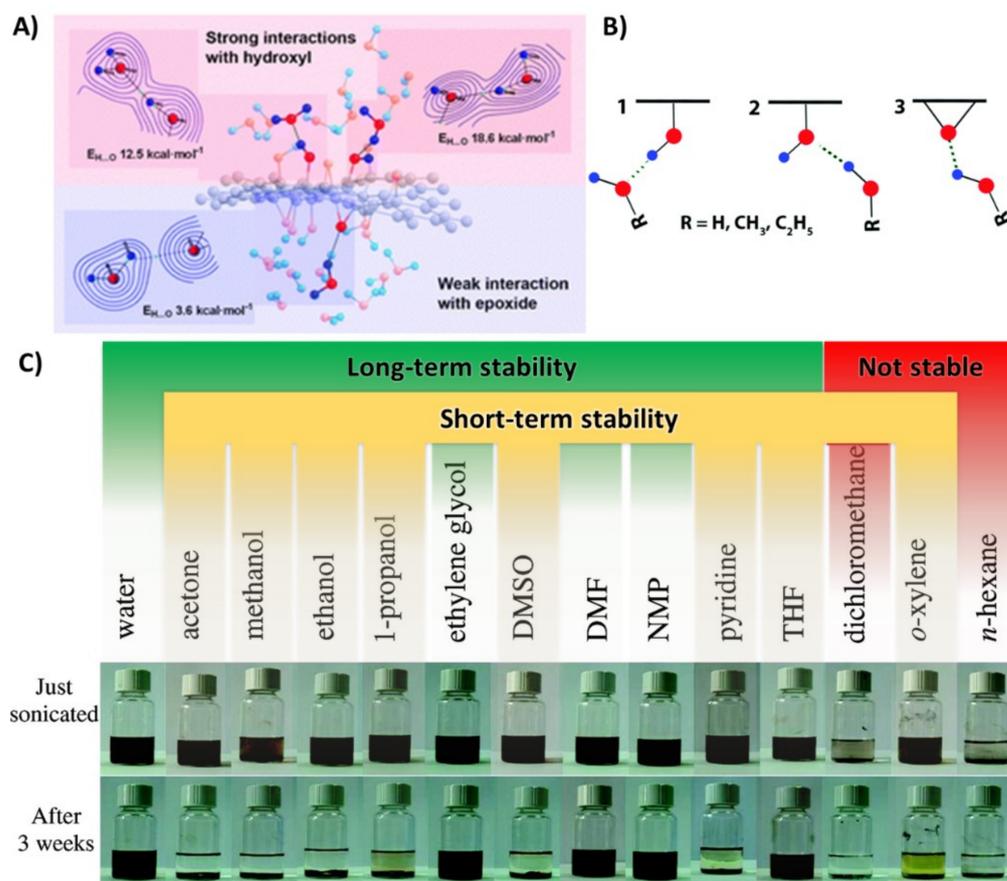


Figure 4. (A) Optimized structures of the solvates of graphene oxide with water based on a theoretical approach (B) Schematic representation of the three types of hydrogen bonding in the graphene oxide (GO) solvates. where red balls denote O atoms and blue balls denote H atoms. (1) and (2) show the bonding to the tertiary alcohol. (3) shows the bonding to the epoxide group. Reprinted (adapted) with permission from [47]. (C) Graphene oxide relative stability in different solvents immediately after sonication and after 3 weeks. Reprinted (adapted) with permission from Ref. [49] Copyright 2012 American Chemical Society.

Prior to the electrosynthesis process, exfoliation of graphene oxide in solution is necessary to ensure that the sheets are dispersed, reducing the possibility of aggregation to achieve more efficient electrodeposition. This step is extremely important to achieve electrodeposition of a few layers of graphene oxide. This issue is easily resolved by applying an ultrasound bath for a brief period that can vary from a few minutes to a few hours, depending on the conditions of electrosynthesis and the power of the ultrasound device. However, it is important to note that the application of ultrasound can also alter the characteristics of graphene oxide sheets, such as changes in the oxidation rate of GO and generation of defects in the sheets, and both parameters play a significant role in the formation of the composite as well as the desired characteristics [50,51].

Graphene oxide influences the pH of the medium on its sheets as a function of the proton balance with its oxygenated groups [48,52,53]. Thus, for the direct electrodeposition of graphene oxide sheets on conductive electrode substrates (glassy carbon, Pt, Au, Ni, etc.), the chosen pH value will influence the residual charge of the graphene oxide sheets depending on whether or not their oxygenated groups are protonated [54,55]. This will directly influence the potential required for electrodeposition, as well as the interaction between graphene oxide and the monomer/polymer during the formation of the composite material [48]. For most studies of electrodeposition of graphene oxide on electrodes, phosphate buffer solutions (PBS) at pH values close to 7 are commonly used [46,56]. The pH 7 buffer solution is used to ensure that the H^+ concentration in the solution does not change during the process of reducing oxygenated groups. However, several studies have shown satisfactory electrodeposition at varying pH values [6,57–62]. Indeed, Hilder and collaborators demonstrated that graphene oxide is stable and has no disadvantage in electrodeposition performance in the pH range of 1.5 to 12.5 [44].

