Chapter 7

Graphene-Polymer based Nanocomposites for Electrochemical Sensing of Toxic Chemicals

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Abstract

This chapter (with 94 refs.) gives an overview of the progress in the past few years on the development of graphene-polymer based sensors and analytical tools for the determination of toxic chemicals. Sensing of toxic molecules is critical to environmental monitoring, control of chemical processes, agricultural, and medical applications. In particular, the detection of heavy metal ions such as mercury, cadmium, arsenic, chromium, thallium and lead which are extremely harmful pollutants in the biosphere due to their toxicity and even trace amounts of them pose a detrimental risk to human health. Graphene and their polymer composites are synthesized by using various synthesis techniques. Following details is an overview of the significant synthesis techniques of graphene-polymer based nanocomposites that have been reported in the past few years. We also discussed the various analytical electrochemical detection methods for toxic chemicals such as potentiometric, voltammetric and electrochemical impedance spectroscopy methods. Subsections cover electrochemical sensors on graphene-polymer based nanocomposites with different kind of polymers used, and finally their detection sensors on toxic chemical containing heavy metal ions.

Keywords

Polymerization, Graphene Derivatives, Electroanalysis, Nanohybrid, Biosensor, Potentiometric Technique, Voltammetric Technique

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1. Introduction

A toxic chemical is a substance or a particular mixture that can be poisonous or cause damage to the organism. Many chemicals can be obtained persistently from organic pollutants such as flame retardants (PBDEs), dioxins/furans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) [1-4] that can be found on waste sites, heavy metals/metalloid concentrations and even industrial waste. Any chemical can be toxic because they can harm us when it contacts or enters the body. The toxicity level of any chemical is described by the types of effects it causes and its potency under a certain condition. Different chemical causes different type of effects. For example, ingesting gasoline can cause burns, vomiting, diarrhea and, in very large amounts, drowsiness or death, but not cancer. However, there are certain chemical such as asbestos and benzene which may have no noticeable effects at the beginning of exposure but can cause cancer after years [5]. The health effects depend on the amount of chemical exposure, for example, two aspirin tablets can help to relieve a headache, but taking an entire bottle of aspirin can cause stomach pain, nausea, vomiting, headache, convulsions and even death.

Meanwhile, heavy metals include mercury (Hg) [6,7], cadmium (Cd) [8], arsenic (As) [9], chromium (Cr) [10], thallium (Tl) [11], and lead (Pb) [12] are extremely harmful pollutants in the biosphere due to their toxicity and even trace amounts of them pose a
detrimental risk to human health. Although, heavy metals are naturally abundant elements found from earth’s crust, but most environmental contamination can occur from anthropogenic human activities such as mining and smelting operations. Human exposure through industrial activities include metal processing in refineries, coal burning in power plants, petroleum combustion, nuclear power stations and high tension lines, plastics, textiles, microelectronics, wood preservation and paper processing plants can risk harmful health effects [13]. Among the harmful health effect of heavy metals, they can induce multiple organ damage, even at low degree of exposure. They are also classified as human carcinogens (known or probable) according to the U.S. Environmental Protection Agency, and the International Agency for Research on Cancer [14-16].

Since these chemicals can be toxic, it is crucial to know the amount of a substance that enters or exposes a person. Thus, it is necessary to have a rapid, sensitive, and simple analytical method for the detection and monitoring of these environmental pollutants. The development of a sensor for the precise and selective measurement for metal ions in the presence of potential biomolecules interference at the abnormal levels characteristic of living systems can make a great contribution to disease diagnosis. Although many sensor materials reported showed good potential in detecting toxic chemicals, this chapter will emphasize on graphene and their hybrids with different kind polymer composites. These graphene-polymer based composites are material mainly used for detecting heavy metals and hazardous chemicals in respective detection techniques. The graphene-polymer nanocomposites have recently received a great attention among worldwide researchers in the field of sensors due to its novel chemical, optical and physical properties. Some of its unique properties of graphene-polymer composites are related to their high simplicity and flexibility [17,18]. Polymer–carbon composite is another sensing material that received significant attention since it was introduced many centuries ago. As a filler component, it can improve mechanical properties, chemical inertness and stability, versatile processing techniques and low cost [19]. The graphene-polymer also performed an important role in the sensitivity and selectivity especially in the sensing platform [20,21]. Likewise, the functionalized graphene acts as an efficient nanofiller in polymer composites to improve its engineering properties. Moreover, even with a small quantity of functionalized graphene can improve the mechanical, electronic, optical, thermal and magnetic properties significantly [22-25]. The mechanical properties of a nanocomposite material are evaluated based on the enhancement of the performance as characterized by the elastic modulus, tensile strength, elongation, and toughness [26,27]. Therefore, interfacial interactions play key roles to achieve these mechanical properties. Even more, graphene-polymer nanocomposites possess an impressive functional properties, such as electrical (semi-) conductivity, unique photonic/optical transportation, anisotropic transport, low
permeability, and fluorescence quenching [28,29]. Some interesting properties of graphene-polymer based nanocomposites are summarized in Figure 1.

