Analytica Chimica Acta 1272 (2023) 341449

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Graphene derivatives-based electrodes for the electrochemical determination of carbamate pesticides in food products: A review

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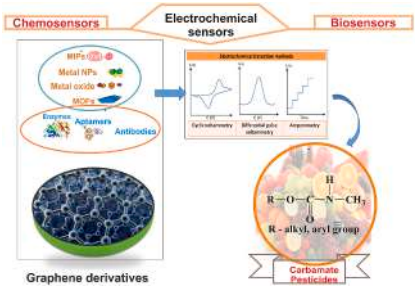
HIGHLIGHTS

- Graphene-based electrochemical detection of carbamate pesticides in food is reviewed.
- Characterization of graphene and its derivatives using instrumental methods is discussed.
- Analytical characteristics of carbamate pesticides determination by electrochemical methods are discussed.
- Graphene electrodes modified by enzymes, nanoparticles, and polymers are discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Devoted to the memory of Professor Jaroslav Heyrovsky to commemorate 100 anniversary of the discovery of polarography.

Keywords:
Carbamate pesticides
Graphene derivatives
Electrochemical sensors
Food products
Green chemistry

ABSTRACT

Graphene (GR) composites have great potential for the determination of carbamates pesticides (CPs) by electrochemical methods. Since the beginning of the 20th century, GR has shown remarkable promise as electrode material for various sensors. The contamination of food products with harmful CPs is a major problem as they do not always damage human health immediately, but can be harmful after prolonged exposure. A range of advantages can be gained from their electrochemical determination, such as high sensitivity, reasonably selectivity, rapid detection, low limit of detection, and easy electrode fabrication. Furthermore, these electrochemical techniques are robust, reproducible, user-friendly, and conform to both "green" and "white" analytical chemistry. This review is focused on results published in the last ten years in the field of electrochemical determination of CPs in food products using GR and its derivatives.

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https://doi.org/10.1016/j.aca.2023.341449
Received 7 March 2023; Received in revised form 26 May 2023; Accepted 29 May 2023
Available online 2 June 2023

1. Introduction

In recent years, emerging pollutants have gained global attention due to their impacts on the environment [1]. A pressing challenge is obtaining enough food and fresh water. Water and food requirements are expected to increase by 30% and 40% by 2030, respectively [2]. Therefore, environmental pollution and its effects on water, soil and food [3–5] are key economic and political issues. The food production and clean water is outlined in guidelines developed by the United Nations (UN) [6]. In the pest control industry, carbamate pesticides (CPs) are among the most widely used substances. Large amounts of CPs used in agriculture can cause several adverse environmental problems. Since the 1970s, CPs have been increasingly used in crop protection because of their high effectiveness and other positive properties [7]. However, due to their widespread use in fruits, vegetables, and cereals, these pesticides pose a serious health risk to humans [8]. In spite of their importance [9] for ensuring food security and economic growth, their incorrect and undifferentiated use can be detrimental both to human health and the environment [10]. There are many factors to consider in evaluating whether chemicals are beneficial or harmful, including concentration and duration of exposure [11]. Moreover, it is necessary to keep in mind that people mostly rely on plants as a primary source of food and nutrition [12].

CPs (carbamic acid derivatives, carbamates) are esters of carbamic acid, widely used in agriculture as active ingredients of pesticides. Carbamates include well-known insecticides (carbofuran, carbosulfan, methomyl, propoxur, carbaryl (CBR)), herbicides (prosulfocarb, phenmedipham), and fungicides (propamocarb hydrochloride). Further, carbamates-insecticides will be considered in detail, since they are highly toxic for warm-blooded organisms and preparations based on them belong to the I and III classes of danger to humans when ingested [13–15]. The mechanism of action of carbamate insecticides is a blocking effect on the functions of the neuromuscular system (they inhibit acetylcholinesterase (AChE) of the nervous system). AChE promotes hydrolysis of neurotransmitter acetylcholine (ACh) into choline and acetic acid [16]. With the inhibition of AChE by carbamate ether, the hydrolysis of ACh does not occur. Thus, the concentration of ACh remains high in the ligaments, causing incessant muscle stimulation, leading to extreme exhaustion and tetany [17]. There is an accumulation of ACh and a violation of the normal passage of nerve impulses to the muscular systems. They become frequent, spontaneous, convulsions and paralysis occurs [18,19]. Thus, it is necessary to use modern analytical methods for the detection and quantification of carbamates for food control.

Electrochemical (EC) approaches are widely recognized as having significant advantages when compared with conventional laboratory-centralized methods for detecting CPs [20–24]. Advantages of EC methods include high sensitivity, low detection limits, and high cost-effectiveness and easy portability [25]. Additionally, they are simple to operate, give rapid analytical results, and usually require no sample pretreatment [26]. Moreover, they have fast response time, simple preparation procedures, and high target specificity and their performance in complex matrixes is less affected by chemical interferences [27,28].

Due to its impressive physicochemical properties (e.g. high conductivity, electrocatalytic properties, large electrochemical potential, mechanical strength, chemical stability, high elasticity, thermal conductivity, etc.), GR has attracted enormous scientific and technological interest [29,30]. Moreover, many other carbon structures can be formed using GR as a precursor. For electrochemical assays, GR has two main advantages over well-known and extensively applied carbon nanotubes: no metallic contaminants and easy and inexpensive preparation from graphite. In GR sheets, electron transfer is enhanced by the highly concentrated edges per material amount, and it appears to be independent of the multiple of layers [31]. Therefore, GR is unique because of its individual sheets. In electrochemistry, graphene oxide (GO) and reduced graphene oxide (rGO) are the most commonly used forms; both are easily functionalized due to oxygen-containing groups, which reduce GR's hydrophobicity and tendency for aggregation in aqueous electrolytes [32,33]. Their popularity has led to exploration in a variety of applications. Electrochemical (bio) sensors based on GR-derivatized nanomaterials have become popular applications in Ref. [34] for environmental analysis.

Fig. 1 shows the number of publications per year on the development of the electrochemical sensors based on GR derivatives. It also shows the development of electrochemical methods for the determination of the carbamate pesticides on graphene derivatives based electrodes. It has been estimated that the number of publications on graphene-based electrochemical sensors for carbamate pesticide determination has increased by more than 60% in the last five years.

In this review paper, a comprehensive evaluation of GR and its derivatives as electrochemical sensors for determination of CPs (e.g. CBR, carbosulfan, carbofuran, fenobucarb, propoxur, methomyl, etc.) in food products takes into account both promising advantages (e.g. quick electrode production, low limit of detection, high reproducibility, long term stability in some cases) and existing disadvantages (e.g. such as long time for electrode modification, slow production, low reproducibility and short term stability in another cases). GR derivatives present remarkable potential for electrochemical sensor research by providing better sensors for the determination of a wide range of pesticides. Electrochemical sensors find immense applications for detecting CPs in food products and agriculture, and they are used for environmental monitoring. This review is divided into sections, which include preparation methods and characterization of GR and its derivatives, application of electrochemical sensors based on GR and its derivatives for determination of CPs in food and application of electrochemical biosensors based on GR and its derivatives for determination of CPs in food products. In the last section, conclusive remarks and future scope are presented.

2. Preparation methods of graphene and its derivatives

2.1. Preparation of graphene

In 2004, Novoselov and Geim isolated GR using the peel-off method with a scotch tape [35]. In GR, carbon atoms in this form are arranged in a single layer in 2D allotropic honeycombed form (Fig. 2) [36,37]. Since this 2D nanomaterial exhibits exceptional thermal, optical, chemical, and mechanical properties, it has attracted considerable attention. Graphene quantum dots (GRQDs) are other interesting derivatives of GR. Furthermore, GR-derived nanomaterials can be functionalized easily, have high electron mobility and a high surface area to volume ratio and they are biocompatible for a variety of applications [38–42]. This is why they can be used to develop highly sensitive and low cost electrochemical sensors [43].

The high charge carrier mobility and large specific surface area of GR make it ideally suited for sensor applications [44]. Solvents such as N-methyl pyrrolidone and sodium dodecyl benzene sulphonate solution have been reported to peel graphite [45]. GR has been frequently prepared on a large scale using this technique because of its low fabrication cost and fewer processing steps. However, the process is arduous and has poor reproducibility, making it unsuitable for large scale GR production [46–48]. GR has been also fabricated by chemical vapor deposition (CVD) in many fields [49–52]. Additionally, it can also be prepared by reduction of GO., but the resulting material has many defects in comparison with GR synthesized from graphite. Various approaches to GR preparation are shown in Fig. 3.

There are two key reasons GR has such excellent electrochemical properties: (1) its large surface area creates electroactive properties which improves sensitivity and (2) its stability over a wide temperature range makes it an excellent conductive material for electrochemical sensors [53]. GR's applicability is sometimes hindered by agglomeration

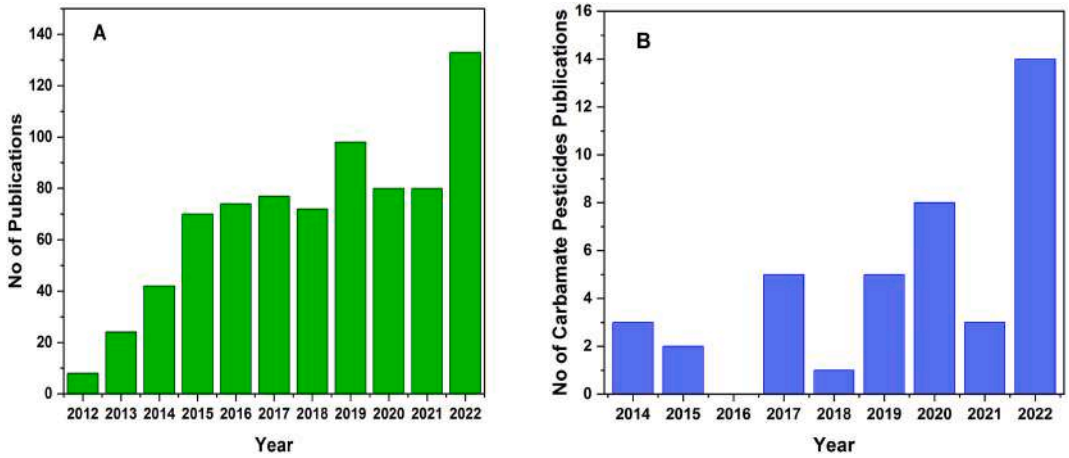

Fig. 1. Number of publications between 2012 and 2022: A) Development of electrochemical sensors based on graphene derivatives, B) Development of electrochemical sensors based on graphene derivatives for carbamates determination. Obtained from Scopus database using keywords: graphene derivatives, electrochemical sensor (A) and keywords: graphene derivatives, electrochemical sensor, carbamates (B).