Another key point is the applied potential, or potential range, in the graphene electrodeposition process. The values for this parameter vary widely between different studies, depending on the chemical constitution of the chosen electrode and the pH values of the medium, but most studies report the application of a potential of approximately -1.0 V (vs. SCE) [56]. The intense cathodic potential aims to promote the reduction of the oxygenated groups of the graphene oxide sheets, making their deposition on the electrode possible [61,63–66]. When reduced or partially reduced (depending on the conditions, the electrodeposited graphene oxide will be partially reduced), the sheets become more insoluble and stick to the surface of the conductive material [56,61,64,65]. However, it was verified in a recent study by our research group that electrodeposition with cathodic limit potentials of -0.30 V (vs. SCE) is also viable [67]. Indeed, some studies have shown graphene oxide electrodeposition in the anodic regime due to the electrostatic attraction between the positively charged electrode surface and negatively charged graphene oxide sheets [68,69].

The amount of electrodeposited material (the number of layers or its thickness) on an electrode surface will depend mainly on the application time of the cathodic potential (time or number of cycles used), which may result in the deposition of a few monolayers or coarse deposits [70]. Again, the choice of morphology will depend on the need and purpose of applying the material. However, thicker deposits tend not to show satisfactory electrochemical responses. One possibility to guarantee the deposition of only a few sheets of graphene onto an electrode is to apply electroexfoliation after electrodeposition. This occurs by means of pulses of cathodic potentials applied to force the removal of graphene sheets with low conductivity quality [70]. Through the application of an alternating pulse, sufficiently cathodic potentials are applied in small time intervals, sufficient for local generation of H_2 gas in the conductive regions and exfoliation of the material. However, there is not enough time for total material degradation. The result is that reduced graphene monolayers are obtained on the electrode surface (Figure 5).

As mentioned, the reduction of graphene sheets plays a significant role in the deposition mechanism. Additionally, the conductivity of graphene oxide has a direct relationship with the number of oxygen species present in its sheets, and this step can be strategically used to modulate or achieve certain desired characteristics in the material (Figure 6) [71–74]. In this sense, in electrochemical sensors, the common aim of the presence of graphene oxide is to guarantee good charge transfer in the system [25,75,76]. Thus, with the intention of reaching the highest conductivity, some works carry out the electrochemical reduction process after electrodeposition [6,70,77]. To perform electroreduction, a constant cathodic potential is applied for periods that can vary from a few minutes to a few hours to ensure that graphene is at its lowest oxidation state. This process occurs in an electrolytic solution similarly to electrodeposition; however, GO species dispersed in solution are absent. Afterwards, electrochemically reduced graphene oxide (called rGO or ERGO) is obtained [56]. The electroreduction method, in addition to being simple and of low cost, also avoids

the need to handle harmful reagents such as hydrazine and other reagents used during conventional chemical reduction.