Figure 1 Properties of graphene-polymer based nanocomposites.

Frequently, the graphene-polymer based nanocomposites have been used in a wide range of practical demanding applications nowadays. Figure 2 shows multifunction applications of graphene-polymer based nanocomposites. Some conjugated polymer functionalized graphene like polythiophenes or its derivative composites are widely used in photovoltaic devices [30], light-emitting diodes [31,32], transparent conducting electrodes [33], gas barrier membranes [34,35], and biosensors [36-38]. Meanwhile, conducting polymers such as polyaniline and polypyrrole functionalized graphene composites show a great potential application in supercapacitors [39,40] and lithium-ion battery electrode [41]. As for supercapacitor devices based on graphene/PANI composite film, it exhibits large electrochemical capacitance value of 210 F g⁻¹ at a discharge rate of 0.3 A g⁻¹ [39]. Another example of a composite that has been used for supercapacitor devices is based on the rGO/polypyrrole composite which shows a higher specific capacitance value of 424 F g⁻¹ [36]. Besides that, non-covalently polymer functionalized graphene composites
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contribute a variety of sensor applications [42,43], e.g. GO/methylcellulose and GO/poly(vinyl alcohol) hybrid system acts as a good sensor for the detection of nitroaromatics [38] and Au (III) ions in aqueous media, respectively [44]. The poly(ethylene glycol) functionalized nanographene is used as new vectors for the delivery of cancer drug into the cells [45]. Another branch of biomedical applications by using graphene-polymer based including controlled drug release, enzyme immobilization, sensors and actuators, and as tissue culture substrates.

Figure 2  Multifunction of graphene-polymer based nanocomposites applications.

2. Methods of detection

Various techniques for detecting heavy metal ions have been developed as a result of the rapid development of nanotechnology, and each technique has its advantages and disadvantages. Along with the production of a variety of techniques for the detection. To date, there are various analytical techniques, such as atomic absorption spectrometry [46], inductively coupled plasma mass spectrometry [47], inductively coupled plasma atomic emission spectrometry [48], capillary electrophoresis [49], X-ray fluorescence spectrometry [50], Neutron activation analysis [51], Ion chromatography [52] and UV-VIS spectrometry (UV-VIS) [53], have been performed for heavy metals quantification. However, these spectrometric methods require expensive instruments and not suitable for in situ analysis due to the ponderous and also needing professional operators to handle complicated instruments. Thus, a simple and inexpensive method that not only detects but
also quantities heavy metal ions is desirable for the real-time monitoring of environmental, biological, and industrial samples. On the contrary, the electrochemical method considered as an alternative to these expensive spectroscopic techniques has been acknowledged as an efficient method to detect heavy metal ions [54-58]. Advantages of electrochemical analysis, including has high sensitivity, high accuracy, wide measuring range, simple device, economical, user-friendly, reliable and suitable for in-field applications [59]. For metal analysis, the principal electrochemical techniques used are potentiometric, voltammetric and electrochemical impedance spectroscopy methods [60]. The brief principal aspects of electrochemical operation are explained as below.

2.1 Potentiometric technique [61]

It is a classical technique in which information about the composition of the sample is provided through the potential appearing between two electrodes. Ion-selective electrodes (ISEs) provide rapid selective potentiometric techniques for the determination of the major cations (metal samples). The detection limit is in the nanomolar range (or even lower).