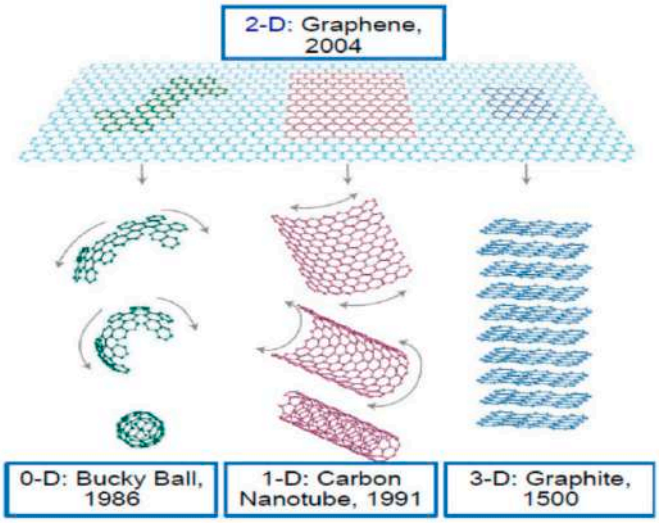

Fig. 2. Various structures of Graphene (Reproduced with permission from Ref. [37]. Copyright 2016 Springer Publications).

caused by the combination of agglutination, physical defects, sheet thickness, and suboptimal aqueous dispersion [54]. Due to this fact, mitigation strategies such as GR conversion into functionalized GO [41] have been explored.

2.2. Preparation of graphene oxide

Chemical oxidation introduces oxygen to GR, producing graphene oxide (GO). Hydroxides, epoxides, carbonyls, and carboxyls enhance the interaction and detection capabilities of its surface. Hummer's method [55], which involves highly oxygenating and acidic conditions before sonicating graphite precursors, has been used for a very long time because it is simple and relatively fast [56]. There are several modified Hummers methods, including nitrate-free [57], two-step [58], co-oxidant [59], and low-temperature and room-temperature [60] methods.

2.3. Preparation of reduced graphene oxide

In order to restore near pristine GR properties, several methods of rGO synthesis can be used. rGO material is characterized by structural defects due to the removal of an enormous portion of oxygen functional

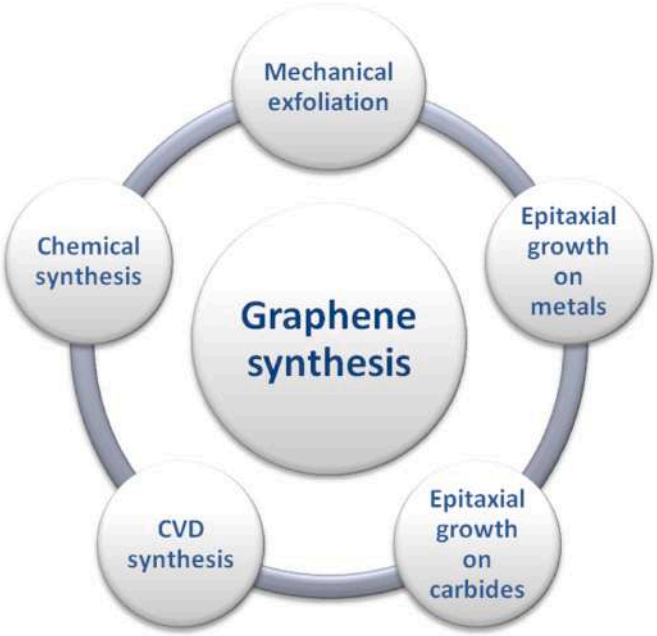

Fig. 3. Different graphene synthesis methods.

groups. rGO, like graphite oxide, does not have a completely homogeneous structure because of the remaining functional groups [61]. A variety of strategies can be used to reduce graphene oxide by removing its oxygen functional groups [62]: electrochemical reduction [63], chemical vapor deposition [64], thermal reduction stimulating the re-emergence of defects by re-hybridized carbon atoms [65], microwave reduction [66], chemical reduction [67] by using a wide variety of reducing agents. Chemical reductants, e.g. sodium borohydride, ascorbic acid, hydroiodic acid, and hydrazine [68] are commonly used to reduce GO into rGO.

3. Characterization of graphene and it derivatives

Surface and electrochemical characterization of various GR materials is of extreme importance for its electroanalytical applications.

3.1. Scanning electron microscopy

Materials with micro- and nanostructures can be characterized using

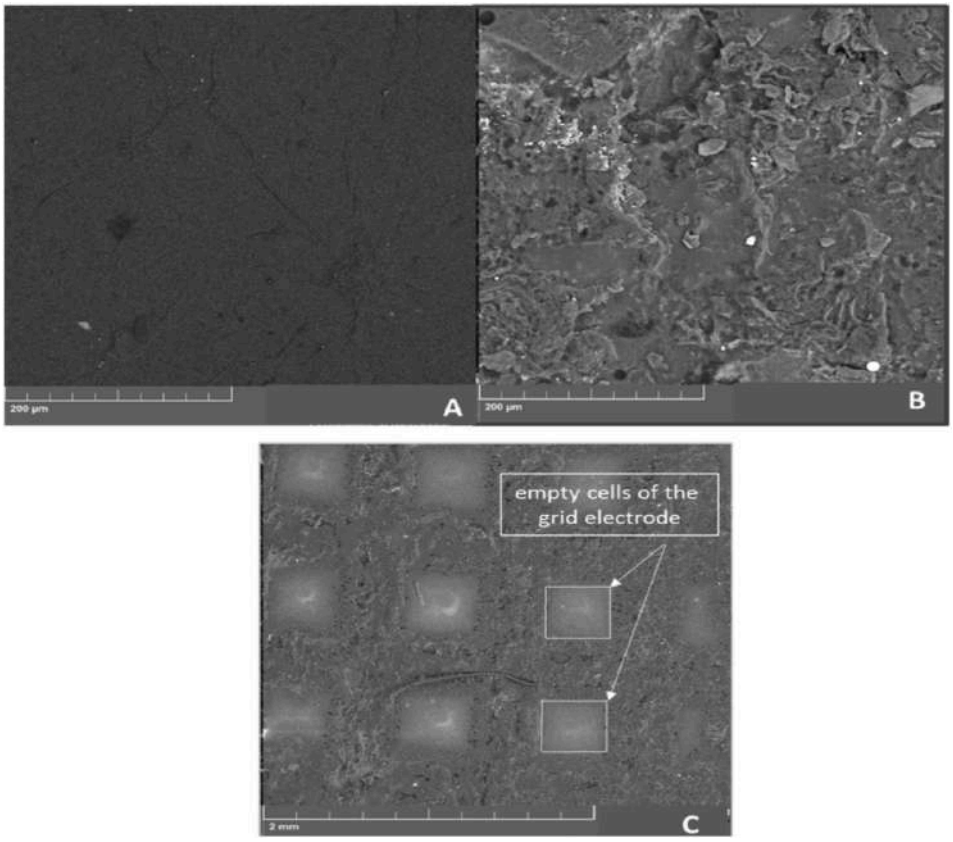

Fig. 4. SEM characterization of (A) graphene oxide electrode (B) laser reduced graphene oxide grid electrode with high resolution and (C) laser reduced graphene oxide grid electrode with low resolution for the voltammetric determination of CBR in fruits (Reproduced with permission from Ref. [73], Copyright 2021 MDPI).

scanning electron microscopy (SEM) capable of identifying nanoscale features of GR, including wrinkles; grain shapes, and fold lines [69]. GO nanosheets with porous morphologies were observed in the SEM images as wrinkled stacks, because of sp^2 carbon-to-carbon bonding, the plane has a flaky appearance [70,71]. In RGO, nanosheets are thin and wrinkled. This occurs when individual sheets are stacked using various self-assembly techniques. This is attributed to GR intrinsic properties [72]. The homogeneous surface of laser reduced GO grid electrode investigated by SEM was used for determination of CBR in the fruits [73]. The laser reduced graphene oxide grid electrode has defects on the surface, which potentially detected the CBR amino groups signal by LSV (Fig. 4). The electrode surface of rGO decorated with cobalt oxide surface examined by SEM was used for determination of CBF and CBR in real objects [74]. Surfaces of rGO decorated with gold nanoparticles have been similarly examined and used for detection of CBR in water; the gold nanoparticles enhanced the determination signal for CBR amino groups [75]. The surface of a screen-printed GO sensor characterized by SEM was used for the determination of carbendazim pesticides in tomatoes [76].

