

2019

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Elsevier

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<https://doi.org/10.1016/j.teac.2019.e00064>

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Article in Trends in Environmental Analytical Chemistry · April 2019

DOI: 10.1016/j.teac.2019.e00064

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# Graphene and graphene like 2D graphitic carbon nitride: Electrochemical detection of food colorants and toxic substances in environment

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## ARTICLE INFO

### Article history:

Received 27 February 2019

Received in revised form 12 April 2019

Accepted 22 April 2019

### Keywords:

Graphene  
Graphitic carbon nitride  
Electrochemical  
Azo dyes  
Residues  
Antibiotic

## ABSTRACT

Excessive consumption of substances such as food colorants, exposure to doses of metal ions, antibiotic residues and pesticides residues above maximum tolerance limit have a detrimental effect on human health. Hence in detecting these harmful substances, the development of sensitive, selective and convenient analytical tools is an essential step. Graphene and graphene like 2D graphitic carbon nitride have shown great promise in the development of electrochemical sensors for determining the levels of these substances in different samples. In this paper, graphene and graphene like 2D graphitic carbon nitride applications on the determination of various food colorants in foods and drinks such as azo dyes (tartrazine, allura red, amaranth, carmine and sunset yellow); metal ions contaminants, antibiotic and pesticide residues in the environment are reviewed.

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## 1. Introduction

Graphene is made up of one layer of  $sp^2$ -hybridized carbon atoms arranged in a rigid two dimensional (2D) honeycomb network. The history of graphene discovery dates back in 2004 when Geim and co-workers from Manchester University succeeded in isolation of single-layer of graphene from graphite for the first time [1]. It has a structure which makes it a fundamental building block in the formation of different dimension carbon materials such as three dimensions (3D) graphite, one dimension (1D) nanotubes and zero dimension (0D) fullerene [2]. Graphene is mechanically very strong with extraordinary thermal ability, excellent electron transfer capacity and large surface area attributed to its chemical structure. Due to these fascinating properties, its application in fields such as sensing, catalysis, electronic devices and energy storage have been of high interest to Scientists [3]. Moreover, graphene or its derivatives such as graphene oxide (GO) and reduced graphene oxide (rGO) have been applied in detection of chemical substances in different samples. For instance in electrochemical concentration determination, graphene

has been used to detect dopamine, rutin from human samples [4–6], food colorants in food and drinks [7,8], metal ions [9], antibiotic residues [10], pesticides residues [11] and 4-nitrophenol [12] from contaminated environment just to mention a few.

Recently, the extraordinary properties of graphene have arisen interests in graphene like 2D nanomaterials. These graphene like 2D materials are called that way owing to their structures which resemble that of graphene. They include graphitic carbon nitrides ( $g-C_3N_4$ ), boron nitride (BN), transition-metal dichalcogenides (TMDs) (such as  $MoS_2$ ,  $MoSe_2$ ,  $SnS_2$ ,  $WS_2$  and  $WSe_2$ ) and transition metal oxides (e.g.  $MnO_2$ ,  $MoO_3$ ,  $WO_3$  and  $La_2CuO_4$ ) [13]. The 2D graphene like nanomaterials are either composed of one or just a few atomic layers. The graphene 2D analogs have shown excellent novel catalytic, mechanical, optical, thermal and electrical properties. Due to these extraordinary abilities, recently their potential applications in the areas of electronic, catalysis, chemical and biological sensors, super capacitors and energy storage have gained tremendous attention [14–19].

Among the graphene like 2D materials mentioned earlier, graphitic carbon nitride ( $g-C_3N_4$ ) is a typical polymeric metal free semiconductor. The early discussions on carbon nitride can be traced back to 1834 when Liebig and Berzelius observed and named the material to be “melon” which is (linear polymers of connected tri-s-triazines via secondary nitrogen) [20]. From 1990, the material started receiving much attention. Graphitic carbon nitride is described to be the most super material among the  $C_3N_4$  allotropes being most stable at

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ambient conditions [21,22]. Its structure is demonstrated as a 2D frameworks of s-triazine or tri-s-triazine connected via tertiary amines [23]. The tri-s-triazine ring structure with the high degree of condensation makes the material to be very thermal stable (up to 600 °C) in air and in chemicals such as acid, base and organic solvents and an electronic structure being a medium-band gap, indirect semiconductor [24]. Furthermore, graphene like 2D material has arisen interest due to the strong electron donor nature of nitrogen present in g-C<sub>3</sub>N<sub>4</sub>, which is not found in graphene [25]. Since it is defect rich (N-bridged poly (tri-s-triazine)), the defects and nitrogen atoms work as active sites for electron conductivity [26].

Graphitic carbon nitride is a wonder material in today's world which has been applied in diverse areas such as chemical and biological sensors development [27,28], drug delivery [29], fuel and photocatalysis [30]. Furthermore, Scientists inspired by its properties, have been able to design and develop different sensors employing the unique properties of g-C<sub>3</sub>N<sub>4</sub>. These sensors include, electrochemiluminescent (ECL) [22,31–34] photoluminescent (PL) [35], photoelectrochemical (PEC) [36–39], catalytic (chemo catalysis, photocatalysis and electrocatalysis) [40] which have been used in detection of various chemical molecules, (Fig. 1). Moreover g-C<sub>3</sub>N<sub>4</sub> has found its use in fluorescent sensors [22,31,41–43], voltammetric and amperometric electrochemical sensors. In addition ultra-sensitive and selective sensors are also needed to enable determination of ultra-trace chemical molecules from the target samples.