2.2 Voltammetric technique

It is a method in which information about the composition of electrolytic solutions is provided by measuring the current as a function of applied potential [62]. For voltammetry, stripping analysis is one of the most widely used in metal ion analysis due to highly sensitive voltammetric method, which makes possible to determine minimal concentrations of analyte (sub-nanograms) [63,64]. In contrast to conventional analytical techniques, these techniques can provide the best limit of detection (LOD) but low cost, environmentally friendly, quicker and easy to apply for analysis of heavy metal ions in a variety of real samples. There are several voltammetric techniques currently use for metal ions detection including cyclic voltammetry (CV), differential pulse voltammetry(DPV), linear scan voltammetry (LSV), chronoamperometry (CA), square wave voltammetry (SWV), differential pulse anodic stripping voltammetry (DPASV) and square wave anodic stripping voltammetry (SWASV). The comparison of different voltammetry with graphene-polymer modified electrodes have comprehensively summarized in Table 1.
### Table 1  Analytical performances of various methods of modified electrodes for metal ions determination.

<table>
<thead>
<tr>
<th>Modified electrode</th>
<th>Methods</th>
<th>Ion/compound</th>
<th>Detection limit</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-(IL-rGO/AuNDs/Nafion/GCE)</td>
<td>SWV</td>
<td>Iron</td>
<td>35 nM</td>
<td>[65]</td>
</tr>
<tr>
<td>PGMGPE</td>
<td>CV</td>
<td>Hg^{2+}</td>
<td>6.6 μM</td>
<td>[66]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb^{2+}</td>
<td>0.8 μM</td>
<td></td>
</tr>
<tr>
<td>Nafion-G</td>
<td>DPASV</td>
<td>Pb^{2+} and Cd^{2+}</td>
<td>0.02 μg L^{-1}</td>
<td>[67]</td>
</tr>
<tr>
<td>3D rGO@PANI</td>
<td>CV</td>
<td>Pb^{2+}</td>
<td>0.035 nM</td>
<td>[6]</td>
</tr>
<tr>
<td>PPy–RGO</td>
<td>SWASV</td>
<td>Hg^{2+}</td>
<td>15 nM</td>
<td>[68]</td>
</tr>
<tr>
<td>G/PANI/PS</td>
<td>SWASV</td>
<td>Pb^{2+}</td>
<td>3.30 μg L^{-1}</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd^{2+}</td>
<td>4.43 μg L^{-1}</td>
<td></td>
</tr>
<tr>
<td>sGO/PPy</td>
<td>DPASV</td>
<td>Pb^{2+}</td>
<td>0.07 ppb</td>
<td>[70]</td>
</tr>
<tr>
<td>RGO-CS/PLL</td>
<td>DPASV</td>
<td>Cd^{2+}</td>
<td>0.01 μg L^{-1}</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb^{2+} and Cu^{2+}</td>
<td>0.02 μg L^{-1}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.02 μg L^{-1}</td>
<td></td>
</tr>
<tr>
<td>PEI-RGO</td>
<td>DPASV</td>
<td>Cu^{2+}</td>
<td>0.3 μM L^{-1}</td>
<td>[72]</td>
</tr>
<tr>
<td>GR-CD/PPy</td>
<td>DPV</td>
<td>Hg^{2+}</td>
<td>0.47 nM L^{-1}</td>
<td>[73]</td>
</tr>
<tr>
<td>PA/PPy/GO</td>
<td>DPV</td>
<td>Cd^{2+}</td>
<td>2.13 μg L^{-1}</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb^{2+}</td>
<td>0.41 μg L^{-1}</td>
<td></td>
</tr>
</tbody>
</table>

