chemosensors

Review

Synergism between Graphene and Molecularly Imprinted Polymers in Developing Electrochemical Sensors for Agri-Food and Environmental Analyses

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Abstract: In recent years, new sensor-based technologies have been developed to meet the demand for rapid and accurate analysis of food and environment, as food safety and environmental monitoring are very important concerns nowadays. In this context, considerable attention has been paid to the development and design of electrochemical sensors, as these offer a number of advantages, such as portability, ease of use, low costs and fast response times. Molecularly imprinted polymers (MIPs) are robust synthetic polymers with special cavities designed for a target molecule, and they are used as selective tools through a mechanism of molecular recognition. Graphene is a 2D crystalline carbon that forms either a single or a coupled layer of hexagonally arranged carbon atoms and is referred to as a "wonder material". The use of these two structures in the development of electrochemical sensors gives the newly created analytical tool enhanced properties, such as improved sensitivity and selectivity, low detection limit, good stability and reusability. This review presents an overview of the recent research regarding the use of MIPs and graphene in the development of electrochemical sensors for food and environmental analyses, critically discusses the pros and cons, and gives perspectives for further developments in this field.

Keywords: molecularly imprinted polymers; graphene; electrochemical sensors; environment; agriculture; food

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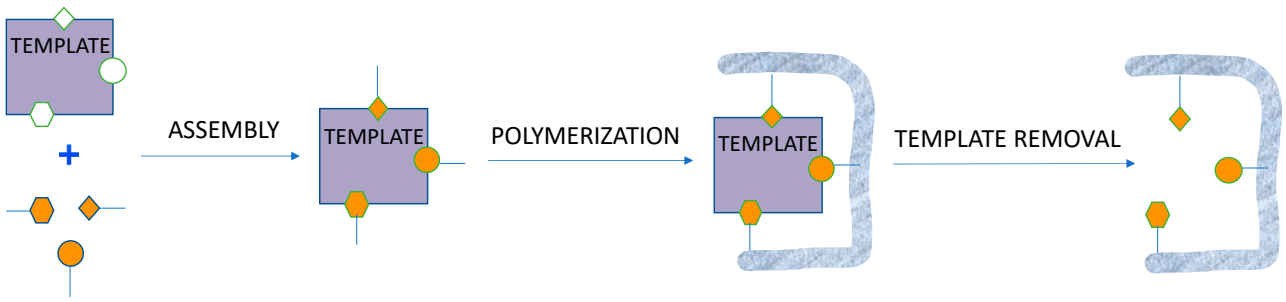
1. Introduction

The European Union (EU) notes that the agricultural sector has had great success in achieving its production objective in recent years. However, this has often been at the expense of environmental degradation, soil and water pollution, negative impacts on biodiversity and a high carbon footprint. Therefore, one of the EU's current targets is for at least 75% of all soils in the EU to be healthy for food, people, nature and the climate by 2030 [1]. Furthermore, Barhoum et al. found that an intrinsic relationship between food quality and environmental quality is naturally established; therefore, monitoring environmental quality and promoting safety measures is essential to preserve food quality. A large number of casualties is generated by pollution, regardless of whether air, soil or water is the contaminated source, with 9 million premature deaths being reported annually [2]. Pesticides, insecticides, herbicides, artificial fertilisers, veterinary pharmaceuticals and fisheries drugs are widely used by farmers and producers in crop cultivation to improve crop yield and fulfil quantitative market demand [3]. At the various stages of food preparation, e.g., manufacturing, processing, packaging, distribution and retail, food is exposed to contaminants, including plasticisers, heavy metal ions, additives, preservatives, food colourings and artificial fragrances. Consumption of these chemically and biologically hazardous substances and microorganisms has adverse health effects on consumers, e.g., hypertension,

allergic reactions, high blood pressure, hormonal disorders and inflammation. Normally, techniques such as UV-Vis spectroscopy, fluorescence, liquid or gas chromatography and capillary electrophoresis are used for the analysis of real samples from agri-food and environment, but they are expensive, time-consuming, require well-trained personnel, consume large amounts of reagents, etc. With this in mind, electrochemistry is at the heart of many sensors developed for the agri-food sector, environmental analysis and other important areas [4]. Electrochemical sensors are the most important tools in electrochemistry, and the need to use new materials with improved properties is a desideratum. The development of electrochemical sensors is gaining interest because they are inexpensive, have good sensitivity to a wide range of analytes, do not require trained personnel, are easily miniaturised, can be used in the field and, above all, require little power consumption [5,6]. The most important aspect when developing an electrochemical tool is related to the proper choice of the working electrode material as this is key to obtaining high sensitivity and good selectivity. Development of electrochemical sensors generally followed the evolution of conductive materials [7] used for electrode preparation and consequently was based on the use of different conductive supports, starting from inert electrode materials as metals—gold, platinum and silver [8–12]—and carbon-based materials—glassy carbon, carbon nanostructures, graphite and doped diamond-based materials [13–19]. It should be mentioned that historical evolution of electrode materials involved even mercury; accordingly, dropping mercury electrodes (DMEs) were used in electrochemical sensor development [20].

An interesting alternative in preparation of conductive materials is molecularly imprinted polymers (MIPs), which are synthetic materials obtained by polymerisation, having as specific features tailored shapes and functional groups designed to ensure the complementarity fit to the target molecule (Scheme 1). MIPs offer several advantages, including fast and easy fabrication; high chemical, mechanical and thermal stability; reusability; low manufacturing costs; and high specificity. They can be regarded as synthetic analogues of nature's enzyme–substrate systems, which function according to Fischer's lock-and-key mechanism [21].



Scheme 1. Schematic representation of the synthesis of molecularly imprinted polymer preparation.

It is 50 years since Wulff published the first paper on the molecular imprinting of synthetic polymers. It arose from the desire to produce catalysts that imitate enzymes [22–24]. In general, MIPs are obtained by bulk polymerisation (3D). In this process, it is used as a target template, the polymerisation reaction occurring, at its level, between organic and inorganic functional monomers in the presence of cross-linking reagents. After polymerisation, the template molecules are removed, and a polymer matrix with complementary sites to imprinted molecule is obtained. Thus, the obtained structure is able to interact with the target molecules [25].

Graphene, the magical material, as it was named by the researchers working in the nanomaterials area, consists of a single layer of sp^2 carbon atoms arranged in a two-dimensional honeycomb lattice. The researchers' fascination lies in its powerful properties, such as high surface area, excellent thermal conductivity and high Young's modulus, which makes it the strongest material ever measured. Graphene was discovered in 2004 [26] by Andre Geim and Konstantin Novoselov, who received the Nobel Prize in Physics for this

in 2010. Due to its properties, graphene is used in many areas such as electronics, energy storage, biotechnologies and sensors/biosensors [27]. There are several forms of graphene that have been used in the development of electrochemical sensors, including graphene nanoribbons (thin bands of graphene nanosheets having nanometre width) [28], graphene oxide (layered and oxygenated graphene sheets containing oxygen functional groups) [29] and reduced graphene oxide [30,31].

These special properties of MIPs and graphene materials make them very suitable for electrochemistry, especially for the construction of electrochemical sensors. The coupling of MIPs and graphene leads to higher sensor performance, lowers the detection limit and makes electrochemical sensors a powerful approach as they are free from interference since the interfering substances do not have the same structure as the target analytes. According to the Scopus database, the first electrochemical sensor that has used both MIP and graphene was the one developed by Liu et al. in 2012 for the determination of 2,4-dinitrophenol [32]. In recent years, researchers have used graphene together with MIP in the development of electrochemical sensors to improve the electrical conductivity of the sensor, increase the surface area and thus increase the sensitivity.

The aim of this article is to provide an overview of the most recent progress in the field of electrochemical sensors based on both MIPs and graphene, which are used in the agri-food industry and in environmental analysis. In this review, some brief information regarding MIPs, graphene and electrochemical sensors is presented, followed by recent advances in "electrochemical sensors", "molecularly imprinted polymers" and "graphene". The important data that have applications in the food or environmental field are analysed and, at the end of the article, future perspectives and challenges together with conclusions are given.

2. Molecularly Imprinted Polymers

MIPs are synthetic materials formed by the polymerisation of functional monomers in the presence of an analyte to form cavities for target molecules and deposit them on various types of electrode surfaces. After the analytes are removed, complementary imprinted cavities suitable for the target molecules remain [33]. The MIPs obtained are stable and resistant to a wide range of pH values, temperatures, solvents, etc. [34].

Regarding MIP synthesis, the first step consists of the formation of pre-polymerisation complexes between the target analyte (template) and the functional monomers. Considering the nature of the interaction between the functional monomers and the template during both the polymerisation and rebinding processes, there are three different strategies: covalent (the first approach described in the 1970s), semi-covalent and non-covalent. In the case of covalent interaction, reversible covalent bonds are formed before polymerisation, followed by removal of the template with cleavage of the covalent bonds, which then reform by binding to the target molecules. The second type of interaction, semi-covalent, consists of a covalent interaction between the template and monomer, but the rebinding occurs through non-covalent bonds. Finally, the non-covalent approach consists of the formation of weak interactions such as hydrogen bonds, electrostatic interactions and van der Waals forces between the monomer and the template before polymerisation. Analyte rebinding occurs by the same interactions. The non-covalent approach is the most commonly used for the preparation of MIPs due to its simplicity and wide range of chemical functionalities [35]. The second step consists of polymerising the functional monomer around the template in the presence of a cross-linker, creating the rigid MIP network. The next step is to remove the template from the MIP, creating voids that correspond to the shape and size of the analyte. The final step is to immerse the MIP in the analyte solution so that the voids recognise the target analyte. MIPs can recognise very small to very large molecules, such as proteins, which makes them extremely useful in the field of electrochemical sensors. At the same time, synthesis of a non-imprinted control polymer is carried out using the same procedure as for MIP synthesis but omitting the addition of the template.