3.2. Transmission electron microscopy

Transmission electron microscopy (TEM) is used for characterization of graphene electron transition, A TEM image shows transparent, corrugated, or wrinkled structures of GO and RGO nanosheets. It can be described as the morphology of an ultrathin silk veil with an edge that folds and scrolls [72,77,78]. The GO nanoribbons with multiwall carbon nanotubes sensor surface morphology was characterized by TEM to develop the biosensor for determination of CBR [79]. The morphology of rGO decorated by Cu/CuO Ag nanocomposite was investigated by TEM to develop a sensor for CBR and Ag NPs helped to detect the CBR signal (Fig. 5) [80]. The GR surface aggregation was similarly characterized by TEM for the determination of CBR [81].

3.3. Atomic force microscopy

Atomic force microscopy (AFM) is a powerful technique to measure atomic steps on a surface and it helps to determine the Z-height and number of layers in the sample. In the reduction of graphene oxide, rGO sheets become thinner, which is a clear indication that oxygen has been removed from graphene oxide. However, several studies have found that rGO sheets are thicker than GO, which can be attributed to the binding either of capping agents to the sheets or the restacking of sheets without stabilizer molecules [82]. Furthermore, the GR family was characterized with AFM in terms of their size, shape, absorption/dispersion, and aggregation [69,83,84]. AFM images were used to characterize GO and B-rGO (bacterial reduced graphene oxide) nanosheets' surface morphology and thickness, which help to understand thickness of graphene [85]. rGO decorated with gold nanoparticles dispersed on its surface characterized by AFM was used for the determination of the CBR in water [75].

3.4. Raman spectroscopy

Raman spectroscopy (RS) is used to characterize crystalline, nanocrystalline, and amorphous carbons [83]. GR family materials are easily characterized using RS because it detects vibrations in bonds and allows detecting the pesticides [86–88]. The surface enhanced Raman spectroscopy (SERS) technique has been widely used to detect pesticides residues in food. A SERS method detects molecules adsorbed on metal nanoparticles (gold, silver, copper), producing physical and chemical enhancements that increase Raman signal intensity [89]. In Ref. [90] quantitation of pesticide residues in fruits was achieved by using silver nanoparticles as the substrate enhancing the SERS signal. Pesticides with

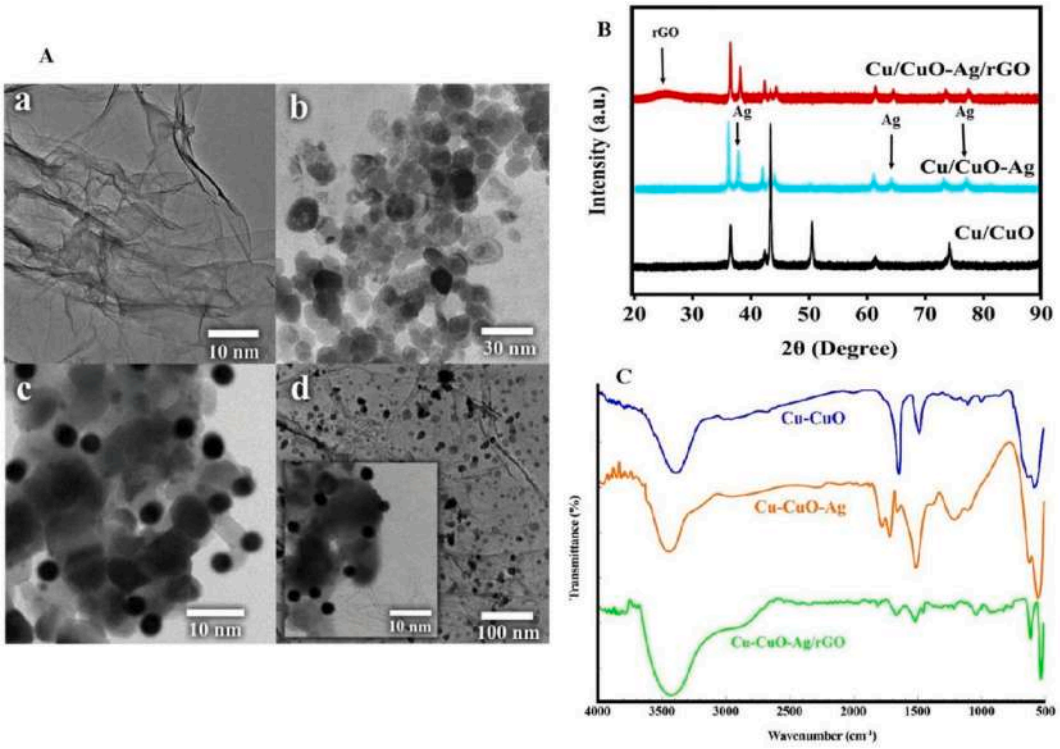

Fig. 5. A) TEM images of a) graphene, b) Cu/CuO, c) Cu/CuO–Ag, and d) rGO/Cu/CuO–Ag nanocomposite; B) XRD patterns of Cu/CuO, Cu/CuO–Ag and rGO/Cu/CuO–Ag nanocomposite, C) FT-IR spectra of Cu/CuO, Cu/CuO–Ag, and rGO/Cu/CuO–Ag nanocomposite (Reproduced with permission from Ref. [80], Copyright 2019 Elsevier B.V.).

e.g. carboxyl, hydroxyl, thiol, or amine functional groups that can bind to Au and Ag substrate strongly are good targets to get Raman signal [91]. Moreover, RS characterized chemically functionalized graphene (CFG) at different reaction times by monitoring D and G bands of GR [92].

3.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) uses X-rays to focus on the surface of a sample and measures the kinetic energy and number of electrons emitted from it [93]. XPS was used to confirm the presence of different elements composition in GR confirming the atomic composition as well as C/O ratio dividing the C1s peaks area by the area of the O1s peak multiplied by the ratio of the photoionization cross sections [78,94,95]. In Ref. [75] GO was examined by XPS to identify present elements. In spite of its tremendous capability, the main drawback of XPS is costly equipment and the need of highly qualified personnel.

3.6. X-ray diffraction

X-ray diffraction (XRD) is a valuable analytical tool to observe the intensity of scattered X-rays as a function of scattering angle and to characterize GR nanocomposites, both intercalated and exfoliated [96–98]. There are distinct peaks in the XRD patterns of graphite and GR, which allows them to be distinguished from one another [99]. Phase determination and confirmation of different patterns of graphene reduction by XRD is reported in Ref. [100]. rGO decorated with TiO_2 [72], with silver nanoparticles (Fig. 5) [80], or with cobalt oxide [101] was examined by XRD to understand the degree of GR formation.

3.7. Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FT-IR) is another powerful tool to detect the chemical structure of carbon oxides [102]. To study the functional interactions between GR and pesticide pollutants, FT-IR was used to understand the characteristic functional bonds present in GR materials. The FT-IR indicated the presence of oxygenated carbon and hydrogen functional groups to enhance the signal for pesticides determination. Moreover, silver nanoparticles enhanced the signal with rGO electrode for CBR detection (Fig. 5) [80]. The graphene-coated silica prepared for the determination of pesticides was investigated by FT-IR [78,103] as well. Bands were observed at different wavelengths due to absorption of oxygen containing functional groups [104,105].

3.8. UV spectroscopy

When GR is oxidized to GO with oxygen-containing functional groups, such as -C-O, –C═O, –COOH, corresponding UV signals can be observed [105,106]. The difference between GO and rGO degree of oxidation can be monitored by this technique [97,107,108].

3.9. High resolution transmission electron microscopy

Graphene's atomic structure and interfaces can be characterized very effectively by high resolution transmission electron microscopy (HRTEM). HRTEM of GR samples was used to investigate thickness and number of layers at various locations [109]. Morphology of Fe_2O_3 decorated on the GR surface was investigated and 30–50 nm particle size was confirmed by HRTEM [110]. The morphology of rGO was examined by HRTEM in Ref. [69].

Methods used for characterization of GR and its derivatives and composites are summarized in Table 1.

4. Application of electrochemical sensors based on graphene and its derivatives for determination of carbamate pesticides in food

Preparation of samples for the determination of carbamates in fruits

Table 1
Methods used for characterization of GR composites.

Technique	Parameters	Ref.
Scanning Electron Microscopy	Structure, size, shape	[69–76]
Transmission Electron Microscopy	Structure, shape, size	[72,77–81]
Atomic Force Microscopy	Number of layers	[69,75, 82–85]
Raman Spectroscopy	Structure and quality of matter	[83,86–92]
X-ray Photoelectron Spectroscopy	Quantitative analysis of functional groups	[75,78, 93–95]
X ray Diffraction	Interlayer distance	[72,80, 96–101]
Fourier transform infrared spectroscopy	Presence of oxygen functional group	[78,80, 102–105]
UV–vis spectroscopy	Transition of molecules	[97, 105–108]
High Resolution Transmission Electron Microscopy	Structure, size, shape	[69,109,110]

and vegetables is usually carried out in several stages. The first stage in all works is the grinding of samples (cutting, blending), followed by the extraction of carbamates from the crushed object of analysis with various solvents, e.g. ethanol, methanol, acetonitrile. After extraction, the obtained samples are centrifuged; the supernatant is collected and filtered. Sometimes the supernatant is evaporated to dryness after filtration and solvents are added to the dry residue. Further, for enzyme-free sensors, alkaline hydrolysis is carried at increased temperature in some works. This is not required for enzyme sensors. Hoverer, the sample pretreatment and possible preconcentration are out of the scope of this review.

From the last decade, carbon materials, especially GR and its derivatives (GO, rGO), have proven themselves highly effective for the development of electrochemical sensors for the determination of carbamates (Fig. 1) and currently they are widely used for the development of highly efficient electrochemical sensors [111]. Unique properties of GR-based materials and its derivatives, help to improve analytical and technical characteristics of sensors, which evoked interest of researchers to use it as primary substance for development of high-efficiency sensors (Table 2). However, GR and its derivatives have their own limitations, which will be discussed below.