IL-rGO/AuNDs=ionic liquid-reduced graphene oxide (IL-rGO) supported gold nanodendrites; PGMGPE=polyglycine-modified graphene paste electrode; G=graphene; 3D rGO@PANI=three-dimensional reduced graphene oxide and polyaniline; PPy–RGO=polypyrrole/reduced graphene oxide; G/PANI/PS=graphene/polyaniline/polystyrene; sGO/PPy=cysteine-functionalized graphene oxide/polypyrrole; RGO-CS/PLL=reduced graphene oxide-chitosan/poly-l-lysine; PEI-RGO=Polyethyleneimine-reduced graphene oxide; GR-CD/PPy=polypyrrole decorated graphene/β-cyclodextrin; PA/PPy/GO=phytic acid functionalized polypyrrole/graphene oxide

#### 2.3 Electrochemical impedance spectroscopy (EIS)

EIS is a non-destructive method used for detecting and determining the target species concentrations based on electrical impedance changes the sensor analyte interface [75]. It is a highly sensitive characterization technique used to study a variety of electrochemical systems since EIS can provide accurate error-free kinetic and mechanistic information using a variety of techniques and output formats. The EIS is a modulation technique in which impedance measured by applying a small amplitude sinusoidal excitation signal to
the system under study (electrochemical system) and measuring the response signal [76]. Impedance measurement provides information such as processes occurring on electrode surfaces, the conductivity of the solution and ability numerical expression of an aqueous solution to carry electric current [77]. One-step fabrication of DNA-modified three-dimensional reduced graphene oxide and chitosan nanocomposite (CS@3D-rGO@DNA) was reported for highly sensitive detection of Hg$^{2+}$ in drinking water [78]. The direct adsorption of Hg$^{2+}$ onto the nanocomposite detection was investigated by EIS with a detection limit of 0.016 nM. The authors measured the sensitivity of CS@3D-rGO@DNA-modified electrode based on EIS Nyquist plots toward different concentrations of Hg$^{2+}$ from 0.1 nM to 10 nM are shown in Figure 3a. Whereas, the linear plot and the dependence of Rct on the concentration of Hg$^{2+}$ (0.1 to 10 nM) were calculated by using software shown in Figure 3b.

![Figure 3](https://example.com/figure3.png)

*Figure 3* (a) EIS Nyquist plots for the detection of different concentrations of Hg$^{2+}$ ions with concentrations are of 0 to 10 nM. (b) The linear fit plots $R_{ct}$ as function of the logarithm of Hg$^{2+}$ concentration [78].

### 3. Electrochemical sensors using graphene-polymer nanocomposites

Many approaches are used for the modification of the working electrode surface by using graphene incorporated polymer based composites. Generally, traditional fabrication routines include solution-based processing [79-82] and melt-based processing [83,84]. The most widely used for the fabrication of graphene-polymer based nanocomposites approaches are in situ polymerization, chemical grafting, latex emulsion blending, layer-by-layer (LbL) assembly, and directed assembly [85-87]. For the in situ polymerization method, intercalated monomers within expanded graphite clusters can promote their
efficient exfoliation into single sheets throughout the polymer matrix caused by catalysis reactions [88].

3.1 Sensors using graphene modified conducting polymer

3.1.1 Graphene-polyaniline (PANI) nanocomposites

Yang et al. synthesized nanorod-like nanocomposite of three-dimensional reduced graphene oxide and polyaniline (3D-rGO@PANI) by an in situ chemical oxidative polymerization method for detecting Hg$^{2+}$ in aqueous solution [6]. The synthesis schematic illustration is shown in Figure 4. The results demonstrated that the electrochemical biosensor based on 3D-rGO@PANI nanocomposite showed high sensitivity and selectivity toward Hg$^{2+}$ within a concentration range from 0.1 nM to 100 nM with a low detection limit of 0.035 nM. The authors proved that the presence of 3D-rGO within the nanocomposite further improves the specific surface area and electrochemical performance.

![Figure 4 Schematic diagram of the detection of Hg$^{2+}$ nanorod-like nanocomposite of three-dimensional reduced graphene oxide and polyaniline (3D-rGO@PANI) by an in situ chemical oxidative polymerization method [6].](image)

Muralikrishna et al. prepared PANI/GO hydrogels for highly sensitive electrochemical determination of Pb$^{2+}$ [89]. They synthesized hydrogels via in situ polymerization of aniline in the presence of GO nanosheets followed by hydrogel formation at an elevated
temperature as shown in figure 5. The synthesized nanomaterial exhibits significant properties for the highly sensitive electrochemical determination as well as removal of environmentally harmful lead ($\text{Pb}^{2+}$) ions. The detection limit obtained for this electrode is 0.04 nM with the longer linear concentration range. The sensor showed excellent repeatability and reproducibility and successfully tested by using real water samples.