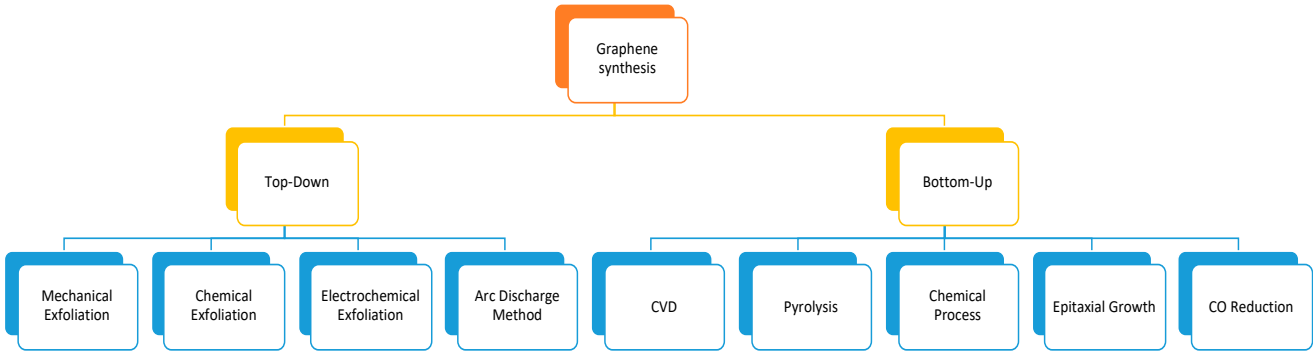
Another important aspect in the production of stable MIPs with suitable recognition properties is the correct choice of template, monomers, cross-linker and solvent as well as polymerisation conditions, as each of them leaves an important fingerprint on the final product [36]. The most important element in the creation of an MIP is the template. Nevertheless, the choice of monomer is also crucial, as it depends on the type of template (e.g., acidic monomers for basic templates and basic monomers for acidic templates). The most common monomers successfully used in the development of MIPs are methacrylic acid, pyrole and 4-vinylpyridine. The role of the cross-linker is to form the network that maintains the shape of the binding site, and it also affects the polarity, surface area, pore size and adsorption capacity. The amount of cross-linker is very important in the production of MIPs to avoid the formation of structures that are too rigid. The solvent is the challenging aspect during the process as it must dissolve all the components but not interfere with the template or monomer. For example, as it has already been mentioned that non-covalent approaches are usually used, non-polar aprotic solvents must be used as they have a low capacity for donating or accepting hydrogen bonds.

MIPs, which are characterised by their high selectivity and stability, are used for numerous applications, such as separation processes, drug delivery, solid-phase extraction and, most importantly, as detection elements for electrochemical sensors and biosensors [37]. Normally, sensors and biosensors are not very selective, but when you use MIPs, they become selective/specific for the analyte of interest.

3. Graphene

Some disadvantages of MIP-based sensors and biosensors are slow mass transfer and low binding capacity. However, these drawbacks have been overcome by increasing the porosity, conductivity and surface area of the transducer using graphene materials. Graphene, as mentioned in the Introduction, is the "wonder material" of recent years. Due to its unique properties, it is used in many fields, such as sensors and biosensors [38,39], electronics [40], optoelectronics [41] and biosystems [42].

There are two main approaches to graphene synthesis: top-down methods, in which the stacked graphene layers are broken up by extracting thin layers, and bottom-up methods, in which graphene is synthesised [43]. Top-down methods involve mechanical, chemical or electrochemical exfoliation of graphite, while bottom-up methods form graphene by assembling molecules into a single or multiple graphene layers through chemical vapor deposition (CVD), thermal or chemical processes (Scheme 2) [4].



Scheme 2. Graphene synthesis methods.

Another property that makes graphene an interesting material for sensory applications is its ease of functionalisation through covalent or non-covalent bonds [44]. In the case of covalent functionalisation, the sp^2 structure of graphene is changed, leading to a change in the electronic configuration and thus to higher stability. However, non-covalent functionalisation is preferred to covalent functionalisation because the graphene structure is not changed and different molecules can be physically adsorbed onto the graphene nanosheets.

One more added value of graphene is that it can be an environmentally friendly material [29]. This and other properties such as biocompatibility, high electrical and thermal conductivity, large electrochemical potential window and a large surface area have led to its use in the field of electrochemical sensors. Other graphene-related materials that are successfully applied in the field of electrochemical sensors are graphene oxide (GO) [45] and reduced graphene oxide (rGO) [46]. These compounds have different chemical and mechanical properties when compared to graphene.

GO, the oxidised form of graphene, consists of a monatomic layered material of carbon, hydrogen and oxygen molecules and can be produced on a large scale from graphite using strong oxidising agents such as $NaNO_3$, $KMnO_4$ and concentrated sulphuric acid [47]. The best known method for producing GO from graphite is the Hummers method [48], which uses a mixture of $KMnO_4$ and concentrated sulphuric acid. It is worth noting that Hummers' work has more than 26,000 citations. Due to the strong oxidation, the GO obtained in this way has numerous defects that are useful in the development of electrochemical sensors. Another important property of GO is that it is very hydrophilic due to the presence of oxygen.

rGO is obtained by reducing GO using physical, chemical, photochemical or electrochemical methods. The most commonly used reducing agents to produce rGO are the highly toxic hydrazine hydrate and milder compounds such as sodium borohydride, vitamin C, reducing sugars and urea [49]. Compared to GO, rGO does not dissolve as easily as it tends to form aggregates. However, rGO has a higher electrochemical conductivity than GO.

4. Electrochemical Sensors

Electrochemical sensors are a relatively new and powerful tool for the determination of many analytes from different fields because they are portable, inexpensive, easy to use, fast, reliable and sensitive, and because of these characteristics, they are the most commonly used sensors. The basic principle of the electrochemical sensors is that they convert the interaction between a target analyte and a receptor located on the surface of a sensing electrode into a measurable analytical signal [50]. Electrochemical sensors usually consist of a three-electrode system, namely, a working electrode (WE) where the electrochemical reaction takes place, a reference electrode (RE) and a counter electrode (CE). Depending on the measured electrical signal, the electrochemical sensors can be classified into three major classes, amperometric, potentiometric and conductometric [51]. In the case of amperometric sensors, a potential is applied between the working and reference electrodes to reduce or oxidise the electroactive compounds of interest and the resulting current is measured. For potentiometric sensors, the variation of potential between working and reference electrodes is measured which gives information about the analyte concentration. Conductometric sensors measure the conductivity of a film or other material that is influenced by the target analyte. The ideal electrochemical sensor has to be selective and sensitive towards the targeted compound and these aspects are fulfilled by MIPs and graphene, respectively.

5. MIPs and Graphene Electrochemical Sensors for Agri-Food Analyses

One of the potential disadvantages of electrochemical sensors is the lack of selectivity. However, this can be countered by using MIPs in combination with graphene as specific detection elements. To increase the sensitivity of MIP-based electrochemical sensors, the sensing surface of the electrode could be increased by using various nanomaterials such as carbon derived materials and noble metal nanoparticles [52]. Graphene is the perfect material for developing electrochemical sensors, because it has a large surface area with many electroactive sites and is therefore very well suited for detecting the molecules adsorbed onto the surface of the electrode [53].

Looking at both materials, it is clear that a "mixture" of the two results in electrochemical sensors with better performance, so we can say that synergism occurs between them. An extremely important aspect when developing an MIP-based sensor is the choice of the

monomer in order to obtain a good selectivity. Electrochemical sensors based on both MIPs and graphene used in agri-food are shown in Table 1.

Table 1. Electrochemical sensors based on both MIPs and graphene used in agri-food.