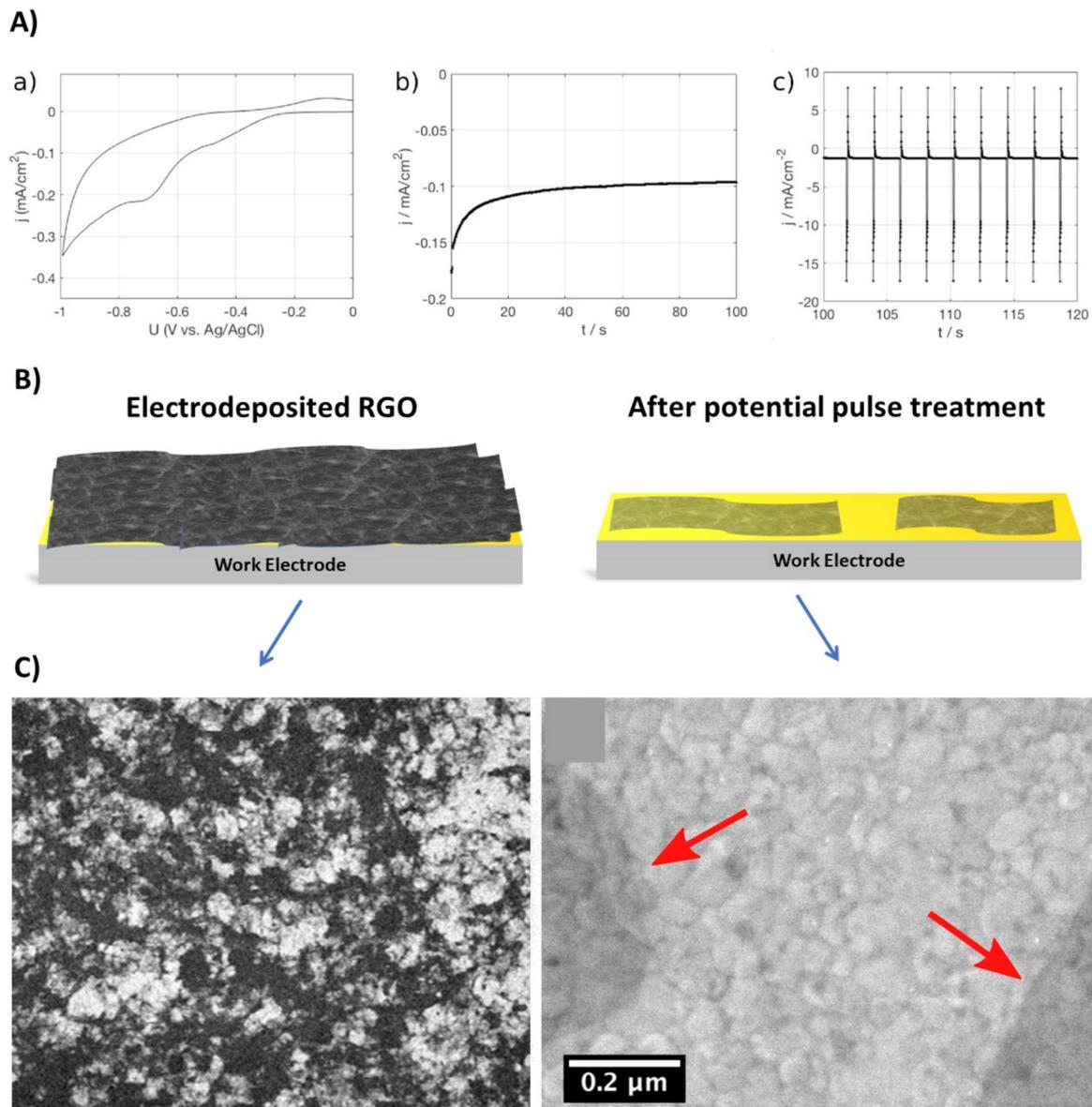


Figure 5. (A) (a) Cyclic voltammogram (50 mV/s) for a gold electrode in 1 mg/mL GO immediately before deposition, (b) reduction of GO onto gold at -0.8 V/Ag/AgCl for 100 s in 0.1 M phosphate-buffered saline (PBS) electrolyte, (c) current during the 20 s time period during the pulse treatment period between -0.5 V Ag/AgCl for 2 s and -1.5 V Ag/AgCl for 0.1 s on a graphene/GO-modified gold electrode in 0.1 M phosphate buffer (pH = 7.4). (B) Schematic representation of an electrode modified with graphene before and after the application of a potential pulse. (C) Scanning electron microscopy of electrodes covered with graphene before and after application of a potential pulse. Reprinted with permission from Ref. [70] Copyright 2019 Elsevier Ltd.

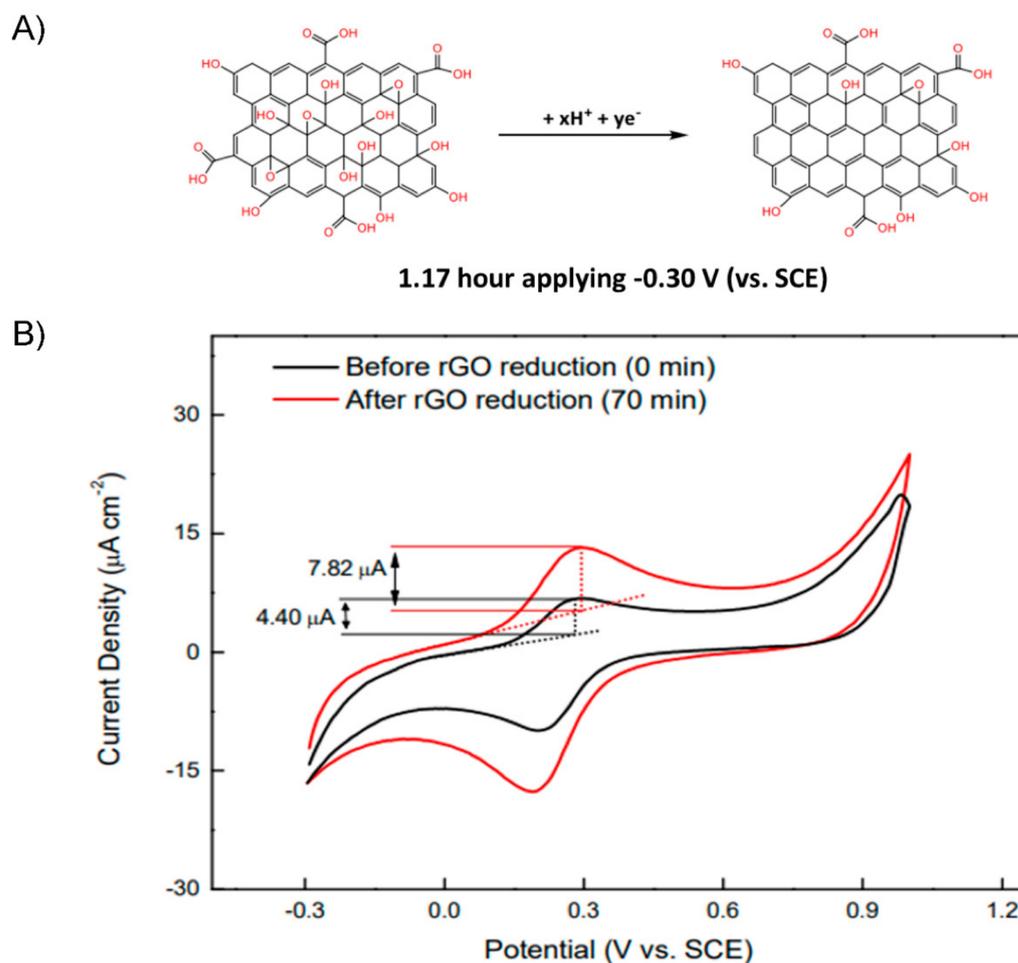


Figure 6. (A) Graphene electrochemical reduction representation after applying a fixed potential of $-0.30\text{ V (vs. saturated calomel electrode)}$. (B) Voltammetric response to poly(azo-BBY)-rGO in $\text{KCl } 0.50\text{ mol L}^{-1}$ ($\text{pH } 2.0$) solution under N_2 atm before (black line) and after (red line) electrochemical reduction. Scan rate = 25 mV s^{-1} . Reprinted (adapted) with permission from Ref. [6] Copyright 2020 from the American Chemical Society.