The analytical signal of carbamates is obtained both by direct method and from carbamate-phenols formed after alkaline hydrolysis (Fig. 6).

The relatively high potential required for the detection of these pesticides greatly affects the detection limits and selectivity. According to earlier studies, carbamate derivatives hydrolyzed with an alkaline solution exhibited a much lower anodic potential for fast electrochemical oxidation, minimizing interferences and significantly increasing the sensitivity of the electrode [74,112,113]. Alkaline hydrolysis is often used to determine CBF, since it is electrochemically inactive on non-enzymatic sensors [112,114–118].

Metal nanoparticles, metal oxides, polymers and, more rarely, metal-organic frameworks (MOFs) are used to determine carbamates in food using sensors based on GR and its derivatives, due to which both the sensitivity of carbamate determination, the linear dynamic range and selectivity of sensors are increased.

4.1. Graphene based sensors

Properties of GR such as good electrical conductivity, impermeability to gasses and liquids, fast electron transfer and excellent mechanical flexibility marked the beginning of its wide application in electrochemical analysis [119–121]. In addition, due to their large surface area, two-dimensional GR sheets provide a large number of electroactive centers for the recognition of the target molecule, thereby increasing the sensitivity of the determination of carbamates [111].

As can be seen from Table 2, the inclusion of GR in the composition of the electrochemical sensor modifier for the determination of carbamates is rarely used. In Ref. [122] a disposable electrochemical sensor based on a screen-printed carbon electrode (SPCE) with the inclusion of MnO_2 nanoparticles and graphene nanoplatelets (GNPs) was developed for the individual and simultaneous determination of three carbamate pesticides – carbaryl (CBR), fenobucarb (FNB) and carbosulfan (CBS) in jasmine rice samples (Fig. 7). GNPs have a unique size and morphology due to one or more layers of graphite planes with a total thickness in the range of 5–10 nm. However, GNPs have the disadvantage of stacking aggregation between GNP layers caused by π–π interactions. To avoid such a problem, nanomaterials based on metal oxides deposited on the surface of GNPs were used [123,124]. Thus, in paper [122] a sensor for simultaneous detection of three pesticides was successfully developed with a wide linear dynamic range (LDR) over 1–30 μM for CBR, 5–80 μM for FNB, and 50–400 μM for CBS, thanks to the inclusion of MnO_2. Sensor based on MnO_2-GNPs/SPCE has good analytical characteristics, but LOD is too high and the stability for a non-enzymatic sensor is limited.

The analytical signal was obtained from carbamate-phenols after alkaline hydrolysis of three carbamate pesticides for improving electroactivity (Fig. 8).

The limited use of GR for the creation of electrochemical sensors for the determination of carbamates can be explained by its hydrophobicity. It makes its use incompatible with aqueous electrolyte solutions, which creates a significant obstacle in the electron transfer process. In addition, the presence of π–π stacking and electrostatic interaction in GR based sensors is both an advantage and a disadvantage, since such stacking contributes to the easy absorption of various molecules, including carbamates, but at the same time the electrode becomes less stable. Some of the useful and unique properties of GR can be realized only after its functionalization with ionic liquids, metal oxides or organic groups such as hydroxyl-, carboxyl- and amino-groups. However, this is often a very long process (it takes on average 10–24 h), which greatly increases the analysis time.

4.2. Graphene oxide based sensors

Electrochemical sensors based on GO for the determination of carbamates in food are more frequently used than GR-based (Table 2). GO contains chemically active oxygen with functional groups such as carbonyl, hydroxyl and epoxy groups, which makes it one of the best materials for creating sensors, since a stable colloidal suspension is formed and its individual layers are hydrophilic [125–127]. It is assumed that the stability of the GO suspension is due to negative electrostatic repulsion due to the ionization of phenolic hydroxyl and carboxyl groups.

Thus, a suspension of GO dispersed in ionic liquid (IL) (namely 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6)) was prepared for voltammetric determination of CBR in fruit samples [128]. The fabricated GO/IL/GCE showed high reproducibility, stability and selectivity due to the synergistic effect of GO and IL, which, when used together, increase the peak current and reduce the oxidative potential of CBR. GO exhibits the same properties when designing sensors together with metal nanoparticles for the determination of carbamates [114, 129]. Another example of incorporating GO into a sensor is the creation of a (MIL)Fe)-101@GO/GCE, where it also justifies itself as having a large surface area and high catalytic activity. Since MIL(Fe)-101 belongs to the metal-organic frameworks (MOF) family, the sensor without GO has low electrical conductivity [130]. Thanks to this combination, it was possible, under optimal conditions, to determine CBR and CBF with low LODs of 1.2 and 0.5 nM within LDR of 5–200 nM and 1–300 nM, respectively. However, most sensors based on GR derivatives have relatively low stability and rather complex fabrication despite good analytical characteristics.

Thus, the inclusion of GO in the composition of the modifying

Table 2
Determination of carbamate pesticides by sensors based on graphene and its derivatives.

Graphene composites	Electrode substrate	Sensing materials	Carbamate pesticide(s)	Method	LDR, μmol·L^{-1}	LOD, μmol·L^{-1}	Analytical characteristics		Characteristics of the electrode		Matrix	Ref.
							Adv.	Disadv.	Adv.	Disadv.		
GR	SPCE	MnO_2	carbaryl carbosulfan fenobucarb	DPV	[a]1–40 [c]50–600 [d]5–150	[a]0.30 [c]14.90 [d]1.30	B, C, D	T	J	X, Y	jasmine rice	[122]
	GCE	MIP/IL-Au/CS-AuPt NPs	carbaryl	DPV	0.030–6.0	0.008	A, B, C, D	–	–	X, Y, Z	cabbage, apple peel	[138]
3D GR	GCE	Au	carbaryl	DPV	0.004–0.3	0.0012	A, B, C, D	–	–	X, Y, Z	peach, apple, grape, tomato, cucumber	[139]
GO	GCE	Ag	carbofuran	Amp	1–1000	0.01	A, B, C	W	E, J	Y	celery, lettuce	[101]
	SPCE	Au NPs	carbofuran	DPV	1–30 30–250	0.22	B, C	T, W	–	X, Y, Z	cucumber, rice	[119]
	Pt disk (the contact)	graphite powder/Hem	carbofuran	SWV	5.0–95	0.009	A, C, D	–	E	Y, Z	carrot, tomato	[120]
	GCE	35MIL(Fe)-101	carbaryl carbofuran	DPV	[a]0.001–0.3 [b]0.005–0.2	[a]0.0005 [b]0.0012	A, B, C, D	–	–	X, Y, Z	cucumber, orange, tomato, cabbage	[125]
	GCE	IL	carbaryl	SWV	0.10–12.0	0.02	A, B, C, D	–	E, F, J	–	tomato, grape	[128]
	PET plastic	PEDOT/PSS	carbofuran	LSV	1–90	0.1	B, C, D	T	E	Y, Z	tomato, wine	[129]
	BDD	–	carbaryl	DPV	1–6	0.07	A, D	U, V	E, J	Y	apple juice	[140]
	CPE	Hem/nickel (II) 1,48,11,15,18,22,25-octabutoxy-29H, 31H-phthalocyanine complex	carbofuran	Amp	5.0–140	1.67	B, C, D	T	–	X, Y, Z	carrot, soil	[141]
rGO	PET	–	carbaryl	LSV	1.2–640	0.49	B, C	T, W	J	X, Y	apple and orange juices	[73]
	GCE	CoO	carbaryl carbofuran	DPV	[a]0.0025–0.99 [b]0.0009–0.32	[a]0.037 [b]0.019	A, B, C, D	–	F	X, Z	grape, orange, tomato, cabbage	[74]
	GCE	Cu/CuO–Ag	carbaryl	DPV	0.05–20.0	0.005	A, B, C, D	–	–	X, Y, Z	grape, orange, tomato, cabbage	[80]
	GCE	Gd_2S_3	carbofuran	DPV	0.001–1381	0.012	A, B, D	V	F, J	X	potato	[117]
	ITO	PDDA/MNP/PSS	carbofuran	DPV	0.83–11.4	0.407	B	T, V, W	–	X, Y, Z	soil	[118]
	GCE	Au NPs/4-HTP	carbofuran	SWV	0.001–10	0.00033	A, B, C, D	–	F	X, Z	orange, cornmeal, cowpeas, potato	[134]
	GCE	MIP/rGO@Au	carbofuran	DPV	0.05–20	0.02	A, B, C, D	–	F, J	X	cabbage, cucumber	[135]
	SPCE	Micellar CTAB	carbofuran	SWV	0.18–90	0.045	A, B, C	W	J	X, Y	soy bean, rice, tomato	[142]

[a] – carbaryl. [b] – carbofuran. [c] – carbosulfan. [d] – fenobucarb.
Analytical characteristics.
Adv: **A** low LOD; **B** wide LDR; **C** selective electrode; **D** high reproducibility.
Disadv: **T** high LOD; **U** narrow LDR; **V** non-selective electrode; **W** low reproducibility.
Characteristics of the electrode.
Adv: **E** easy modifier preparation; **F** long-term stability; **J** low cost.
Disadv: **X** complex modifier preparation; **Y** short-term stability; **Z** high cost.

mixture makes it possible to improve its properties, since a unique feature of GO in comparison with GR is solubility in various solvents. In addition, GO is a relatively simple material for flexible, inexpensive and mass scaling, and it is also easy to apply. However, the chemical details (oxidation/reduction mechanisms and detailed chemical structures) need to be better understood. For example, for a long time there is no exact model of the chemical structure of GO, although it is known that GO is an infinitely thin sheet of oxidized graphite [125]. Currently, a number of structural models have been proposed, such as the Lerf-Klinowski model (the most acceptable now) [131], Scholz-Boehm [132], Ruess [133], Decany [101], etc. In this regard, GO-based materials are difficult to characterize due to its amorphous and non-stoichiometric atomic composition.