Electrode Material	Electrochemical Technique	Monomer	Template/Analyte	Samples	LoD, mol L^{-1}	Ref.
[a] mag-MIP/Gr-UiO-66/SPE	[i] CV	Methacrylic acid	Cannabidiol	CBD products	5.00×10^{-8}	[54]
[b] Pt-NPs-NH_2-r-GO/GCE	[ii] EIS	Indole-6-carboxylic acid	Fluxapyroxad	Apple, cabbage	1.00×10^{-10}	[55]
[c] MIP/graphene/GCE	[iii] DPV	Acrylamide	Phoxim	Cucumber	2.00×10^{-8}	[56]
[d] MIP/rGO@Au/GCE	DPV	Methacrylic acid	Carbofuran	Cucumbers and cabbage	2.00×10^{-8}	[57]
[e] CS–PtNPs/GR–AuNPs/MIPs/gold electrode	[iv] CA	$HAuCl_4$, 2-mercaptonicotinic acid (MNA)	Erythromycin	Milk, honey	2.30×10^{-8}	[58]
[f] MIP@GO/GCE	DPV	Pyrrole	Glyphosate	Corn	1.10×10^{-5}	[59]
[g] RGO/Fe_3O_4-MIP/GCE	DPV	1-vinyl-3-butylimidazolium hexafluorophosphate ([VC4mim][PF6])	Diphenylamine	Lake water, pear peel, apple peel	5.00×10^{-8}	[60]
[h] MIP/Fe_3O_4/GO/GCE	[v] SWV	1-ethyl-3-methylimidazolium tetrafluoroborate	Patulin	Apple and pear juices	3.33×10^{-13}	[61]
[i] GCE-EG-MIP	DPV	Pyrrole	Ascorbic acid	-	1.00×10^{-4}	[62]
[j] MIPs/HA -MWCNTs/PPy-SG/GCE	CA	Pyrrole	Tryptamine	Cheese, lactobacillus beverage	7.40×10^{-8}	[63]
[k] GO /CCNTs/ IL /AuNPs/MIPs	DPV	Pyrrole	Vanillin	Tap water	6.20×10^{-9}	[64]
[l] MIPs/PPy/DGr/GCE (MIECS)	DPV	Pyrrole	Olaquindox	Fish and feedstuff	7.50×10^{-9}	[65]
[m] MIP/Au-PB/SH-G/AuNPs/GCE	DPV	*o*-aminophenol and resorcinol	Tebuconazole	Cucumber, green vegetable, strawberry	1.25×10^{-8}	[66]
[n] PEI-rGO-Au-NCs@MIP	DPV	Choline chloride	β-lactoglobulin	Milk	See text	[67]
[o] PtNPs@MIP/SPGrE	[vi] ASV	Methacrylic acid	Paraquat	Cabbage, cucumber, yardlong bean, kale, tomato, onion, lettuce	2.00×10^{-8}	[68]
[p] PDDA-Gr-(Pd-Cu) @MIP-PDA /GCE	DPV	Dopamine	Amaranth	Soft drinks	2.00×10^{-9}	[69]
[q] GCE/GO–PtCo@MIPDA	DPV	Dopamine hydrochloride	Tartrazine	Orangeade, yellow wine, ice cream, jelly, instant juice powder, candy, cookie	1.10×10^{-9}	[12]
[r] MIP/GO/GC	DPV	β-cyclodextrin	Epigallocatechin gallate	Tea samples	8.78×10^{-9}	[70]
[s] MIPs/PtAu-GrCNTs/GCE	CA	*o*-phenylenediamine	Propyl gallate	Oil samples	2.51×10^{-8}	[71]
[t] GCE/rGO-MIP	DPV	Phenylboronic acid	Fructose	Orange, apple and grape juices	3.20×10^{-15}	[72]
[u] MIP/ERGO/GCE	DPV	*o*-phenylenediamine and resorcinol	Thiabendazole	Orange juice	1.25×10^{-7}	[73]
[v] GN/MIPs/GCE	[vii] LSV	*p*-Vinylbenzoic acid	Imidacloprid	Rice	1.00×10^{-7}	[74]
[w] MIP-GN/GCE	LSV	*p*-Vinylbenzoic acid	Thiamethoxam	Brown rice	4.00×10^{-5}	[75]

Table 1. *Cont.*

Electrode Material	Electrochemical Technique	Monomer	Template/Analyte	Samples	LoD, mol L^{-1}	Ref.
[x] MGO@AuNPs-MIPs	DPV	Methacrylic acid	Dibutyl phthalate	Wine samples	8.00×10^{-10}	[76]
[y] MIP/Ag/Ni-MOF/N-GQDs/GCE	DPV	Aniline	Olaquindox	Fish muscle, swine muscle, chicken breast	2.20×10^{-9}	[77]

[a] mag-MIP/Gr-UiO-66/SPE: magnetic molecularly imprinted polymer/graphene UiO-66/screen-printed electrode; [b] Pt-NPs-NH_2-r-GO/GCE: platinum nanoparticles amino-functionalised graphene glassy carbon electrode; [c] MIP/graphene/GCE: molecularly imprinted polymer/graphene/glassy carbon electrode; [d] MIP/rGO@Au/GCE: molecularly imprinted polymer/reduced graphene oxide gold nanoparticles/glassy carbon electrode; [e] CS–PtNPs/GR–AuNPs/MIPs/gold electrode: chitosan–platinum nanoparticles/graphene–gold nanoparticles/molecularly imprinted polymers/gold electrode; [f] MIP@GO/GCE: molecularly imprinted polymer graphene oxide/glassy carbon electrode; [g] RGO/Fe_3O_4-MIP/GCE: reduced graphene oxide/iron oxide–molecularly imprinted polymers/glassy carbon electrode; [h] MIP/Fe_3O_4/GO/GCE: molecularly imprinted polymer/iron oxide/graphene oxide/glassy carbon electrode; [i] GCE-EG-MIP: glassy carbon electrode–exfoliated graphene–molecularly imprinted polymer; [j] MIPs/HA-MWCNTs/PPy-SG/GCE: molecularly imprinted polymers/hyaluronic acid–multiwalled carbon nanotubes/polypyrrole sulphonated graphene/glassy carbon electrode; [k] GO/CCNTs/IL/AuNPs/MIPs: graphene oxide/carboxylated multiwalled carbon nanotube/ionic liquid/gold nanoparticles/molecularly imprinted polymers; [l] MIPs/PPy/DGr/GCE (MIECS): molecularly imprinted polymers/polypyrrole/Dopamine@Graphene/glassy carbon electrode; [m] MIP/Au-PB/SH-G/AuNPs/GCE: molecularly imprinted polymers/gold–Prussian blue/thiolgraphene/gold nanoparticles/glassy carbon electrode; [n] PEI-rGO-Au-NCs@MIP: polyethylenimine–reduced graphene–gold nanoclusters@molecularly imprinted polymers; [o] PtNPs@MIP/SPGrE: platinum nanoparticles molecularly imprinted polymer/screen-printed graphene paste electrode; [p] PDDA-Gr-(Pd-Cu) @MIP-PDA/GCE: poly(dial-lyldimethylammonium chloride)–graphene–palladium–copper nanocomposite@molecularly imprinted polymer/glassy carbon electrode; [q] GCE/GO–PtCo@MIPDA: glassy carbon electrode/platinum cobalt nanoalloy–functionalised graphene oxide@ membrane of molecularly imprinted polydopamine; [r] MIP/GO/GC: molecularly imprinted polymer/graphene oxide/glassy carbon; [s] MIPs/PtAu-GrCNTs/GCE: molecularly imprinted polymers/platinum gold nanoparticles–graphene–carbon nanotubes/glassy carbon electrode; [t] GCE/rGO-MIP: glassy carbon electrode/reduced graphene oxide molecularly imprinted polymer; [u] MIP/ERGO/GCE: molecularly imprinted polymer/electrochemically reduced graphene oxide/glassy carbon electrode; [v] GN/MIPs/GCE: graphene nanoribbon/molecularly imprinted polymer/glassy carbon electrode; [w] MIP-GN/GCE: molecularly imprinted polymer graphene nanoribbon/glassy carbon electrode; [x] MGO@AuNPs-MIPs: magnetic graphene oxide and gold nanoparticles–molecularly imprinted polymers; [y] MIP/Ag/Ni-MOF/N-GQDs/GCE: molecularly imprinted polymer/nickel-based metal-organic framework functionalised with silver nanoparticles/nitrogen-doped graphene quantum dots/glassy carbon electrode; [i] CV: cyclic voltammetry; [ii] EIS: electrochemical impedance spectroscopy; [iii] DPV: differential pulse voltammetry; [iv] CA: chronoamperometry; [v] SWV: square wave voltammetry; [vi] ASV: anodic stripping voltammetry; [vii] LSV: linear sweep voltammetry.

Cannabidiol (CBD) is an important ingredient of cannabis, which is extracted from the hemp plant (*Cannabis sativa* L.). According to various studies, CBD is not addictive and is an important product on the market approved by the U.S. Food and Drug Administration (FDA) for the treatment of seizures. Tang et al. [54] have developed an electrochemical sensor for the detection of CBD. The UiO-66 (zirconium 1,4-dicarboxybenzene) was prepared, then mixed with graphene (Gr) and the resulting Gr-UiO-66 suspension was carefully dropped onto the surface of the working electrode of a screen-printed electrode (SPE) and then allowed to dry. Subsequently, the mag-MIP suspension was dropped onto the working electrode of the Gr-UiO-66/SPE to develop mag-MIP/Gr-UiO-66/SPE and further used for the determination of CBD from CBD products.

Shi et al. [55] have developed a novel electrochemical molecularly imprinted polymer (MIP) sensor for fluxapyroxad (FP). Indole-6-carboxylic acid (6-IAA) and platinum (Pt) nanoparticles (NPs) on a support of amino-functionalised reduced graphene oxide (NH_2-r-GO) formed the basis of the electrochemical MIP sensor. The obtained nanocomposite (Pt-NPs-NH_2-r-GO) was then used to modify the surface of a glassy carbon electrode (GCE), resulting in an electrochemical Pt-NPs-NH_2-r-GO/GCE sensor having an excellent detection limit.