3. Nanocomposite Architecture

As previously mentioned, synthesis based on electrochemical methods allows the creation of different molecular architectures via control of the applied electrochemical parameters. At the level of nanocomposites, it is possible to form structures by alternating the order in which they are electrodeposited, in multiple stages, or even simultaneously in a single stage. Next, we will discuss in detail the possibilities explored in recent works.

3.1. Multiple-Step Strategy

The molecular architecture of a device may vary according to the researcher's objective and may involve one or more processing steps [56,58,77,78]. Construction in two or more steps, as with the first addition of a reduced graphene oxide layer onto an electrode surface followed by electropolymerization of a polymer on an electrode/rGO structure, can be carried out, for example, with the aim of increasing the active area of the electrode and improving the electronic response of the material.

In this sense, Chen and collaborators [79] used cyclic voltammetry to electrodeposit a reduced graphene oxide layer onto a glassy carbon electrode by applying 8 potential cycles in an interval from 0.6 V to $-1.5\text{ V (vs. Ag/AgCl)}$, with a scan rate of 25 mV s^{-1} . The results obtained showed an increase in the capacitance of the system, which is related to the increase in the surface area of the material. Scanning electron microscopy (SEM) images

showed the effective deposition of graphene sheets. Afterwards, the authors successfully realized electropolymerization of polypyrrole (PPy) onto the electrode, applying 8 cycles between -0.2 V and 0.8 V at 100 mV s^{-1} . An increase in the electrochemical performance of the sensor due to the presence of reduced graphene oxide was verified.

Eryiğit and collaborators built their sensory platform based on the strategy of first depositing a poly(3,4-ethyleneoxythiophene) (PEDOT) film followed by the electrodeposition of reduced graphene oxide [80]. For this, a fixed potential of $+1.3$ V (vs. Ag/AgCl) was applied for 30 s in a solution containing 10 mmol L^{-1} 3,4-ethyleneoxythiophene (EDOT) monomer (acetonitrile (ACN)/ LiClO_4 0.1 mol L^{-1}), forming a first layer of conductive polymer on the surface of a gold electrode. Afterwards, the Au-PEDOT set was immersed in a 2.0 mg mL^{-1} GO solution and a -1.0 V cathodic potential (vs. Ag/AgCl) was applied for 60 s, giving rise to a Au-PEDOT-ERGO sensor (Figure 7).

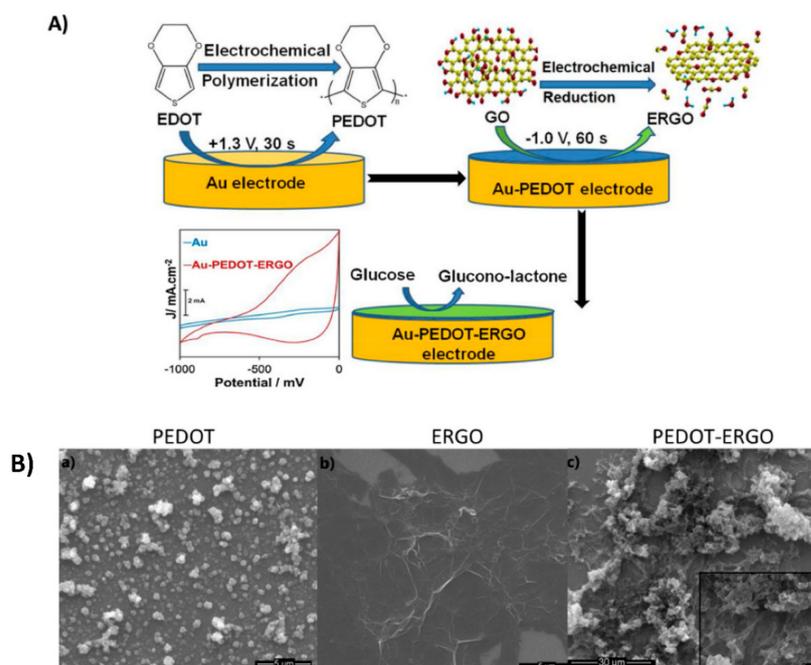


Figure 7. (A) Schematic presentation of the experimental procedure used and (B) scanning electron microscopy for formed films, (a) poly(3,4-ethyleneoxythiophene) (PEDOT), (b) electrochemically reduced graphene oxide (ERGO) and (c) PEDOT-ERGO. Reprinted (Adapted) with permission from Ref. [80] Copyright 2020 Elsevier B.V.