![Diagram](image)

*Figure 5 Schematic diagram of the detection of $\text{Pb}^{2+}$ electrochemical sensor based PANI/GO hydrogels synthesized via in situ polymerization method [89].*

### 3.1.2 Graphene/polyaniline/polystyrene nanoporous fibre

Graphene/polyaniline/polystyrene (G/PANI/PS) nanoporous fibres modified electrode was developed by using electrospinning fabrication for highly sensitive and simultaneous determination of lead ($\text{Pb}^{2+}$) and cadmium ($\text{Cd}^{2+}$) in real water samples [69]. Promphet et al. prepared nanoporous structure on Graphene/polyaniline/polystyrene fibre which increases an electroactive surface area, that leading to enhance electrochemical sensitivity of carbon electrode as shown in Figure 6. The authors employed square-wave anodic stripping voltammetry technique (SWASV) for detecting $\text{Pb}^{2+}$ and $\text{Cd}^{2+}$ in the presence of bismuth ($\text{Bi}^{3+}$) on G/PANI/PS nanoporous fibre-modified SPCE with detection limit of 3.30 $\mu$g L$^{-1}$ and 4.43 $\mu$g L$^{-1}$ respectively.
3.1.3 Graphene-polymerne (PPy) nanocomposites

Palanisamy et al. reported the synthesis of polypyrrole decorated graphene/β-cyclodextrin (GR-CD/PPy) composite for low-level electrochemical detection of Hg$^{2+}$ in various water samples [73]. The GR-CD/PPy composite was synthesized by chemical oxidation of PPy monomer in GR-CD solution using FeCl$_3$. The FeCl$_3$ solution was added into the GR-CD/pyrrole suspension, the mixture was stirred for 1 h for the polymerization of pyrrole to PPy. The result of GR-CD/PPy composite was obtained after a day treated in an air oven at 50 °C. The authors employed the differential pulse voltammetry (DPV) technique for the detection of Hg$^{2+}$, and the results showed the limit of detection (LOD) of 0.47 nM L$^{-1}$ that below the guideline level of Hg$^{2+}$ set by the World’s Health Organization (WHO) and U.S. Environmental Protection Agency (EPA). Figure 7 illustrates the schematic of GR-CD/PPy composite for detecting Hg$^{2+}$.
Figure 7  Schematic diagram of the detection of Hg^{2+} based on GR-CD/PPy composite modified electrode synthesized via polymerization method [73].

Another example for the synthesis of electrochemical sensor based on graphene-polypyrrole nanocomposites is reported by Dai et al. [74]. Dai synthesized polypyrrole/graphene oxide (PPy/GO) nanocomposites via in situ chemical oxidation polymerization and followed by phytic acid (PA) molecules functionalization with nanocomposites through electrostatic attraction. According to the authors, a purified GO nanosheets were obtained by exfoliation of natural graphite are dispersed in water, giving a yellow-brown dispersion with a concentration of 0.5 mg/mL. Then a pyrrole solution is added by magnetic stirring for more than 1 h. Subsequently, the oxidation agent containing FeCl₃-6H₂O is added into the mixture before continued stirring for 4 h at temperature of 0 to 4 °C. The final product of PA/PPy/GO nanocomposites is obtained after sonication PPy/GO nanocomposites into a PA solution for 2 h. The synthesis steps of PA/PPy/GO nanocomposite are shown in Figure 8. The synthesized of phytic acid-functionalized polypyrrole/graphene oxide nanocomposites were then developed for determination of Cd^{2+} and Pb^{2+} simultaneously. The electrochemical determination of Cd^{2+} and Pb^{2+} metal ions were traced by differential pulse voltammetry (DPV) technique revealed the detection limit of 2.13 μg L⁻¹ for Cd^{2+} and 0.41 μg L⁻¹ for Pb^{2+} respectively.
3.1.4 Graphene-poly (3,4 - ethylenedioxythiophene) (PEDOT) nanocomposites