Tan et al. [56] developed an electrochemical sensor using a graphene-modified GCE and a MIP membrane for the determination of phoxim in cucumber samples. Phoxim, an organophosphate pesticide, is widely used in agriculture due to its high efficacy against insects. The sensor was first made by drop-casting graphene suspension and then drying it. In addition, the MIP was prepared using phoxim as the template, acrylamide as the

functional monomer and ethylene glycol maleic acid rosinate acrylate (EGMRA) as the cross-linker. The mixture was also dropped onto the graphene-modified GCE, then polymerised and washed with acetic acid/methanol solution to remove the template molecule. The developed sensor is an example of synergism between graphene and MIPs. The addition of graphene leads to an increase in current intensity and a shift in the reduction peak potential of 0.185 V, which is due to the electrocatalytic effect of graphene. The response of the developed sensor was measured using differential pulse voltammetry. Switching from organophosphate to carbamate compounds, the same group [57] reported the development of an electrochemical sensor, an MIP one, for detection of carbofuran. The MIP sensor was developed using a GCE decorated with reduced graphene oxide and Au nanoparticles, MIP being directly obtained using a targeted compound, carbofuran, as the template molecule. As a cross-linking agent, it also used EGMRA, while methyl acrylic acid was used as the functional monomer, in the polymerisation reaction. The developed sensor was used to determine carbofuran in cucumber and cabbage.

Another molecularly imprinted electrochemical sensor based on Au electrode, this time decorated with chitosan–PtNPs (CS-PtNPs) and graphene–gold nanoparticles (GR-AuNPs), was fabricated for the determination of erythromycin in milk and honey, as erythromycin residues have toxic effects on consumers [58]. Both nanoparticles were "homemade": first, the CS-PtNPs were added to the surface of the Au electrode, followed by the GR–AuNPs. The synergistic effects of CS–PtNPs, GR–AuNPs and MIPs were used to improve the current response and the sensitivity of the sensor.

In 2022, a study reporting the assessment of glyphosate (GPh) content in corn was published, with an electrochemical sensor being developed for herbicide monitoring. MIP nanocomposite was obtained by polymerising pyrrole (Py) on GO nanosheets modified with GCE (MIP@GO/GCE) [59]. The developed electrochemical sensor had a significantly higher peak current and lower oxidation potential than other electrode combinations, which can also be attributed to the synergistic effects between MIP and GO, which result in a larger electroactive surface area and thus better sensitivity.

Liu et al. [60] used two types of ionic liquids in MIP synthesis, namely, the ionic liquid 1-vinyl-3-butylimidazolium hexafluorophosphate ($[VC_4mim][PF_6]$) as the functional monomer and the ionic liquid 1,4-butanediyl-3,3′-bis-l-vinylimidazolium dihexafluorophosphate ($[V_2C_4(mim)_2][(PF_6)_2]$) as the cross-linker. First, the cross-linker $[V_2C_4(mim)_2][(PF_6)_2]$ was obtained in a two-step procedure. Then, RGO/Fe_3O_4, diphenylamine (DPA) and $[VC_4mim][PF_6]$ were dispersed in a mixed solvent to prepare RGO/Fe_3O_4-IL-MIP. Finally, a new composite of RGO/Fe_3O_4-ionic liquid-based MIP (RGO/Fe_3O_4-IL-MIP) was prepared and applied to a GCE for the detection of DPA in water and fruit samples. Afzali et al. [61] have developed a novel electrochemical sensor for the determination of patulin toxin from apple and pear juices. The development of the sensor was based on a GCE modified with a composite material obtained from an ionic liquid-based molecularly printed polymer (MIP) and magnetic nanoparticles/graphene oxide (Fe_3O_4/GO). The group first prepared Fe_3O_4 NPs and then Fe_3O_4/GO (non-covalent imprinting process that used patulin as the template molecule), 1-ethyl- 3-methylimidazolium tetrafluoroborate ($[EMIM]^+[BF4]^-$) as the functional monomer and ethylene glycol dimethacrylate (EGDMA) as the cross-linker agent, while 2,2′-azobisisobutyronitrile (AIBN) was the initiator, followed by a MIP/Fe_3O_4/GO nanocomposite mixed with Nafion for stabilisation and applied to the surface of a GCE. The developed MIP/Fe_3O_4/GO/GCE was used to determine patulin with an extremely low limit of detection. In this case, GO nanosheets with excellent conductivity increased sensor sensitivity, while MIP with unique cavities for patulin molecules improved electrochemical sensor selectivity.

Ascorbic acid (AA) is a powerful antioxidant that is commonly used as a preservative in the food industry. Therefore, Oliveira et al. [62] developed a sensor for the determination of AA using a GCE modified with both electrochemically exfoliated graphene (EG) and MIPs. The electrochemical device proved to be highly selective in the presence of interfering factors such as dopamine and uric acid. The group obtained the EG-modified sensor by

electrochemical exfoliation of graphite followed by deposition on the GCE. The obtained EG-GCE was then immersed in a solution containing $LiClO_4$, Py monomer and AA and the final electrochemical sensor was also prepared by electropolymerisation.

Xing et al. [63] developed an imprinted electrochemical sensor for the sensitive detection of tryptamine. Tryptamine, a biogenic amine synthesised by tryptophan decarboxylation, is found in protein-rich foods such as meat, fish and dairy products and can cause hypertension in high concentrations. The first step of the work was to prepare sulphonated graphene (SG), followed by the addition of Py monomer and their electropolymerisation to obtain PPy-SG/GCE electrodes. Subsequently, the MWCNTs were carboxylated and casted onto the PPy-SG/GCE electrodes to produce the final electrochemical sensor, MIPs/HA-MWCNTs/PPy-SG/GCE, which was successfully used for tryptamine determination in cheese and lactobacillus beverage samples.

Carbon-based composite materials were used to obtain an imprinted electrochemical sensor to assess the vanillin in spiked water samples [64]. The sensor fabrication involved the use of GO/carboxylated multiwalled carbon nanotube/ionic liquid/Au nanoparticles to enhance the sensor sensitivity and the conductivity by improving the efficiency of the electron transfer process, while the response specificity for vanillin was ensured by the MIP membrane which was prepared by electropolymerisation.

Bai et al. [65] developed a molecularly imprinted electrochemical sensor for the sensitive detection of olaquindox (OLA), a feed additive used to improve feed conversion and promote animal growth, which was banned by the European Community and the United States in 1998 because of its toxicity and food safety concerns. The sensor was manufactured as follows: Dopamine@Graphene (DGr) composites were dropped onto a GCE, Py was electropolymerised onto the resulting electrode surface, which stabilised the matrix and significantly improved the current signal. Finally, the homogeneous MIPs' thin film was constructed by electropolymerisation in the presence of OLA template molecules on the surface of the GCE modified with DGr and PPy (Figure 1). The developed MIPs/PPy/DGr/GCE (MIECS) was used to detect OLA in fish and feedstuff.

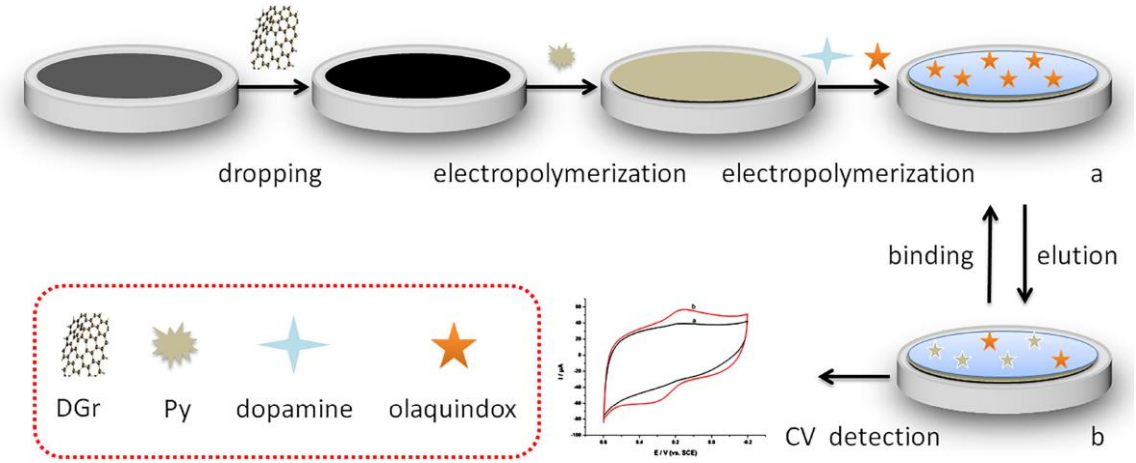


Figure 1. Schematic illustrations of the construction procedure of MIPs/PPy/DGr/GCE. (Reprinted with permission of [65] Copyright © 2020, Elsevier B.V.)

The work of Qi et al. [66] describes the design of a molecularly imprinted electrochemical sensor for sensitive, selective and rapid detection of tebuconazole. Tebuconazole is a fungicide effective against various foliar diseases of cereals and other crops. Based on the specific ability of gold to easily form self-assembled layers with thiol derivatives, gold nanoparticles (AuNPs) were used to modify the surface of a GCE, AuNPs working further as coupling agents for additional modification. Furthermore, AuNPs-GCE-modified electrode was immersed in the thiol graphene (SH-G) suspension to obtain the SH-G-modified electrode, named as SH-G/AuNPs/GCE. The surface of SH-G/AuNPs/GCE was modified

with Au–Prussian blue (Au-PB) to obtain the Au-PB/SH-G/AuNPs/GCE. The MIP film was prepared by electropolymerisation of a solution containing *o*-aminophenol, resorcinol and tebuconazole. The obtained sensor was named MIP/Au-PB/SH-G/AuNPs/GCE and used for the detection of tebuconazole in vegetable and fruit samples.