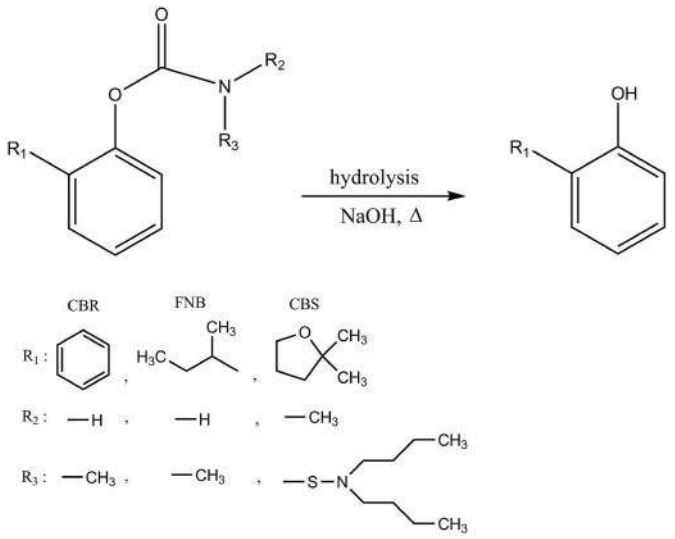

Fig. 6. Example of hydrolysis of some carbamate pesticides.

4.3. Reduced graphene oxide based sensors

Electrode materials with the inclusion of rGO for the determination of carbamates are a large class of graphene materials (see Table 2). rGO has become a good compromise between graphene and GO, because it has properties similar to graphene and it is easy to obtain it in the desired quantities using various methods described in section 2. For the determination of carbamate pesticides, chemical method and electrical recovery are mainly used. rGO has a large surface area and high electrical conductivity, but in order to increase the electron transfer rate and the sensitivity of the determination, it is frequently included in the composition of the electrode material together with metal nanoparticles [134,135], metal oxides [74,80], metal sulfides [117] and polymers [118].

rGO and Au NPs together with a molecular-imprinted polymer (MIP) were used as a modificators of the GCE surface [134]. MIPs were prepared on the electrode surface with CBF as the template molecule, methacrylic acid as the functional monomer, and ethylene glycol maleicrosinate acrylate (EGMRA) as a cross-linker. But, as it is known, MIP causes poor adhesion and a low electrochemical signal, and in this regard, rGO@Au NPs exhibits an excellent synergistic effect to avoid these problems. MIP/rGO@Au/GCE showed high adsorption capacity and good selectivity and was successfully applied to detect CBF in cabbage and cucumber. However, such a sensor is rather expensive for mass production.

rGO is often used in conjunction with Au NPs. rGO@Au NPs were used together with 4-hydroxythiophenol (4-HTP) in Ref. [134]. The sensor was built layer by layer. At first, 4-HTP was self-assembled on the surface of the Au NPs modified layer using Au–S bonds, after this 4-HTP was self-assembled around the CBF using hydrogen bonding (Fig. 9). Finally, the CBF MIP membrane was prepared by electro-polymerization, and the template molecules were eluted using ethanol (75 vol %) and 0.4 mol L^{-1} NaOH solution (25 vol %). This sensor has demonstrated excellent analytical abilities, but with relatively low stability of only 14 days.

In addition to using rGO with metal nanoparticles, metal oxides are also used. CoO/rGO/GCE was developed for simultaneous determination of CBF and CBR in grape, orange, tomato, and cabbage samples [74]. The sensor showed a wide LDR of 0.2–70 μM for CBF and 0.5–200 μM for CBR. LOD was 4.2 μg/L for CBF and 7.5 μg/L for CBR. CoO and rGO demonstrated high catalytic activity and sensitivity to carbamates. Along with metal oxides, the use of gadolinium sulfide and rGO was also described [111]. Gd_2S_3/rGO was prepared using a single-stage hydrothermal approach without any surfactant or additional reducing agent to determine CBF (Fig. 10). rGO acted as a highly conductive, durable and electrochemically active substrate, and Gd_2S_3/rGO, as well as in Ref. [74], showed increased catalytic activity and excellent conductivity due to the synergistic effects between Gd_2S_3 and rGO. The developed sensor has a low LOD of 0.0128 μM with LDR 0.001−1381 μM. However, there is no information about the selectivity of this sensor.

Nevertheless, there are practically no works in which only rGO was used as a single modifier because such a sensor usually has insufficient analytical characteristics, namely reproducibility and sensitivity.

rGO is quite successfully used, as shown above, for inclusion in the

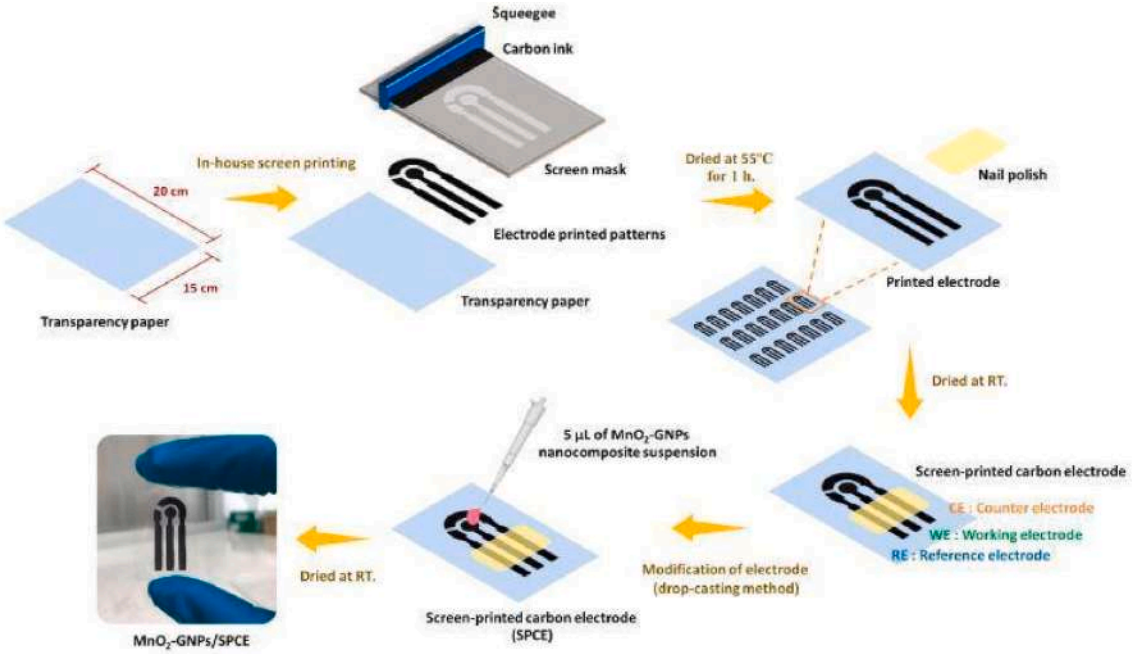

Fig. 7. Fabrication procedures of MnO_2/GNPs/SPCE sensing platform for the simultaneous determination of CBR, FNB, and CBS (Reproduced with permission from Ref. [122], Copyright 2022 Elsevier B.V.).

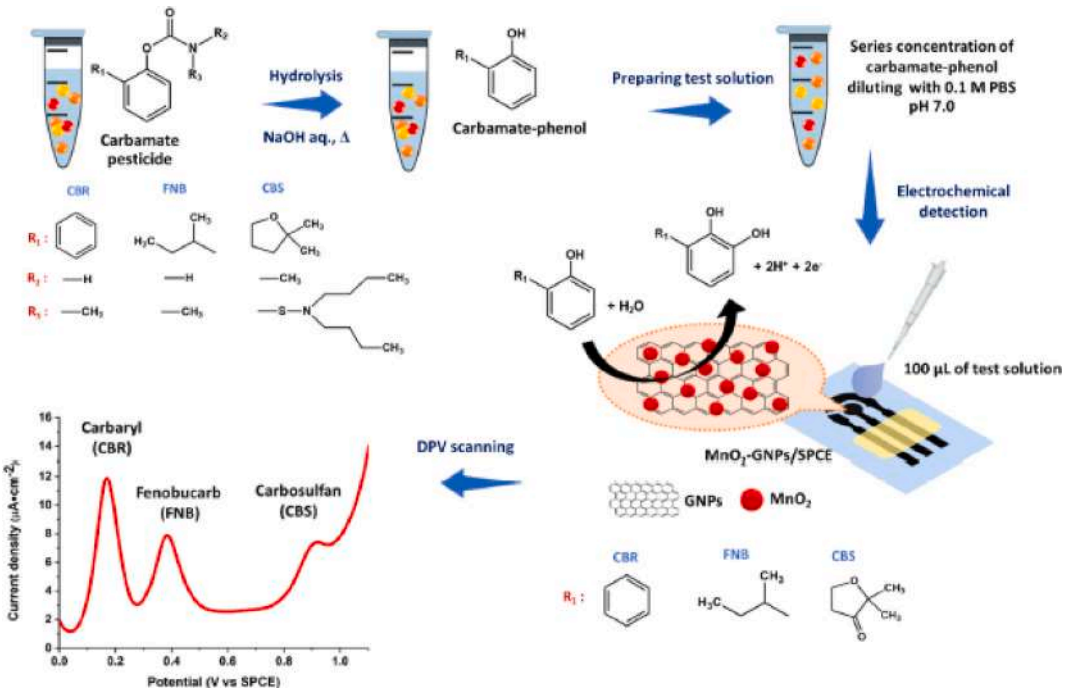

Fig. 8. A disposable MnO_2-GNPs/SPCE sensing platform for the simultaneous determination of CBR, FNB, and CBS (Reproduced with permission from Ref. [122], Copyright 2022 Elsevier B.V.).