Zuo et al. reported an electrochemical determination of Hg$^{2+}$ at trace level based on poly(3,4-ethylenedioxythiophene) nanorods/graphene oxide nanocomposite modified glassy carbon electrode (PEDOT/GO/GCE) by using a simple liquid–liquid interfacial polymerization approach [90]. The differential pulse stripping voltammetry (DPSV) was applied to determine low concentrations of Hg$^{2+}$ on PEDOT/GO/GCE. The electrochemical sensor exhibited a good linear relationship of peak currents and the concentration of Hg$^{2+}$ in range of 10.0 nM to 3.0 μM with detection limit was estimated to be 2.78 nM. The electrochemical sensor showed good selectivity for Hg$^{2+}$ detection and applicable in real water samples testing.

Yasri et al. also reported a partially oxidized graphene flakes (po-Gr) modified with poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) by sonication method [91]. First, the po-Gr flakes were obtained by electrochemical exfoliation of graphite sheet. Then the po-Gr dispersion was mixed with PEDOT:PSS solution by a probe sonicator during sonication process. By using differential pulse stripping voltammetry (DPSV) technique, the final composite of the po-Gr/PEDOT:PSS conducting film exhibited satisfactorily for sensitive and selective detection of Hg$^{2+}$ in real samples with a limit of detection of 0.19 μM.
3.2 Sensors using graphene modified electroactive polymer

3.2.1 Graphene-Nafion nanocomposites

Besides fabrication with conducting polymers, other electroactive polymers including Nafion, poly(dimethylsiloxane) (PDMS), polydopamine, poly-L-lysine (PLL), polyallylamine, and polyethyleneimine have also been widely used in heavy metal ion sensing [92]. Another sensing platform to detect trace levels of toxic elements, such as lead and cadmium by differential pulse anodic stripping voltammetry (DPASV) technique was earlier introduced by Li at al. [67]. Li dispersed graphene nanosheets into Nafion-isopropyl-alcohol solution by using in situ plated bismuth film electrode (BFE) fabrication. Then, the final Nafion-G composite film was obtained after the coated glassy carbon electrode was evaporated under an infrared lamp. The Nafion-G composite film modified GC electrode exhibited enhance electrochemical sensing with the limit of detection around 0.02 μg L⁻¹ for Pb²⁺ and Cd²⁺ as shown in Figure 9.

![Figure 9](image)

*Figure 9* (A) DPASVs for 20 μg L⁻¹ each of Cd²⁺ and Pb²⁺ on an in situ plated Nafion-BFE, Nafion-G-BFE in presence of Bi³⁺ solution, (B) SEM image of Bi film deposited on the Nafion (a) and Nafion-G (b) modified GCE [67].

Another example of Nafion composite fabrication in removal of heavy metal ions is employed when the Nafion cation is introduced into ionic liquid-reduced graphene oxide (IL-rGO) supported gold nanodendrites (AuNDs) [65]. The ionic liquids (ILs) have received great attention because of their tunable structures and unique physicochemical
properties such as can provide a wide electrochemical window, high ionic conductivity, superior thermal stability, good solubility, and biocompatibility [93,94]. Furthermore, the introduction of IL moieties into functional graphene composites can increase their solubility and improve electrochemical performance [65]. The IL-rGO/AuNDs/Nafion modified electrode is applied for iron removal in coastal waters by square wave voltammetry (SWV) technique. The IL-rGO/AuNDs/Nafion modified electrode showed good responses for iron ions with a linear relation with its concentrations ranging from 0.30 to 100 μmol L⁻¹ and the detection limit of 35 nmol L⁻¹. The schematic diagram of the stepwise self-assembly procedures of IL-rGO/AuNDs/Nafion modified electrode is shown as figure 10.

![Schematic diagram of the stepwise self-assembly procedures IL-rGO/AuNDs/Nafion modified electrode for electrochemical determination of iron](image)

*Figure 10* Schematic diagram of the stepwise self-assembly procedures IL-rGO/AuNDs/Nafion modified electrode for electrochemical determination of iron [65].

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