An interesting compound found in milk is β-lactoglobulin, which is a major allergen and the main component of milk skin. It is the β-lactoglobulin that forms a thin gelatinous film on the surface of the milk because it coagulates and denatures when the milk boils. It is important to quantify β-lactoglobulin in milk samples to protect allergy sufferers. Wang et al. [67] developed an electrochemical sensor based on MIP for the detection of β-lactoglobulin. First, the polyethylenimine (PEI)-rGO-Au nanoclusters (Au-NCs) (PEI-rGO-Au-NCs) were prepared, followed by preparation of the imprinted polymers. These MIPs for β-lactoglobulin were prepared using β-lactoglobulin as the template molecule, choline chloride as the functional monomer and EGDMA as the cross-linking agent. Then, the molecularly imprinted polymer was immobilised on PEI-rGO-Au-NCs to develop the PEI-rGO-Au-NCs@MIP sensor having a limit of detection of 10^{-9} mg/mL. The obtained sensor was successfully used for the determination of β-lactoglobulin in milk samples.

Somnet et al. [68] developed an electrochemical sensor based on a screen-printed graphene paste electrode (SPGrE) for the determination of the herbicide paraquat (PQ). This work is the first to use PQ-imprinted polymers synthesised on the surface of PtNPs. The PtNPs@MIP was simply drop-casted onto the SPGrE surface and the resulting sensor, PtNPs@MIP/SPGrE, was successfully used to determine PQ in vegetables and fruits for food safety applications.

Amaranth, an azo dye that gives products a dark red to purple colour is another compound regulated for use in various foods. Li et al. [69] used graphene, poly(diallyldimethylammonium chloride) (PDDA) and Pd-Cu to prepare the PDDA-Gr-(Pd-Cu) nanocomposite. For the imprinted amaranth polymer, the group used amaranth, dopamine hydrochloride solution and the already-prepared PDDA-Gr-(Pd-Cu) nanocomposite. The obtained composite was dropped onto the surface of a GCE to obtain the final sensor, called PDDA-Gr-(Pd-Cu)@MIP-PDA/GCE, which was used to determine amaranth in soft drinks. The synergistic effect of the graphene sheet with large surface area and the MIP with many specific cavities leads to a perfect oxidation peak for amaranth.

Another azo compound commonly used to colour beverages, food, cosmetics, etc. is tartrazine (TZ). TZ is genotoxic to DNA, haemoglobin and lymphocytes and can cause various symptoms such as diarrhoea, allergies and even cancer after long-term excessive intake. For this reason, the use of TC is strictly regulated and the maximum intake of TC should not exceed 7.5 mg/kg daily. Therefore, Cheng et al. [12] developed a novel MIP nanocomposite sensor for TC determination, starting from a matrix surface of platinum cobalt nanoalloy-functionalised graphene oxide (GO-PtCo) and a membrane of molecularly imprinted polydopamine (MIPDA). The PtCo@MIPDA suspension was dropped onto the surface of the GCE, resulting in the GCE/GO-PtCo@MIPDA electrochemical sensor, whose detection limit was 14.8 times lower than the detection limit of the sensor without MIP (GCE/GO-PtCo). The analytical instrument was successfully used for TC determination in various food samples.

Liu et al. [70] proposed a novel electrochemical sensor used for epigallocatechin gallate (EGCG) determination. The molecularly printed polymer (MIP) was obtained by the electrochemical polymerisation of β-cyclodextrins (β-CD) and EGCG on a GO-modified GCE (GO/GCE). The polymerisation reaction of β-CD was due to the oxidation of the primary OH groups, leading to the formation of an aldehyde and/or a carboxylic acid radical, which could react with another β-CD molecule to release a water molecule to form a dimer. In successive cyclic voltammetry (CV) scans, the polymerisation reaction occurred continuously and resulted in the formation of a β-CD-based conductive polymer film on the surface of the electrode. The developed sensor was used for EGCG determination from five extracts of different tea varieties.

Propyl gallate (PG) is a phenolic antioxidant like tertiary butyl hydroquinone (TBHQ) and butylated hydroxyanisole (BHA), compounds commonly used as preservatives in the food industry. PG is added to various foods, such as edible oils, to prevent deterioration of food quality. However, as with BHA and TBHQ, the use of PG can produce toxic products that may affect human health. Therefore, Cui et al. [71] developed a novel electrochemical sensor based on MIPs for sensitive and specific detection of PG. The sensor is based on an *o*-phenylenediamine (*o*-PD) membrane resulting from subsequent electropolymerisation in the presence of PG molecules, the template molecule. For the preparation of the MIPs/PtAu-GrCNTs/GCE, a GCE was used, which was first modified with bimetallic particles (PtAu), embedded with graphene–carbon nanotubes, the PtAu-GrCNTs being synthesised in one-step reaction, by co-reduction starting from MWCNTs. Then, an *o*-PD polymer film was electrochemically deposited on the PtAu-GrCNTs/GCE surface using the PG templates by CV electropolymerisation and the final sensor was obtained (Figure 2). The PtAu-GrCNTs composite gave an exceptionally conductive and large area base for electrodeposition of the MIP material, giving the MIP sensor excellent selectivity towards its target PG. The MIP sensor proved to be more sensitive than other sensors, with a detection limit of 0.0053 µg/mL. Therefore, the sensor can detect PG in oil samples, as 100–200 µg/g of synthetic phenolic antioxidants is allowed.

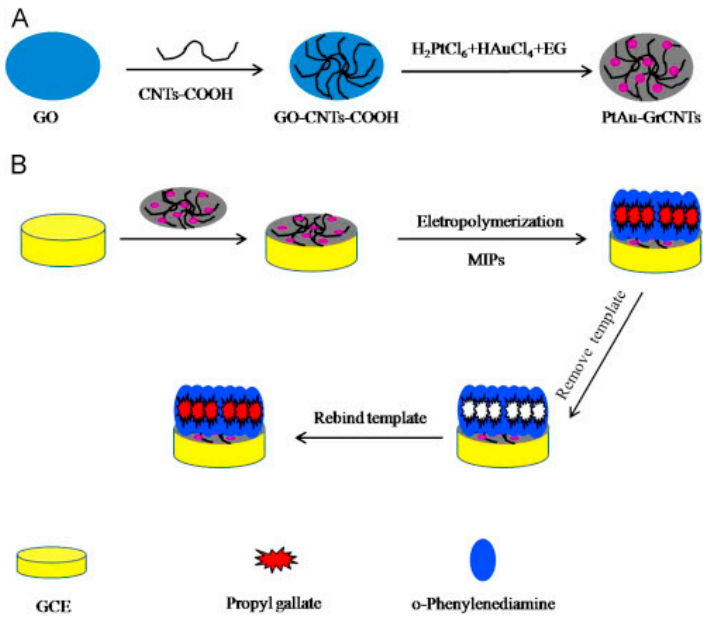


Figure 2. (**A**) Schematic illustration of the preparation process of the PtAu-GrCNTs composite. (**B**) Schematic illustration of the MIP sensor for PG determination. (Reprinted with permission of [71] Copyright © 2015 Elsevier B.V.)

A recent work reported the use of an electrochemical sensor based on MIPs for selective analysis of fructose in different samples of orange, apple and grape juices. The MIP was a film obtained from phenylboronic acid (PBA), as a functional monomer, in the presence of fructose, as a template molecule, using as conductive support a rGO-modified glassy carbon electrode [72]. The use of PBA as functional monomer for MIP ensured the high selectivity for sugar detection. The electrochemical sensor (GCE/rGO-MIP) was prepared by electrosynthesising the MIP film using CV and had an extremely low limit of detection.

Thiabendazole (TBZ) is a benzimidazole pesticide, an anti-infective/anthelmintic mainly used for the treatment of strongyloidiasis, cutaneous larva migrans and visceral larva migrans [78]. It has low acute toxicity by oral and dermal ingestion and is not an eye or skin irritant or sensitiser. The risk of inhalation exposure to vapours or aerosols from the use of TBZ is negligible as it has a low potential for vaporisation or aerosol formation [79]. TBZ has been used to preserve fruits and vegetables in recent years and could have negative

effects on human health due to the fact that it degrades extremely slowly. Therefore, Li et al. [73] developed an electrochemical sensor with TBZ imprinting by first dispersing GO and then dropping it onto the surface of a GCE. Then, the electrochemically reduced GO modified electrode was obtained by indirect electrochemical reduction. Two functional monomers were used to prepare the MIP, namely, *o*-PD and resorcinol (REC), which were mixed with TBZ and electropolymerised by CV. The MIP/ERGO/GCE was used for TBZ determination in orange juice samples. An interesting phenomenon was revealed: the response of the electrochemical sensor was proportional to the TBZ concentration within two ranges, indicating that there were two types of binding sites on the imprinted membrane. At low TBZ concentrations, the local TBZ concentration at the electrode surface decreased rapidly due to the non-specific adsorption of ERGO and the voids created, resulting in a high sensitivity of the electrode response. By contrast, at higher TBZ concentrations, the specific adsorption of imprinted cavities for TBZ required a longer time as the mass transfer resistance increased. Together with the non-electroactive property of TBZ, this led to a lower slope of the reaction.