A similar approach was presented by Zhang et al. [81], where first the surface of a glass carbon electrode (GCE) was modified with L-lysine followed by the incorporation of graphene oxide. Modification by L-lysine occurred through electropolymerization by cyclic voltammetry, applying 7 potential cycles in a potential range from -1.0 V to 2.2 V (vs. Ag/AgCl) with a scan rate of 50 mV s^{-1} . Afterwards, the electrode was washed and immersed in a solution of 1.0 mg mL^{-1} graphene oxide, and 10 cycles of potentials were applied in an interval of 0.6 V to -1.5 V (vs. Ag/AgCl) at a speed of 25 mV s^{-1} . Electrochemical performance was evaluated comparatively with an electrode containing only graphene oxide and subsequently applied to the simultaneous determination of ascorbic acid, dopamine and uric acid.

Another widely used form is that of the modification reaction, functionalization of graphene sheets with the polymer in a chemical step prior to the electrochemical step. Due to the widespread presence of oxygenated species in graphene oxide sheets (and their derivatives), they can be easily covalently functionalized via chemical reactions such as esterification, amidation, click chemistry, nitrene chemistry, etc. [82] or even functionalized non-covalently through π -aromatic interactions [83,84].

In this sense, Hu and collaborators [85] modified graphene oxide prior to the electrochemical step (Figure 8). A rGO-Polypyrrole set was obtained by adding 500 μL of pyrrole monomer to 10 mL of GO solution. The set was taken to a hydrothermal process in an autoclave for 12 h at a temperature of 180 $^{\circ}\text{C}$. After this period, a 3D material rGO-polypyrrole hydrogel pillar was obtained. This material was used as an electrode and immersed in PBS solution, and electropolymerization of the Py present in the structure was conducted by applying a constant potential of +0.8 V for a period of 30 min.

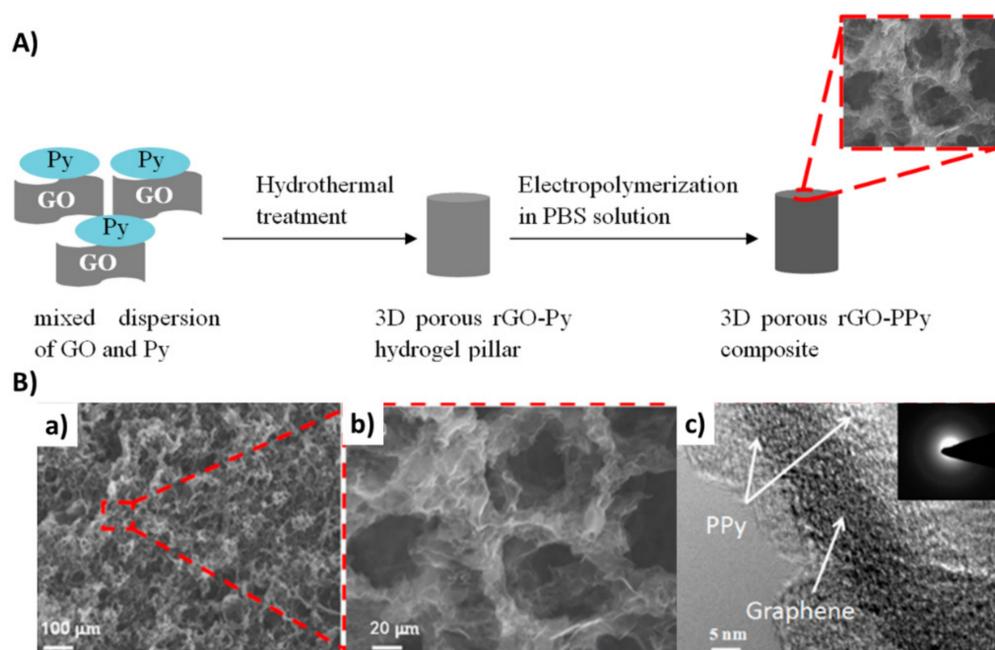


Figure 8. (A) Scheme for the preparation of the three-dimensional (3D) porous graphene-polypyrrole (rGO-PPy) composite and its microscopic analysis (B) for (a) PPy film, (b) rGO-PPy and (c) rGO-PPy. Reprinted (adapted) with permission from [85].

Li and collaborators [86] functionalized graphene oxide by a condensation dehydration reaction to obtain a covalent bond between the carboxylic groups and the amine group of the aminophenylboronic acid (APBA) molecule. The resulting composite, called GO-APBA, was dispersed in Na_2SO_4 0.10 mol L^{-1} solution, and, afterwards, potential cycles were applied in a potential range from -1.2 V to $+1.2$ V (50 mV s^{-1}). The platform formed was evaluated against different glucose concentrations using electrochemical impedance spectroscopy.

3.2. One-Step Approach

Recently, the number of works using the one-step approach has increased. This approach consists of a single step for obtaining the graphene-polymer composite through simultaneous synthesis and deposition (or alternating layers) of the graphene oxide and polymer species by simply modulating the applied electrochemical potential [6,41,78,87–95].

This approach aims to reduce steps, time and cost involved in the construction of the composite material. With this approach, it is possible to build films with a 3D architecture with alternating layers (layers-by-layers), obtaining a remarkable filling of the polymer matrix with the reduced graphene oxide layers [93]. Imae and collaborators built a platform based on graphene-PEDOT through a one-step approach. In a KCl solution containing 3.0 mg mL^{-1} GO and 20 mmol L^{-1} EDOT monomer, pulsed potentials of $+1.0$ and -1.1 V were repeatedly applied, resulting in the formation of a multilayer PEDOT-graphene film.