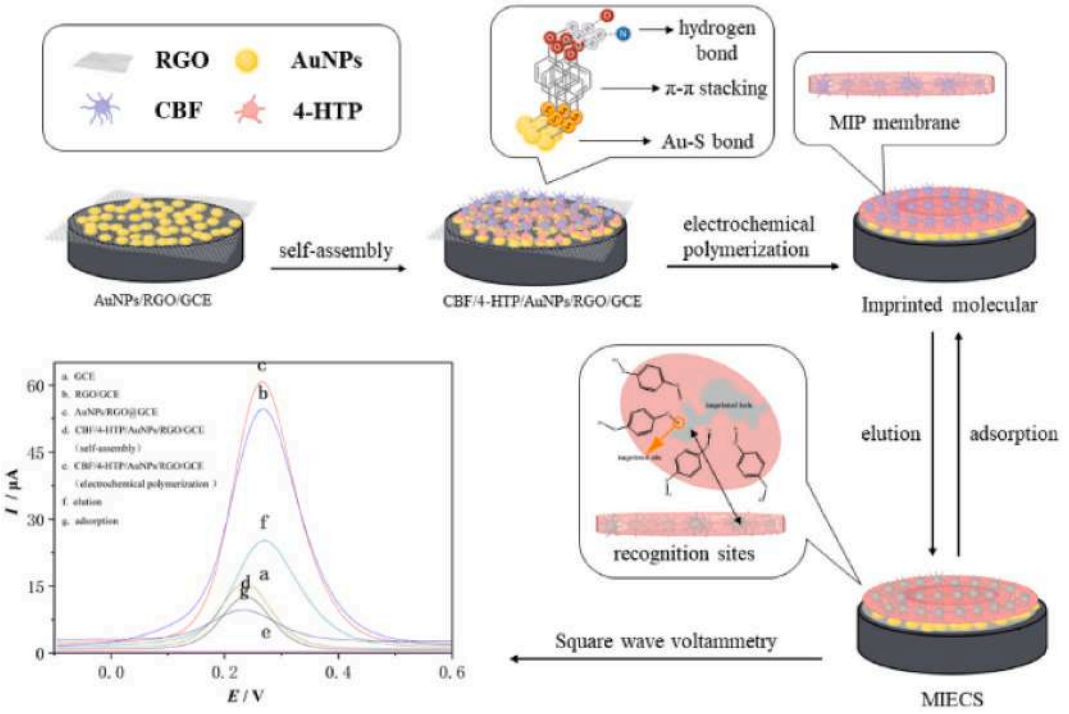

Fig. 9. Molecularly imprinted electrochemical sensor preparation and characterization (Reproduced with permission from Ref. [134], Copyright 2022 Elsevier B.V.).

electrode modificators, due to its unique properties [136,137]. In particular, the synergistic effects resulting from the interaction of various compounds with rGO abound in diversity and, as it has been found, are very useful in the determination of carbamate pesticides. But at the same time, a significant disadvantage of obtaining such sensors is the long time of fabrication (the time to obtain the final sensor reached 29 h) [135]. This approach obviously requires further improvements and new methods for obtaining rGO.

Thus, it has been shown that materials based on GR, GO, and rGO are frequently used to create electrochemical sensors for the determination of carbamates in food. The inclusion of metal nanoparticles, metal oxides, polymers, etc. in GR and its derivatives based electrodes increases its conductivity and catalytic activity, affecting the sensitivity and selectivity of composites in relation to pesticides. However, using GR and its derivatives as an independent sensitive material with sufficient analytical characteristics requires further efforts. In addition, the so far

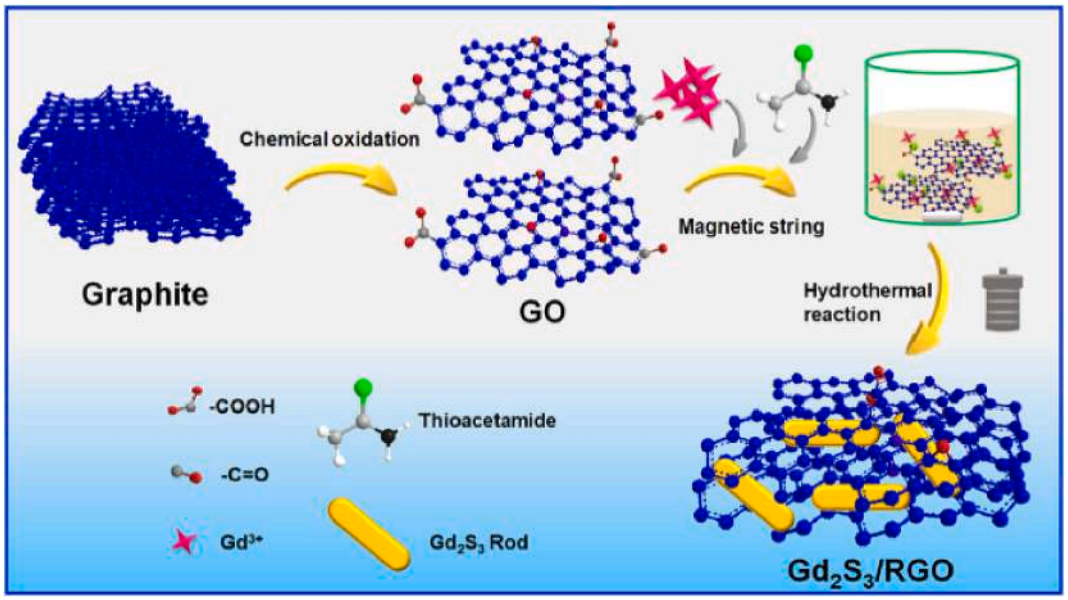

Fig. 10. Formation of Gd_2S_3/RGO composite by a single-step hydrothermal method (Reproduced with permission from Ref. [116], Copyright 2021 ACS Publications).

developed sensors require improvements in two points (1) the development of stable materials with a uniform and controlled distribution of basic materials in the composite material and (2) the creation of cost-effective electrochemical sensors based on GR and its derivatives.

5. Application of graphene and its derivatives based biosensors for determination of carbamate pesticides in food

In the last decade, electrochemical biosensors were in focus for the detection of carbamate pesticides as a promising alternative to optical, piezoelectric and mechanical biosensors due to their high sensitivity [143]. In this review, biosensors were classified according to the immobilized element of bio-recognition (enzymes, rarely antibodies and DNA) on a substrate of GR and its derivatives. In addition, the use of nanomaterials and polymers in the development of biosensors based on GR and its derivatives is a promising tool for improving the efficiency of biosensors in the detection of carbamate pesticides.

The most common group of biosensors for the determination of carbamate pesticides are enzyme biosensors [80,144–149]. Enzymatic detection of carbamate pesticides is mainly based on the inhibition of cholinesterase (ChE) [80,144–149], which have shown satisfactory results for food quality analysis (Table 3). To determine carbamates, monoenzyme biosensors based on acetylcholinesterase (AChE) are used, the substrate of which is acetylcholine (equation (1)):

$$\text{Acetylthiocholine} + H_2O \xrightarrow{AChE} \text{Thiocholine} + \text{Acetic acid} \quad (1)$$

Enzymatic hydrolysis of acetylcholine gives electroactive thiocholine, the electrooxidation signal of which is recorded by various electrochemical methods (e.g. DPV, CV, SWV, Amp) (equation (2)):

$$2\ \text{Thiocholine} + H_2O \xrightarrow[oxidation]{Anodic} \text{Dithiobischoline} + 2H^+ + 2e^- \quad (2)$$

Carbamate pesticides, when introduced into an electrochemical cell, contribute to the inhibition of the enzyme and a decrease in the electrochemical signal of thiocholine. Monoenzyme biosensors are not selective and are used to determine the total carbamate contamination of food in terms of either CBR or CBF. Bi-enzymatic biosensors for the determination of carbamates are also known, but studies in this area are not numerous due to the rise in the cost of biosensors when using two enzymes [81]. The work of such sensors is associated with tyrosinase [150]. In this case, the enzymatic hydrolysis of AChE phenyl acetate gives phenolic compounds characterized by a high oxidation potential. To do this, the enzyme tyrosinase was used, which converts phenol into quinone, a compound that can be electrochemically reduced to catechol (equation (3) and (4)):

$$\text{Monophenol} + O_2 \xrightarrow{\text{Cresolate activity}} \text{Catechol} \quad (3)$$

$$\text{Catechol} + O_2 \overset{\textit{Catecholase activity}}{\rightleftharpoons} \text{O} - \text{quinone} \quad (4)$$

Tyrosinase biosensors have low specificity, since many substrates inhibit the enzyme. Tyrosinase is inherently unstable, which shortens the lifetime of tyrosinase-based biosensors. However, tyrosinase can withstand high temperatures and organic solvents used to extract carbamate pesticides.

A small group of electrochemical biosensors based on GR and its derivatives for the determination of carbamate pesticides is based on DNA biosensors, whose work is based on hybridization between complementary nucleic acid sequences. In these biosensors, a single-stranded DNA probe is complementary to the target DNA. Unfortunately, over the past 10 years, no work has been found on electrochemical immunosensors using GR-based substrates and its derivatives for the immobilization of antibodies or antigens for the determination of carbamates.

5.1. Graphene based biosensors

5.1.1. Cholinesterase-based biosensors

Many studies have shown that pure GR has unsatisfactory electrical conductivity due to the inevitable aggregation [122,155]. The use of GR unique properties for enzyme biosensors is possible after preliminary functionalization of its surface by organic groups such as hydroxyl, carboxyl, and amino [145,146,151]. Functionalized GR sheets are easier to disperse in an organic solvent or polymer matrix. In addition, with the help of functional groups, it is possible to immobilize AChE to the GR surface using covalent linkers, which improves the catalytic properties of the enzyme and increases its lifetime. Thus, it was proposed to functionalize GR by carboxyl groups in a chemical way through conjugation of acetic acid fragments [145]. The composition of the GR composite included NiO NPs to improve electrical conductivity. The

Table 3
Biosensors based on graphene/graphene oxide/reduced graphene oxide for the determination of carbamate pesticides.