A new protocol to obtain MIP based on graphene, without prior modification, was proposed by Zhang et al. [74] for the electrochemical determination of residues of imidacloprid, a neonicotinoid insecticide. MIP was fabricated from a complex obtained from functional monomer *p*-vinylbenzoic acid (VBA) linked to graphene and template molecule, subjected to copolymerisation with EGDMA as cross-linker. The MIP-rGO/GCE was obtained by dropping the resulting mixture directly onto the GCE surface, the extraction of template molecule occurring during an electrochemical reaction (Figure 3). The electrochemical sensor was successfully applied to assess imidacloprid in rice samples. This work is a clear case of synergy between graphene and MIP. The functional monomer is immobilised on graphene, which improves the stability of the electrochemical sensor, while the homogeneous layer of MIP gives stable and very sensitive sensors for the detection of imidacloprid.

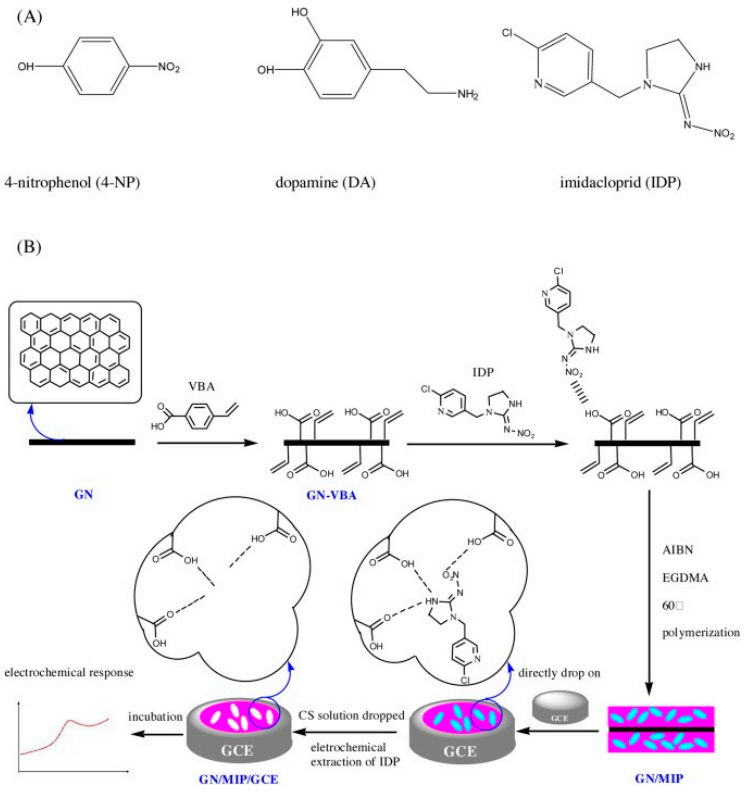


Figure 3. (**A**) Structures of template molecules; (**B**) Schematic procedure for the preparation of GN/MIPs/GCE and the concept for selective electrochemical detection of IDP. (Reprinted with permission of [74] Copyright © 2017 Elsevier B.V.)

Another neonicotinoid, thiamethoxam (TMX), was determined by Xie et al. [75] using an electrochemical sensor based on a MIP and graphene. The same functional monomer, *p*-vinylbenzoic acid, was used as in the above work by Zhang et al., with the GCE modified with both MIP and graphene (Figure 4). The sensor was used for the detection of TMX in organic samples of brown rice.

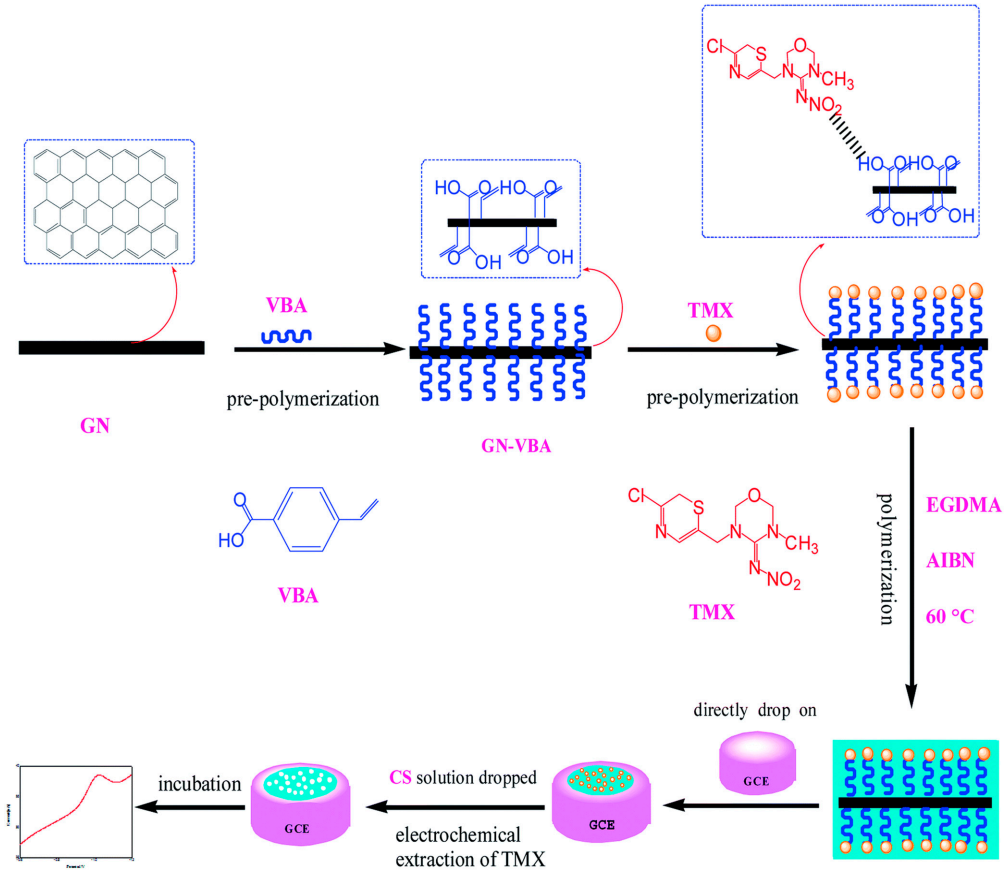


Figure 4. Schematic diagram of the procedure for the preparation of MIP-GN/GCE and the concept for the selective electrochemical detection of TMX. (Reprinted with permission of [75] Copyright © 2017, Royal Society of Chemistry.)

In a widely cited research paper, Li et al. [76] describe the development of a novel composite of magnetic graphene oxide and Au nanoparticles (MGO@AuNPs) and MIPs using dibutyl phthalate (DBP) as a template molecule. The MGO@AuNPs were used as a support material in the MIP matrix to fabricate MGO@AuNPs MIPs and then dropped onto a Au electrode surface. Here, too, GO offers added value, as the current increases after its deposition due to the increased conductivity and adsorption capacity of the electrode. The resulting electrochemical sensor (MGO@AuNPs-MIPs) was successfully used to detect DBP. DBP is a phthalate ester used as an additive in the manufacture of poly(vinyl chloride) plastics to produce flexible plastics. It appears that DBP has low acute and chronic toxicity, so a tool is needed to determine it. The developed MGO@AuNPs-MIP-modified electrode was used for the determination of DBP in wine samples.

A very recent research paper describes the fabrication of a molecularly imprinted electrochemical sensor based on nitrogen-doped graphene quantum dots (N-GQDs) and a nickel-based metal-organic framework functionalised with Ag nanoparticles (Ag/Ni-MOF) (MIP/Ag/Ni-MOF/N-GQDs/GCE) for the detection of OA [77]. OA is a chemically synthesised inhibitor for bacterial growth, mainly used in livestock raising and aquaculture. In the first step, the N-GQDs and Ag/Ni-MOF were prepared (Figure 5). Then, the Ag/Ni-MOF/N-GQDs/GCE was obtained, followed by electropolymerisation of OLA,

to produce the MIP/Ag/Ni-MOF/N-GQDs/GCE, which was used to determine OLA in fish muscle, pig muscle and chicken breast samples. Even the authors said that there is a synergistic effect between the used materials, as the highest peak current was obtained for the final sensor.