Recently, in our laboratory, one-step electrosynthesis was performed to build a graphene nanocomposite film with an azopolymer [6,96,97]. By cyclic voltammetry electropolymerization, a sensory platform was obtained via alternating deposition reduced

graphene oxide and poly(azo-Bismark Brown Y) layers (Figure 9). During the cathodic scan, graphene oxide sheets were electrodeposited, and during the anodic scan, a poly(azo-BBY) layer was obtained. The increase in the conductivity of the material, due to π - π orbital interactions between reduced graphene oxide and π -conjugated azopolymer chains, allowed its application in the sensing of superoxide using electrochemical impedance spectroscopy.

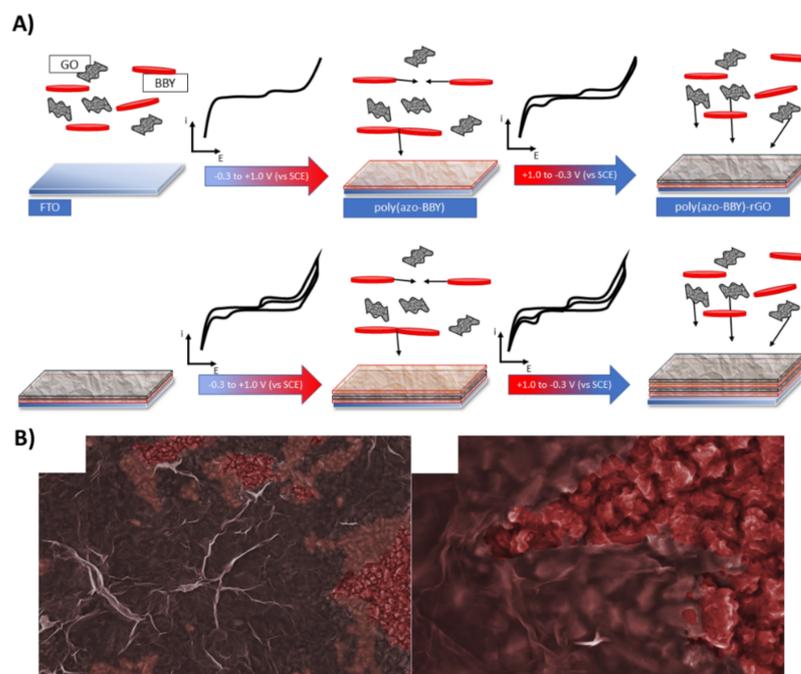


Figure 9. (A) Representative scheme for the formation of a sensory platform via a one-step approach. (B) Scanning electron microscopy (artificially colored) highlighting the graphene sheets over the polymeric film. Reprinted (adapted) with permission from Ref. [96] Copyright 2019 Elsevier B.V.

4. Sensing Applications

Electrochemical sensor-based graphene-polymer composites have shown increasing adhesion due to their versatility and ability to identify and quantify a diversity of analytes, ranging from small inorganic molecules to biological molecules. Below, some recent research related to electrochemically manufactured sensors is summarized in Table 1, and some is highlighted.

Acetaminophen is a drug widely used worldwide due to its analgesic and antipyretic properties. In this sense, Ly and collaborators [94] built a graphene polymer-based sensory platform to detect acetaminophen in traditional medicines. The sensorial platform was built in a single step using an electrochemical cyclic voltammetry technique. The electropolymerization solution consisted of 1.0 mg mL^{-1} GO and 10 mmol L^{-1} EDOT monomer in phosphate-buffered saline (pH 7.4). The solution was sonified for 30 min before electrosynthesis, in which 10 cycles of potentials were applied in a potential range of -1.2 V to $+1.5 \text{ V}$ (vs. Ag/AgCl) with a scan rate of 50 mV s^{-1} . From the obtained voltammogram, the authors identified the typical behavior for the formation of the PEDOT polymer as well as the irreversible peak characteristic of the reduction of the oxygenated groups present in the graphene oxide sheets. The effective formation of the film was confirmed by Fourier transform infrared spectroscopy (FTIR) and SEM. For the detection of the drug, the PEDOT-rGO device presented a sensitivity of $23,515 \text{ } \mu\text{A } \mu\text{mol L}^{-1} \text{ cm}^{-2}$ and a detection limit of $5.74 \text{ } \mu\text{mol L}^{-1}$, which is sufficient for application in real samples of commercial drugs.

Essoussi and collaborators [111] developed a graphene-polymer device based on a molecular imprinting technique to determine a widely used drug, amoxicillin. In a two-stage construction strategy, the authors first formed a reduced graphene oxide layer on the

electrode surface. The electroreduction of graphene oxide sheets on a GCE surface was obtained after the application of 15 cycles of potential in PBS 0.1 mol L⁻¹ solution in a potential range of +0.6 V to -0.7 V (vs. Ag/AgCl). Then, the molecularly imprinted polymer (MIP) was applied to build the device on the GCE/rGO electrode by applying potential cycles (10 scans) in a potential range of -0.2 V to +0.9 V in solution having the pyrrole monomer and the drug amoxicillin as a template molecule. After that, gold nanoparticles were added to the composite. The sensor had a detection limit of 1.22 μmol L⁻¹ over a wide concentration range. The sensor was applied to determine the drug in samples of human serum and milk.

Table 1. Comparison of electrochemical sensors manufactured with different electrochemical synthesis approaches.