Graphene composites	Electrode material	Immobilization of the biocomponent	Carbamate pesticide(s)	Detection technique/ Analytical signal	LDR, μmol·L^{-1}	LOD, μmol·L^{-1}	Matrix	Analytical characteristics		Characteristics of the electrode		Ref.
								Adv.	Disadv.	Adv.	Disadv.	
GR	LACC/TYR/ Au NPs/CS	Electropoly-merization	carbaryl propoxur	SWV/4-amin-ophenol	[a]0.099–2.91 [b]0.499–19.2	[a]0.0198 [b]0.187	orange, tangerine, lemon	A, B, D	V	–	X, Y,Z	[81]
	GCE/GA/ AChE–IL–Gel	Cross-linking	carbaryl	Amp/ thiocho-line	$1.0\cdot10^{-8}$–0.01	$5.3\cdot10^{-9}$	tomato juice	A, B, D	V	F,J	X	[144]
	GCE/NF/ AChE-CS/ NiO-CGR-NF	Entrapment	carbofuran	Amp/ thiocho-line	$1.0\cdot10^{-6}$–0.0001 0.0001–0.01	$5.0\cdot10^{-7}$	apple, cabbage	A, B, D	V	F, J	X	[145]
	PEDOT–PSS/ Au NPs/ AChE	Adsorption	carbofuran	Amp/ thiocho-line	0.0024–0.049 0.94–2.4	–	–	D	T, U, V	E, F, J	–	[146]
GO	GCE/AChE/ MWCNTs	Cross-linking	carbaryl	Amp/ thiocho-line	0.005–5	0.0017	cabbage	A, B, D	V	F, J	X	[79]
	GCE/AChE	Adsorption	carbaryl	Amp/ thiocho-line	0.0015–0.0303	0.00075	cabbage, spinach	A, B, D	V	E, F, J	–	[147]
	Microfluidic chip MIP/Au NPs/DNA aptamer	Cross-linking	carbofuran	DPV/ carbofuran	0.0002–0.05	$6.7\cdot10^{-5}$	Chinese cabbage, chili, lettuce, tomato, apple, banana, tangerine, watermelon	A, B, D	V	–	X, Y, Z	[153]
rGO	GCE/Au NPs/β-CD/ PB-CS/AChE	Adsorption	carbaryl	DPV/ thiocho-line	$2.1\cdot10^{-5}$–0.0049	$5.7\cdot10^{-6}$	caraway, cabbage, rapeseed	A, B, D	V	F	X, Z	[148]
	GCE/AChE/ Con A/PDA-Au NPs	Entrapment	carbofuran	CV/thio-choline	5–40	0.012	tomato	D	T, U, V	F	X, Z	[149]
	GCE/AChE	Adsorption	carbaryl	DPV/thio-choline	0.01–0.05 0.0002–0.001	0.0019	tomato	A, B, D	V	E, F, J	–	[154]

[a] – carbaryl. [b] – propoxur.
Analytical characteristics.
Adv: **A** low LOD; **B** wide LDR; **C** selective electrode; **D** high reproducibility.
Disadv: **T** high LOD; **U** narrow LDR; **V** non-selective electrode; **W** low reproducibility.
Characteristics of the electrode.
Adv: **E** easy modifier fabrication; **F** long-term stability; **J** low cost.
Disadv: **X** complex modifier fabrication; **Y** short-term stability; **Z** high cost.

resulting composite was easily dispersed in Nafion, which was both a matrix for the inclusion of AChE and its protective film. The analytical signal from thiocholine was recorded by the amperometric method. Despite the multi-stage manufacturing of the biosensor, it turned out to be stable for 1 month and suitable for the sensitive determination of CBF in apples and cabbage in LDR 1–100 μmol L^{-1} and 0.1–10 mmol L^{-1} with LOD $5.0\cdot10^{-7}$ μmol L^{-1}.

It is well known that ILs are suitable materials for modification of electrodes due to their high ionic conductivity, biocompatibility, and wide potential windows, which can contribute to increasing the sensitivity of the determination of carbamate pesticides. It is also important that the ILs have a shielding effect on the interaction between GR sheets, contributing to their excellent electrical conductivity. In 2015, Zheng et al. developed a sensor based on a GCE modified with glutaraldehyde with IL functionalized GR, gelatin, and AChE [144]. In this work, in order to avoid GR problems with the shielding effect to the π–π stacking interaction, an IL (1-(3-aminopropyl)-3-methylimidazolium bromide) was used, which contributes to the dispersion of GR sheets and increases sensitivity. So, the modified sensor after covalent crosslinking of AChE on a biocompatible matrix was used with amperometric registration of the analytical signal of thiocholine for CBR determination in tomato juice with LOD $5.3\cdot10^{-9}$ μmol L^{-1} and good reproducibility.

To reduce the biosensor manufacturing time spent on the preliminary functionalization of GR sheets, some authors suggest using commercial materials based on factionalized GR. Sansuk et al. proposed modification of AuNPs/SPCE electrodes by nanocomposite ink (GR-PEDOT:PSS) as a substrate for AChE immobilization [79]. Despite the use of a nanocomposite material based on GR and Au NPs, the author failed to achieve high sensitivity in the determination of CBF in comparison with previous works (Table 3).

5.1.2. *Tyrosinase-based biosensors*

Graphene can enhance the direct electron transfer between enzymes and the electrode in bi-enzymatic biosensors. A bi-enzymatic biosensor obtained in one step by electrodeposition of a hybrid film on a carbon paste electrode doped with graphene (GPE) [81] was used for the determination of two carbamate pesticides (CBR and propoxur), The hybrid film consisted of laccase (LAC), tyrosinase (TYR) and Au NPs enclosed in a chitosan polymer matrix (CS). In this case, GR was used as a transducer mixed with carbon paste in a ratio of 20:80% (w/w). Chitosan-based polymer film with Au NPs has membrane-forming ability, high water permeability and electrical conductivity, good adhesion and biocompatibility with enzymes. It provides a suitable microenvironment for electro-immobilization of enzymes on the electrode surface. The selected carbamates were quantified based on their capacity to inhibit the catalytic reaction of the substrate 4-aminophenol performed

by the bi-enzymatic system. The biosensor demonstrated wide LDR, low LOD, high accuracy, sensitivity, repeatability, reproducibility and stability (twenty days). However, research conducted on tyrosinase-based biosensors using graphene as a substrate for carbamate pesticides determination is so far limited, because graphene based tyrosinase biosensors have low specificity.

5.2. Graphene oxide based biosensors

GO is one of the most popular materials for opening up new opportunities in the development of biosensors of the next generation. Due to the coexistence of a hydrophobic domain from the primordial graphite structure and hydrophilic oxygen-containing functional groups, GO has good dispersibility in water, biocompatibility and high affinity for certain biomolecules. The properties of GR itself partially depend on the methods of obtaining. These properties of GO have provided many opportunities for the development of new biological sensor platforms [152].

5.2.1. Cholinesterase-based biosensors

A biosensor based on immobilized AChE on GO nanoribbons (NRs) with the inclusion of additionally added multiwall carbon nanotubes (MWCNTs) was used for determination of CBR [79]. (Fig. 11).

MWCNTs together with GO NRs, thanks to covalent binding technology, have higher enzymatic activity with respect to ATCl than MWCNTs. Thus, based on changes in the electrochemical reaction based on enzymatic activity induced by CBR, an electrochemical method with an excellent LDR (5–5000 nM), LOD 1.7 nM, and acceptable reproducibility (RSD 7.3%) has been successfully developed. However, the developed biosensor has to be prepared a long time before the experiment: MWCNTs/GO NRs are applied to the sensor, then 0.1 mol l^{-1} phosphate buffer solution containing N-hydroxysuccinimide and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride is applied and incubation is required for 6 h at 25 °C. Only then AChE solutions are applied which are incubated at 25 °C for 30 min. This process is very time consuming for practical application.

In [147] an electrochemical biosensor was introduced for detecting CBR in spinach and cabbage, based on the immobilization of AChE on an electrochemically induced porous GO (e-pGO) grid, which was obtained by scanning a modified GO electrode using the method of successive cyclic voltammetry. In this paper, pGO is used to determine a carbaryl pesticide and this approach to its production is simple, one-step and environmentally friendly. Such a modified material – pGO – provides a large surface area, facilitates the interface between biomolecules and the

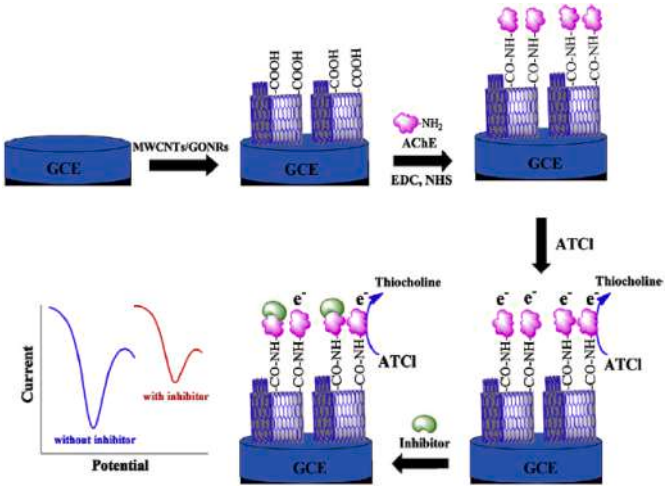

Fig. 11. Stepwise amperometric biosensor fabrication and principle for pesticide determination (Reproduced with permission from Ref. [79], Copyright 2015 Elsevier B.V.).