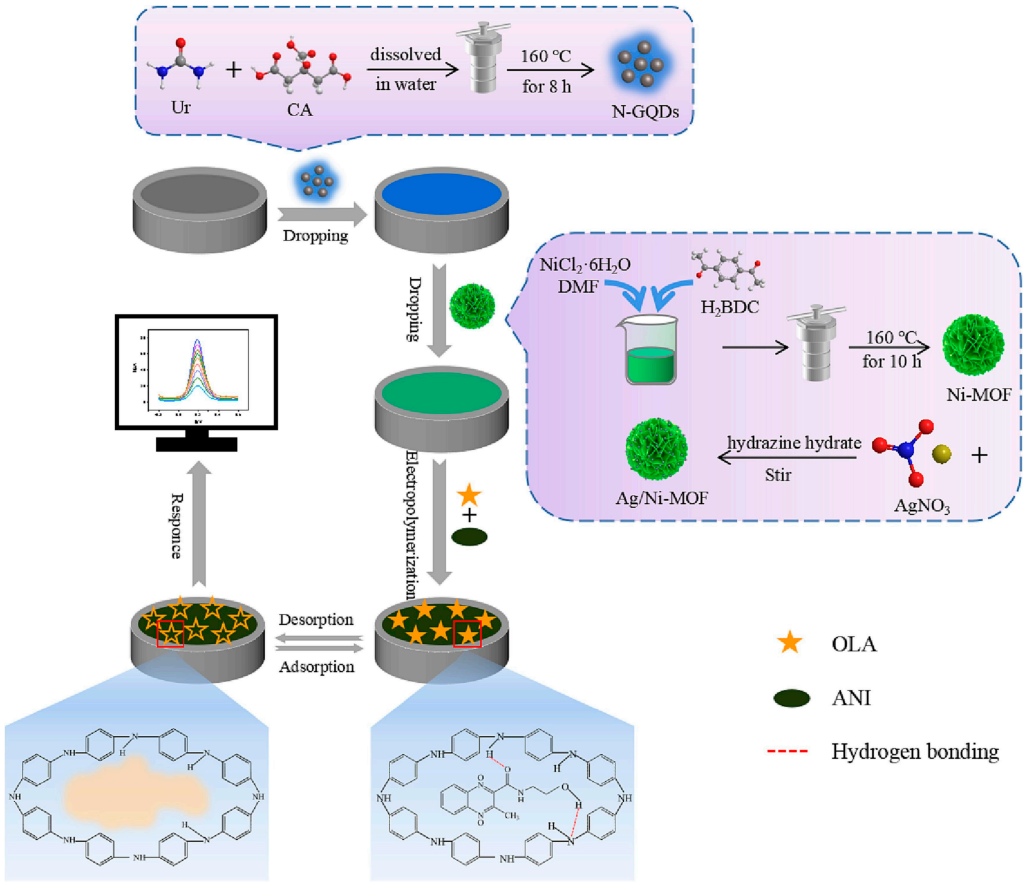


Figure 5. Procedure of the preparation of MIP/Ag/Ni-MOF/N-GQDs/GCE sensor. (Reprinted with permission of [77] Copyright © 2023, Elsevier Ltd.)

6. MIPs and Graphene Electrochemical Sensors for Environmental Analyses

Table 2 summarizes the electrochemical sensors based on both MIPs and graphene applicable in environmental monitoring of emerging contaminants. Further details on several specific examples are provided below.

Table 2. Electrochemical sensors based on both MIPs and graphene used in environmental analysis.

Electrode Material	Electrochemical Technique	Monomer	Analyte	Samples	LoD, mol L^{-1}	Ref.
[a] MIP/rGO/PGE	DPV	Pyrrole	Picric acid	Soil, water	1.40×10^{-6}	[80]
[b] MIP/GO/GCE	DPV	Methacrylic acid	2,4-dichlorophenol	Lake water	5.00×10^{-10}	[81]
[c] MIP/PDA-rGO/GCE	DPV	2,4-dichlorophenol	2,4-dichlorophenol	Lake water	8.00×10^{-10}	[82]
[d] PDDA-G/MIP/GCE	DPV	Methacrylic acid	4-chlorophenol	Tap water, lake water	3.00×10^{-7}	[83]
[e] MIP/HG/GCE	DPV	Methacrylic acid	p-aminophenol	Tap water, lake water	6.00×10^{-8}	[84]
[f] Au@Fe_3O_4@RGO-MIPs	DPV	Methacrylic acid	Ractopamine	Water	2.00×10^{-11}	[85]
[g] Gr/MIPs/ABPE	DPV	4-vinylpyridine	Bisphenol A	Plastic pacifier, one-off plastic spoon, mineral water and the water of Yudai River	9.60×10^{-11}	[86]

Table 2. *Cont.*

Electrode Material	Electrochemical Technique	Monomer	Analyte	Samples	LoD, mol L^{-1}	Ref.
[h] MIP/MXene/Au/GCE	DPV	4-vinylpyridine	Tetrabromobisphenol A	Weihe River, tap water	1.44×10^{-11}	[87]
[i] MIP/NGNRs-IL/GCE	LSV	*o*-phenylenediamine and *o*-toluidine	4-nonyl-phenol	Lake water, river water, tap water	8.0×10^{-9}	[88]

[a] MIP/rGO/PGE: molecularly imprinted polymer/reduced graphene oxide/pencil graphite electrode; [b] MIP/GO/GCE: molecularly imprinted polymer/graphene oxide/glassy carbon electrode; [c] MIP/PDA-rGO/GCE: molecularly imprinted polymer/polydopamine–reduced graphene oxide/glassy carbon electrode; [d] PDDA-G/MIP/GCE: poly(diallyldimethylammonium chloride)/molecularly imprinted polymer/glassy carbon electrode; [e] MIP/HG/GCE: molecularly imprinted polymer/hemin–graphene/glassy carbon electrode; [f] Au@Fe_3O_4@RGO-MIPs: gold-loaded iron oxide–reduced graphene oxide–molecularly imprinted polymers; [g] Gr/MIPs/ABPE: graphene/molecularly imprinted polymers/acetylene black paste electrode; [h] MIP/MXene/Au/GCE: molecularly imprinted polymer/MXene/gold/glassy carbon electrode; [i] MIP/NGNRs-IL/GCE: molecularly imprinted polymer/nitrogen-doped graphene nanoribbons–ionic liquid/glassy carbon electrode.

One particular work presented in Table 2 is that of Karthika et al. [80], who developed an electrochemical sensor based on MIP on a pencil graphite electrode (PGE) coated with rGO for the quantification of picric acid (PA) from soil and water. PA is a very strong organic acid (aromatic compound) that was used as an explosive until the First World War. GO was classically produced using a modified Hummers method and then dispersed in water. The PGE was electrochemically modified with rGO and MIP by immersion in a GO dispersion buffered with sodium bicarbonate (pH 11). Electrochemical reduction was also carried out to obtain the rGO/PGE. Finally, Py was electropolymerised on the surface of the rGO-modified PGE and PA was used as template. After extraction of the PA molecules from the polymer matrix, MIP/rGO/PGE was obtained.

Liang et al. [81] proposed a new electrochemical sensor used for selective determination of 2,4-dichlorophenol (2,4-DCP), an intermediary compound used in the synthesis of several herbicides, preservatives, dyes and disinfectants. The electrochemical sensors were developed based on MIP/GO-modified GCE, and demonstrated a high sensitivity. The MIP was prepared by precipitation polymerisation using 2,4-DCP as template, methacrylic acid (MAA) as the functional monomer and EGDMA as the cross-linking agent. GO was dropped onto the GCE followed by the addition of the MIP. Due to the high binding affinity and π-π interaction between GO and the phenolic pollutants, the MIP/GO/GCE showed high detection performance and electrochemical activity towards 2,4-DCP with an extremely low LoD of 5×10^{-10} mol L^{-1}, again highlighting the synergistic properties of the two materials when combined. The proposed sensor was successfully applied for the determination of 2,4-DCP in lake water samples. Another work on the determination of 2,4-DCP was based on the development of an electrochemical sensor based on polydopamine (PDA)-functionalised graphene and MIP [82]. The bare electrode was also a GCE modified with a black PDA-rGO suspension. The modified electrode was then placed in a solution containing *o*-PD as monomer and 2,4-DCP as template. Electropolymerisation was used to obtain the MIP film and the template was removed with ethanol. On the same topic, another highly selective electrochemical sensor based on MIP and PDDA-functionalised graphene was developed for the determination of 4-chlorophenol (4-CP) [83]. The starting electrode material was also GCE, which was first modified with the mixture of GO and PDDA, followed by the addition of the obtained MIP. The MIP was prepared using 4-CP, and MAA as the functional monomer and the cross-linking agent EGDMA, as in the work of Liang et al. The 4-CP peak intensity increased three times due to the synergy between PDDA and graphene. The imprinted electrochemical sensor was used for the determination of 4-CP from tap water and lake water collected from Wuhan, China. Liu et al. [84] developed a selective electrochemical sensor for *p*-aminophenol (*p*-AP) by modifying the GCE with hemin–graphene composites (HG) and MIP. The modification of the GCE started with the synthesis of GO and hemin–graphene, followed by coating the electrode with HG and then with MIP suspension. The *p*-AP-binding MIP was also synthe-

sised using MAA, AIBN and EGDMA as functional monomer, initiator and cross-linker of polymerisation, respectively.