Electrochemical Approach	Platform	Analyte	Limit of Detection	Ref
One-step	P(ATT)-GO ^a	Lipocalin-2	0.3 nmol mL ⁻¹	[98]
	Pt/rGO/P3ABA ^b	Glucose/Cholesterol	44.3/40.5 μmol L ⁻¹	[99]
	Poly(BBY)-rGO ^c	Dissolved Oxygen	0.36 μmol L ⁻¹	[100]
Two-steps	PPy3C/ERGO ^d	Streptomycin	0.5 nmol L ⁻¹	[97]
	GO-poly(p-ABSA) ^e	Dopamine/Serotonin	0.09/0.2 μmol L ⁻¹	[101]
	MIPPy/GR/GCE ^f	Melamine	10.2 nmol L ⁻¹	[102]
	PPy/rGO	NH ₃	1 ppm	[103]
Multiple steps	MIP-rGO/GCE	Adrenaline	3 nmol L ⁻¹	[104]
	r-GO/poly(CoOBImpC) ^g	Hydrazine	33 nmol L ⁻¹	[105]
	MIP/AuNPs/RGO/GCE	Lactic acid	8.9 × 10 ⁻¹¹ mol L ⁻¹	[106]
	MIP@ERGO/GC	Domperidone	3.8 nmol L ⁻¹	[107]
	PPy-RGO-(AuNPs-GOD)4/GCE	Glucose	5.6 μmol L ⁻¹	[108]
	Eβ-CD/B-RGO/GCE ^h	Flunitrazepam	0.6 nmol L ⁻¹	[109]
	rGO:PSS-PEDOT:PSS	Ion-sensor	-	[110]

^a ATT—3-amino-1,2,4-triazole-5-thiol; ^b 3ABA—(3-aminobenzoic acid); ^c BBY—Bismark Brown Y; ^d Py3C—poly(pyrrole-3-carboxy acid); ^e ABSA—aminobenzenesulfonic acid; ^f GR—graphene; ^g CoOBImpC—octabenzimidazole phthalocyanine; ^h Eβ-CD—β cyclodextrin.

Wang and collaborators [75] used electrodeposition and electropolymerization techniques to develop an ion-printed sensor for the identification and quantification of trace concentrations of Cd(II) metal in river water. The sensor was built in two stages: the first involved the electrodeposition of reduced graphene oxide layers onto the GCE electrode surface by applying a potential range from -1.5 V to +1.0 V at 50 mV s⁻¹ for 10 cycles in 2.0 mg mL⁻¹ graphene oxide solution (KCl 0.1 mol L⁻¹). Subsequently, the GCE/ERGO electrode was washed, dried in a flow of N₂ and immersed in a solution containing 40 mmol L⁻¹ of the monomer o-phenylenediamine (acetate buffer pH 5.4 as electrolyte) to form poly(o-phenylenediamine) (PoPD) on the GCE/ERGO electrode surface by applying 20 cycles in a 0.0 V to +0.8 V potential window (vs. Ag/AgCl) at 50 mV s⁻¹. At the end of the sensor construction, the template ion was removed, and the analytical characteristics of the sensor were investigated (Figure 10). The sensor had an impressive detection limit of 0.13 ng/mL in addition to expressive selectivity compared to other ions, such as Hg(II), Fe(II), Cu(II) and Ni(II), depending on the printed cavity built specifically for the Cd(II) ion. With these skills, the sensor was applied to real water samples collected from rivers in the Beijing region.

Figure 11 shows the one-step approach for the glucose sensor developed by Zhang and collaborators [112]. The GCE electrode was first modified by cyclic voltammetry (8 cycles, range from -1.5 V to +2.2 V vs. Ag/AgCl) in PBS solution containing 1.0 mg mL⁻¹ of GO and 1.0 mmol L⁻¹ of L-lysine. After the construction of the sensor, the enzyme glucose oxidase was immobilized on the surface. Finally, a last layer of Nafion was applied to the GCE/ERGO-PLL/GOx set to protect against sensor degradation. SEM verified the alternate deposition of materials, resulting in a 3D structure that had a positive effect on the electrochemical response performance of the composite. The sensor showed impressive sensitivity compared to some other composite glucose biosensors.