GO surface, and improves the diffusion and mass transfer of reagents. The developed sensor does not require long preparation and shows excellent LOD 0.15 ng mL^{-1} with LDR 0.3–6.1 ng mL^{-1}.

5.2.2. DNA-aptamer

Li et al. has developed an electrochemical microfluidic chip with the inclusion of gold nanoparticles based on GO, which increases the sensitivity of the determination of CBR (LOD 67 pM) [153]. A molecularly imprinted polymer film (MIP) and a DNA aptamer were also included in the chip as dual recognition units, thus increasing the selectivity of the developed chip. This microfluidic chip for CBF determination has attractive characteristics, such as its potential for high throughput, a high degree of automation and a high degree of integration. However, the stability of such a sensor has not been fully studied, especially considering that a DNA aptamer is used.

5.3. Reduced graphene oxide based biosensors

The excellent current density, chemical inertia and biocompatibility of rGO make it suitable material for surface modifications with biocomponents. Unfortunately, the total surface area of rGO can be reduced due to the interlayer effects of van der Waals interactions and repacking of GR sheets. It is observed that the fixation of inorganic nanoparticles on rGO sheets can prevent aggregation, as well as improve the electrochemical properties of biosensors [154].

5.3.1. Cholinesterase-based biosensors

In paper [155] it is proposed to use rGO as a substrate for the immobilization of the enzyme (AChE), followed by the application of a bio composite to a GCE. Despite the lack of selectivity, a biosensor based on rGO and ChE represents fast and inexpensive way to determine carbamate contamination in terms of CBR in tomatoes with LOD 0.0019 μmol L^{-1}.

The sensitivity of the determination of carbamate pesticides in food is affected by conformational changes or the stability of the enzyme during immobilization on the surface of rGO. Most of the AChE immobilization protocols are associated with simple adsorption on the surface of rGO, which leads to the occlusion of the enzyme and loss of its activity. In paper [150], it was proposed to use concanavalin A (Con A) as a modifier that specifically binds to AChE mannose, which solves the problem of biosensor stability. In addition, the use of polydopamine as part of a complex modifier allowed improving the hydrophilicity of the rGO surface, and the use of Au NPs to catalyze the oxidation of thiocholine. However, the use of additional biocomponents in the modifier increases the cost of the biosensor.

In 2015 Zhao et al. developed an ultra-sensitive and selective sensor based on GCE using a modifying mixture including electrochemically reduced GO and Au NPs, β-cyclodextrin (β-CD), Prussian blue (PB), chitosan (CS), and AChE [148]. The synergy of AuNPs and rGO increased electron transfer and amplified the thiocholine electrooxidation signal. GO was reduced by single-stage electrochemical deposition of GO-Au NPs by chronoamperometry in a stirred 0.1 M PBS containing 1.25 mM $HAuCl_4$ and 0.15 mg mL^{-1} β-CD with a fixed potential of +1.4 V for 720 s (Fig. 12). Besides, β-CD could interact with substrate by reversible bonding, which contributed to increase the enrichment of the substrate and improve the selectivity and sensitivity of the biosensor. The integration of ERGO-AuNPs-β-CD with PB-CS provided an advantageous and high-performance platform for sensing applications. The PB effectively catalyzed the oxidation of TCh at low potential. The developed biosensor showed wide LDR 4.3–1.0·10^3 pg mL^{-1} with low LOD of 1.15 pg mL^{-1} for CBR. However, the fabrication of such a biosensor is rather time consuming which is sometimes impractical.

Thus, the most widely presented in the article are cholinesterase-based biosensors based on GR and its derivatives for the determination of carbamate pesticides in food. To increase the sensitivity of the

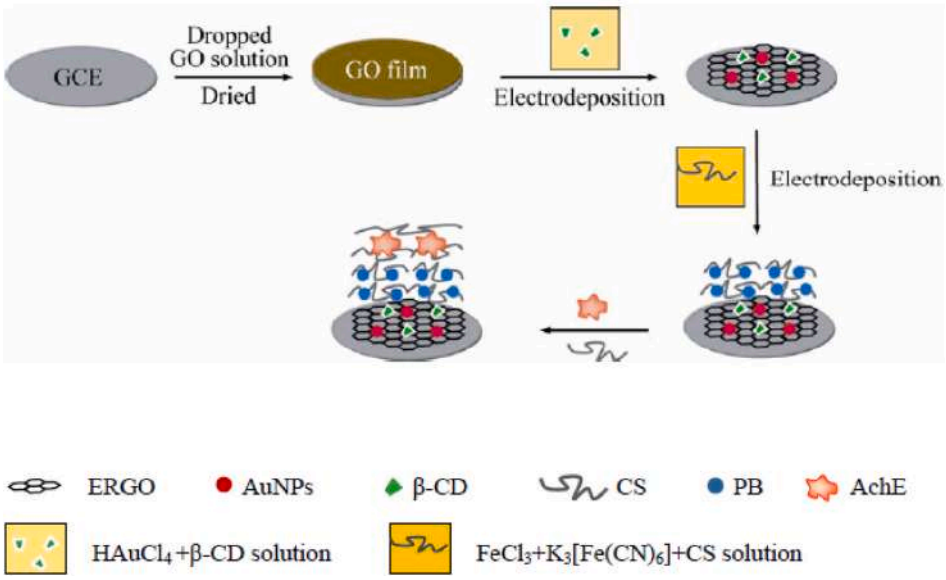

Fig. 12. Fabrication of CS/AChE/PB-CS/AuNPs-ERGO-β-CD/GCE (Reproduced with permission from Ref. [148], Copyright 2015 Elsevier B.V.).

determination of pesticides, manufacturing technologies for electrode substrates based on GR and its derivatives include the use of metal nanoparticles, polymer chitosan coatings, allowing receptor molecules to maintain their native conformation and activity. It should be noted that in most of the cases considered, the proposed electrochemical biosensors are manufactured in non-standardized conditions in labor-intensive ways. Often there is no information about the stability, storage conditions and working time of biosensors for the determination of carbamates. This may affect the inability of analytical laboratories to use electrochemical biosensors on a daily routine basis, preferring simpler and more reliable methods for determining carbamate pesticides.

Despite the still existing limitations in the widespread use of electrochemical biosensors for the determination of carbamates, their potential in terms of high sensitivity, low consumption of the studied objects (at the level of μL), ease of use and reasonable cost, is really impressive.

6. Conclusion and expected trends

This review summarizes the use of GR and its derivatives for electrochemical sensing of carbamate pesticides. The GR and its derivatives integration with different nanoparticles, enzymes, molecules, and polymers further enhance the potential to improve the limit of detection, selectivity, sensitivity, and reproducibility. GR and its derivatives are more sensitive and selective towards pesticides when nanoparticles are incorporated into them because it increases the conductivity and catalytic activity of GR. Furthermore, other factors like surface defects, nanoparticle size, and surface morphology also effect detection of pesticides. In the future, the problem of selectivity could be solved by electrochemical immunosensors or DNA-based biosensors, where graphene and its derivatives could act as a promising substrate. Furthermore, nanocomposites based on GR also require new novel techniques for synthesis that are cost effective and easy to use. In order to enhance GR and its derivatives sensing applications in the future, it is necessary to continue the study of highly stable materials based on GR and its derivatives for pesticide determination.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

This research was supported by the TPU development program and by the State Assignment of the Russian Federation “Science” (Project FSWW-2023-0008). J.B thanks the Czech Science Foundation (Project GACR 20-01589S) for the financial support.

List of abbreviations

4-HTP – 4-hydroxythiophenol
AChE – acetylcholinesterase
Adv – advantage
AFM – atomic force microscopy
Amp – amperometry
B-rGO – bacterial reduced graphene oxide
BDD – boron-doped diamond
CD – cyclodextrin
CFG – chemically functionalized graphene
CGR – carboxylic graphene
Con A – concanavalin A
CPs – carbamate pesticides
CPE – carbon paste electrode
CS – chitosan
CTAB – cetyltrimethylammonium bromide
CV – cyclic voltammetry
CVD – chemical vapor deposition
Disadv – disadvantage
DNA – deoxyribonucleic acid
DPV – differential pulse voltammetry
EC – electrochemical
FTIR – Fourier-transform infrared spectroscopy
GA – glutaraldehyde
GCE – glassy carbon electrode
Gel – gelatin
GO – graphene oxide
GRQD(s) – graphene quantum dot(s)
GR – graphene
Hem – hemin

HRTEM – high resolution transmission electron microscopy
IL – ionic liquid
LACC – laccase
LDR – linear dynamic range
LOD – limit of detection
LSV – linear scan voltammetry
MIL – Matériaux de l'Institut Lavoisier
MIP – molecularly imprinted polymer
MNP – magnetite nanoparticles
MWCNTs – multiwall carbon nanotube(s)
NF – nafion
NPs – nanoparticle(s)
PB – Prussian blue
PDA – polydopamine
PDDA – poly(diallyldimethyl ammonium)
PEDOT – poly(3,4-ethylenedioxythiophene)
PET – polyethylene terephthalate
PPY – polypyrrole
PSS – poly(styrene sulfonate)
RS – Raman spectroscopy
rGO – reduced graphene oxide
SEM – scanning electron microscopy
SERS– surface enhance Raman spectroscopy
SPCE – screen-printed carbon electrode
SWV – square-wave voltammetry
TEM – transmission electron microscopy
TYR – tyrosinase
UN – United Nations
UV–vis spectroscopy – ultraviolet–visible spectroscopy
XPS – X-ray photoelectron spectroscopy
XRD – X-ray diffraction

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