Li et al. [85] developed a MIP-based electrochemical sensor with Au-loaded Fe_3O_4/graphene for the rapid detection of trace levels of ractopamine (RAC) in water using the reversible addition fragmentation chain transfer (RAFT) polymerisation technique. GO was prepared using a modified Hummers method. Subsequently, rGO decorated with Fe_3O_4 was obtained and reacted with $HAuCl_4$ to give Au-deposited Fe_3O_4@RGO (Au@Fe_3O_4@RGO). To obtain the Au@Fe_3O_4@RGO-RAFT, the Au@Fe_3O_4@RGO was dispersed in water; then, NaOH and $NaClO_3$ were added and subjected to sonication to convert hydroxyl groups to carboxyl groups on Fe_3O_4. The Au@Fe_3O_4@RGO-COOH was then rinsed with ethanol to obtain a pH of about 7.0. Au@ Fe_3O_4@ RGO-COOH, 2-hydroxylethyl-2-bromoisobutyrate (HEBrIB) and anhydrous toluene were mixed under nitrogen and anhydrous triethylamine was added to the solution to give Au@ Fe_3O_4@RGO-Br. Phenylmagnesium bromide solution (PMB) was dissolved in ultra-dry tetrahydrofuran (THF) and then mixed with carbon disulphide, and Au@ Fe_3O_4@RGO-Br was added to the above mixture to obtain Au@Fe_3O_4@RGO-RAFT. The active ingredient together with methacrylic acid (MAA), divinyl benzene (DVB) and RAC produced the final product, Au@ Fe_3O_4@RGO-MIP, which was drop-casted onto a GCE.

Wu et al.'s [86] work on the detection of bisphenol A (BPA) is very interesting since the electrode material, called acetylene black paste electrode (ABPE), was produced and further modified with MIP and graphene sheets. Graphene was obtained by improving the classical Hummers method, while BPA MIPs were prepared by dissolving BPA and 4-vinylpyridine (4vp) in methylbenzene. The mixture was ultrasonically dispersed and EGDMA and 2,2′-azobis(2-methylpropionitrile) (AIBN) were added, followed by polymerisation. To fabricate the electrochemical sensor, AB powder was mixed with solid paraffin and then GO and MIPs were dropped onto the ABPE surface. The Gr/MIPs/ABPE was used to determine the BPA from four different samples.

Shao et al. [87] developed an electrochemical sensor constructed by dropping molecularly imprinted polymer onto MXene and gold nanoparticle-modified glassy carbon electrode was used to detect tetrabromobisphenol A (TBBPA) in water samples. The detailed preparation procedure is shown in Figure 6.

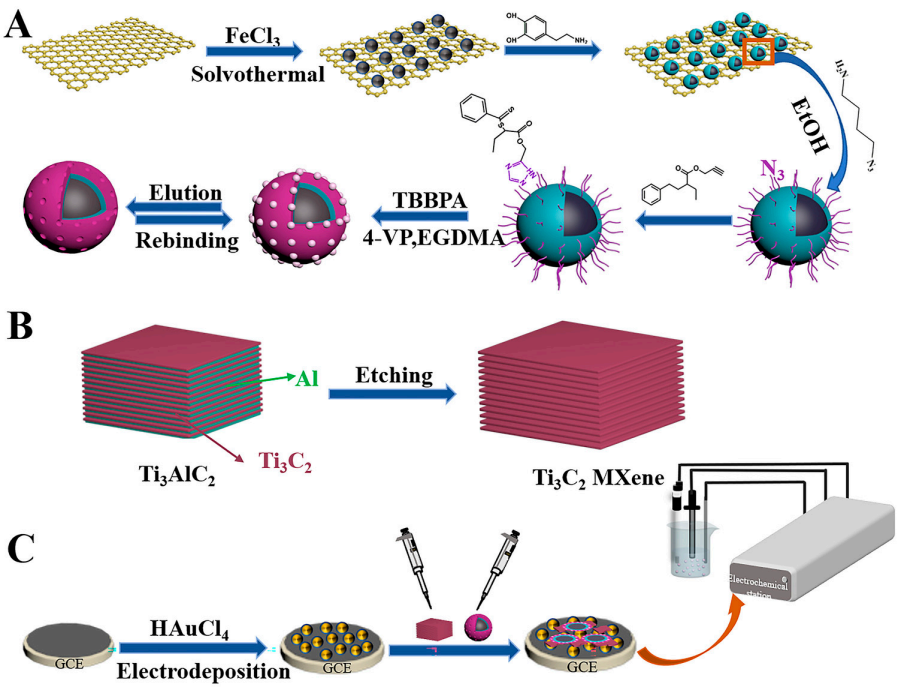


Figure 6. Scheme of the preparation procedure of GO@Fe_3O_4@MIP (**A**), MXene (**B**) and TBBPA-imprinted electrochemical sensor (**C**). (Reprinted with permission of [87] Copyright © 2022, Springer.)

In their work, Pan et al. [88] presented a novel electrochemical sensor for 4-nonylphenol (NP) based on the molecularly imprinted poly(*o*-phenylenediamine-co-*o*-toluidine) on nitrogen-doped graphene nanoribbons (NGNRs)–ionic liquid (IL) composite film (Figure 7), used to increase response sensitivity. The selectivity of the constructed sensor was ensured by the MIP. The obtained sensor was used for the detection of NP in water samples.

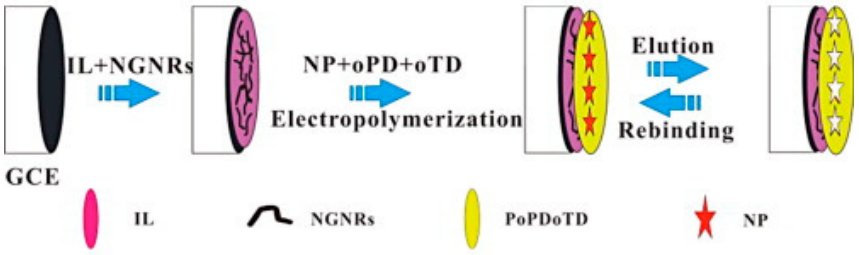


Figure 7. The preparation route for MIP/NGNRs-IL/GCE. (Reprinted with permission of [88] Copyright © 2014 Elsevier Ltd.)

17β-estradiol (17β-E2) is a natural hormone commonly detected in the aquatic environment defined by the U.S. Environmental Protection Agency (EPA) as an endocrine disrupting chemical (EDC) since 17β-E2 negatively impacts humans and wildlife, even at low concentrations. The lowest observed adverse concentration of 17β-E2 in ponds is between 1 and 10 ng L^{-1}. In agricultural soils, for example, concentrations of 425 ng L^{-1} of 17β-E2 have been detected in groundwater. Against this background, Li et al. [89] have developed a novel electrochemical sensor with molecular imprinting based on Fe_3O_4 nanospheres immobilised on graphene (Fe_3O_4-MIP@RGO) to detect 17β-estradiol (17β-E2) in water. Reaction is based on the reversible addition fragmentation chain transfer (RAFT) technique. The Fe_3O_4-MIP@RGO-based sensor demonstrated high selectivity and sensitivity to 17β-E2.

7. Future Perspectives and Challenges

The use of MIPs and graphene for the development of electrochemical sensors has increased in the last decade. Both materials are of great interest to researchers in many fields, with each offering its own added value to the field of sensing. Graphene has properties such as high conductivity, a larger electroactive surface area and direct electrochemistry, while MIPs are cheap, flexible and selective, properties necessary for electrochemical sensors. For MIP synthesis, insulating materials are usually used, thus lowering the electrode signal. Therefore, coupling MIPs and graphene leads to increased sensing performances, lowers the detection limit and makes electrochemical sensors a powerful approach as they are free from any interferences since the interfering substances do not have the same structure as the target analytes.

Methacrylic acid and pyrrole are the most commonly used functional monomers for the preparation of MIPs in the case of MIP-based electrochemical sensors for agri-food and environmental analysis, but it is not clear which monomer has the best yield. An important aspect in the synthesis is the choice of the right monomer and the right solvent to obtain the best MIP. In addition, the case of the reviewed papers, it was observed that electropolymerisation is the preferred synthesis route because it is easy to use and reproducible. Regarding the electrochemical technique, differential pulse voltammetry is predominantly used for MIP–graphene sensors.

However, work needs to be conducted to develop stable electrochemical tools with good repeatability, and the amounts of monomer, cross-linker and initiator need to be extremely well balanced. Another drawback is that electrochemical sensors based on MIPs are usually disposable. Research must make progress to overcome this disadvantage. Repeatability and reproducibility are key factors in the development of commercial electrochemical sensors. If these aspects are improved, a step forward will be made in the field of sensor technology with applications in the food and environmental sectors. The use of

ionic liquids as functional monomers in the fabrication of MIP–graphene sensors could be a step forward in the agri-food and environmental analysis, as the compounds of interest are usually found in aqueous matrices. Electrochemical MIP graphene sensors also have the advantage of potential use for on-site analysis as they are cheap, do not require trained personnel, can be portable and the results are available quickly.

8. Conclusions

This review paper aims to provide useful information on the latest research in the field of electrochemical sensors based on molecularly imprinted polymers and graphene for food safety and environmental applications, two very important research areas. The use of these materials had a synergistic effect, highly enhancing the electron transfer efficiency and widening the range and number of active molecular recognition sites. This resulted in improving and amplifying the sensor signal and the response selectivity, and contributed to increasing the sensors' stability and the repeatability of the sensors' response. It can be observed that MIPs significantly increase the selectivity of the analytical procedure regardless of the external environment, while graphene, with its property of fast electron transfer and increasing the electrical surface area of the transducer with the binding sites in the outer layer of the MIP composite, improves access to the target species. We have noticed that more and more research is looking at electrochemical sensors based on MIPs and graphene, which is perhaps a sign that the technology in this field is maturing.

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