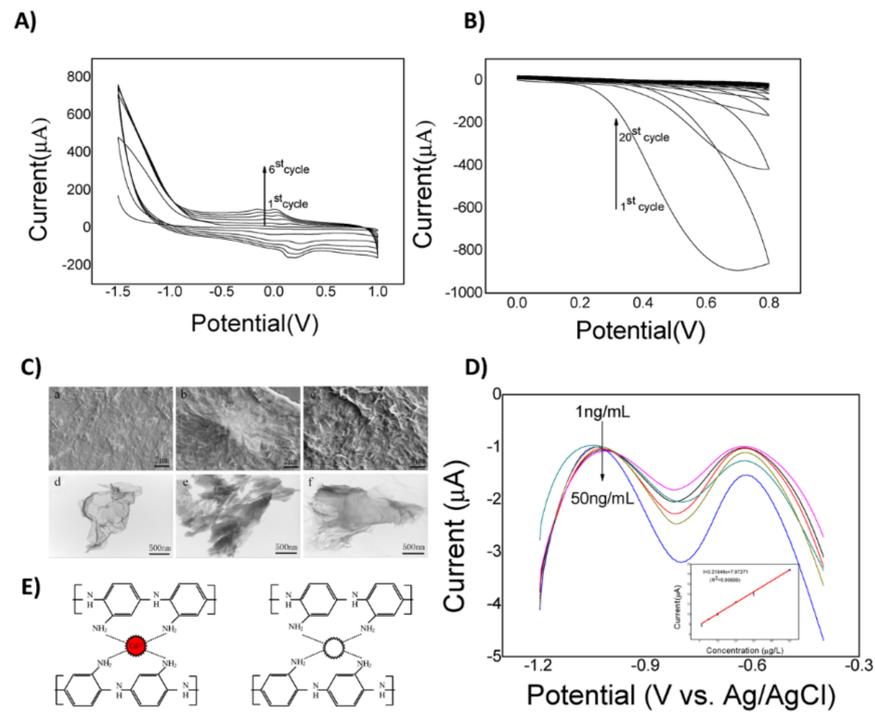


Figure 10. Cyclic voltammetry for GO electrodeposition (A) and o-phenylenediamine (oPD) electropolymerization (B) steps. (C) Morphological characterization of the PoPD/ERGO/GCE sensor. (D) Square wave anode stripping voltammetry (SWASV) response curves at different concentrations. The inset shows the linear relationship between the current response and concentration. (E) Schematic representation of the response mechanism. Reprinted (adapted) with permission from [75].

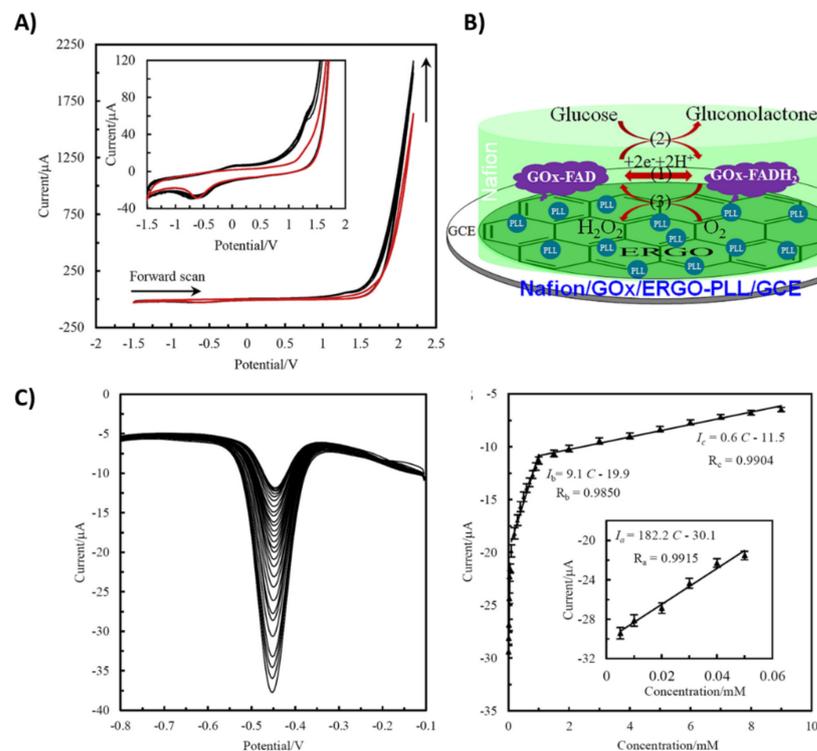


Figure 11. (A) Cyclic voltammogram for the GO-L-lysine electrosynthesis process. (B) Schematic representation of a glucose sensor. (C) Sensor response and analytical curve. Reprinted (adapted) with permission from Ref. [112] Copyright 2019 Elsevier B.V.

5. Conclusions

The main strategies for the electrochemical synthesis of thin films based on reduced graphene oxide nanocomposites with conductive polymers are discussed in this review. The construction of nanocomposite films by electrochemical techniques has several advantages over conventional methodologies based on chemical synthesis. The main benefits include the formation of a nanocomposite film directly on the surface of the desired substrate, with the possibility of high control over its structure, which increases the reaction yield and decreases the process time and cost. Electrochemical sensors are crucial components for achieving low-cost analysis. Electrochemical synthesis also facilitates the modeling and architecture of sensory platforms. Different configurations can be achieved using different solutions and techniques or even different techniques in a single solution (one-spot). From the presented well-illustrated examples, it is possible to follow a variety of construction strategies for realizing sensory platforms as well as infer a wide possibility for applications, ranging from metal ions to biological molecules.

Despite this, the variety of polymers used for the construction of sensorial platforms had been enough explored. Main work had limited to the use of conductive polymers based on EDOT, PPy and PANI. Thus, new conductive polymers need could be study for. For example, polymers with different functional groups could achieve new properties and characteristics, in addition to enabling new ways of anchoring biomolecules. Recently, works increase the use of photosensitive materials in sensory applications. In this sense, for example, the use of polymers with photoresponse characteristics could expand the range of applications or even improve the sensitive response to the analyte, bringing to a photosensitive system all the advantages presented by the graphene-polymer set.

In addition, a promising perspective on composite materials due to the constant improvement of electrochemical equipment. Increased resolution and reduced device dimensions, plus the ease of acquisition and management of the data generated for different platforms make the graphene-polymer nanofilms a promising material for application in miniaturized, smart, and wearable devices.

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