In this review, the discussion is focused on the applications of graphene and graphene like g-C<sub>3</sub>N<sub>4</sub> in development of sensors for detecting food colorant and determination of environmental contaminants which are metal ions, antimicrobial residues and pesticide residues, (Fig. 1). These chemical substances need rapid, simple, cheap analytical tools for determination of their concentration and monitoring their effects in the end consumers who are human beings because they are harmful.

### 1.1. Synthesis of graphitic carbon nitride

Scientists are conducting research day by day to develop new materials with better properties, low cost and better functionality

than the existing ones. They develop novel physical and chemical methods to come up with improved materials for a wide range of application. In synthesizing bulk g-C<sub>3</sub>N<sub>4</sub>, methods such as physical vapor deposition (PVD), chemical vapor deposition (CVD) and thermal nitridation, are used to polymerize precursor materials such as cyanamide, dicyandiamide and melamine [44], Fig. 2 (A). Other methods include solvothermal [45,46] and solid state reaction [47,48]. Li and coworkers [49] produced graphite-like nanobelts and nanotubes from melamine/dicyandiamide by CCl<sub>4</sub> (4.5–5 MPa) at temperature 220 °C. Lotsch and Schnick did tricyanomelaminates thermal decomposition at > 450 °C and observed graphitic like materials [50]. Furthermore, exfoliation method is used in obtaining ultrathin unilamellar g-C<sub>3</sub>N<sub>4</sub> nanosheets. The recent development in exfoliation of 2D g-C<sub>3</sub>N<sub>4</sub> nanosheets include exfoliation methods such as thermal oxidation exfoliation, chemical exfoliation and ultrasonic exfoliation, Fig. 2(B). Although both thermal oxidation and ultrasonic exfoliation methods can synthesize 6 layered g-C<sub>3</sub>N<sub>4</sub> nanosheets with >2 nm thick, ultrasonic exfoliation produces g-C<sub>3</sub>N<sub>4</sub> nanosheets which show superior dispersion and stability in aqueous solution. On the other hand, chemical exfoliation has shown success in synthesizing single layer nanosheets and superior characteristics such as high exfoliation efficiency, acceptable cost effectiveness and functionalization of the nanosheets surface. Hence chemical exfoliation is the most superior compared to ultrasonic exfoliation and thermal oxidative exfoliation [51–53].

## 2. Sensing applications of graphene and graphene like 2D graphitic carbon nitride

### 2.1. Electrochemical detection of colorants in foods products and beverages

Food colorants which are synthetic, have been highly used in food and beverage industry due to low production cost, stability in pH, oxygen and light compared to natural colorants [54]. The main artificial food colorants include azo dyes (tartrazine, amaranth, carmine, sunset yellow, and allura red), triphenylmethane dyes,

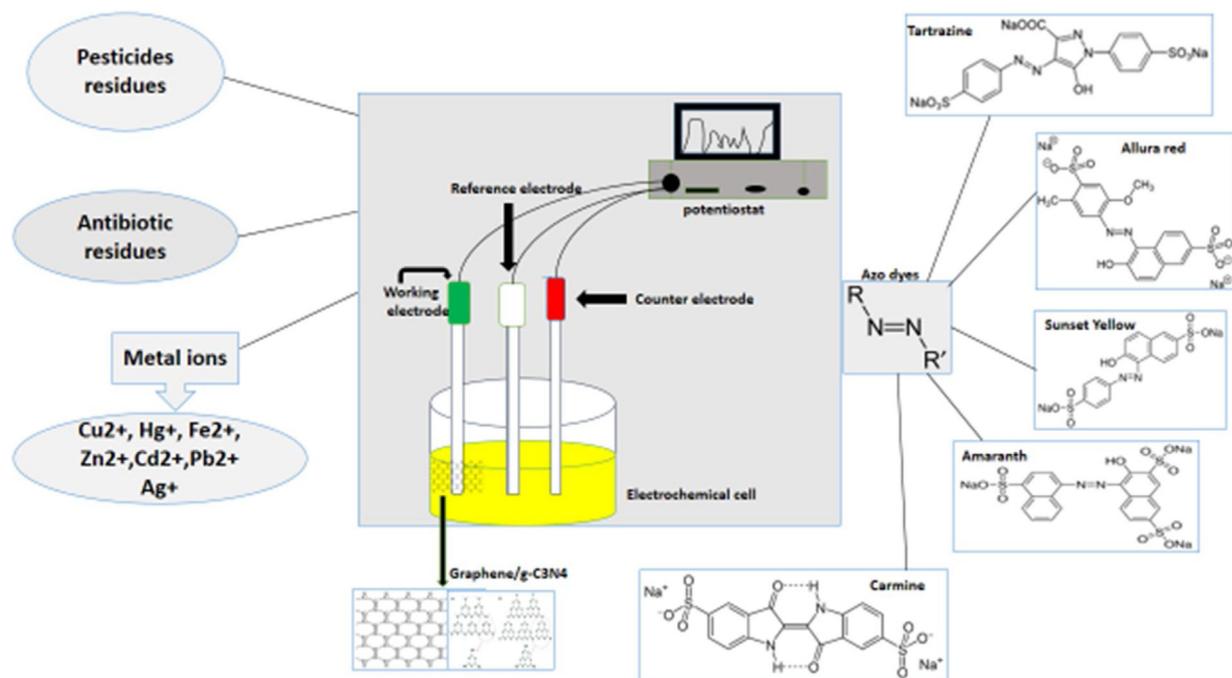
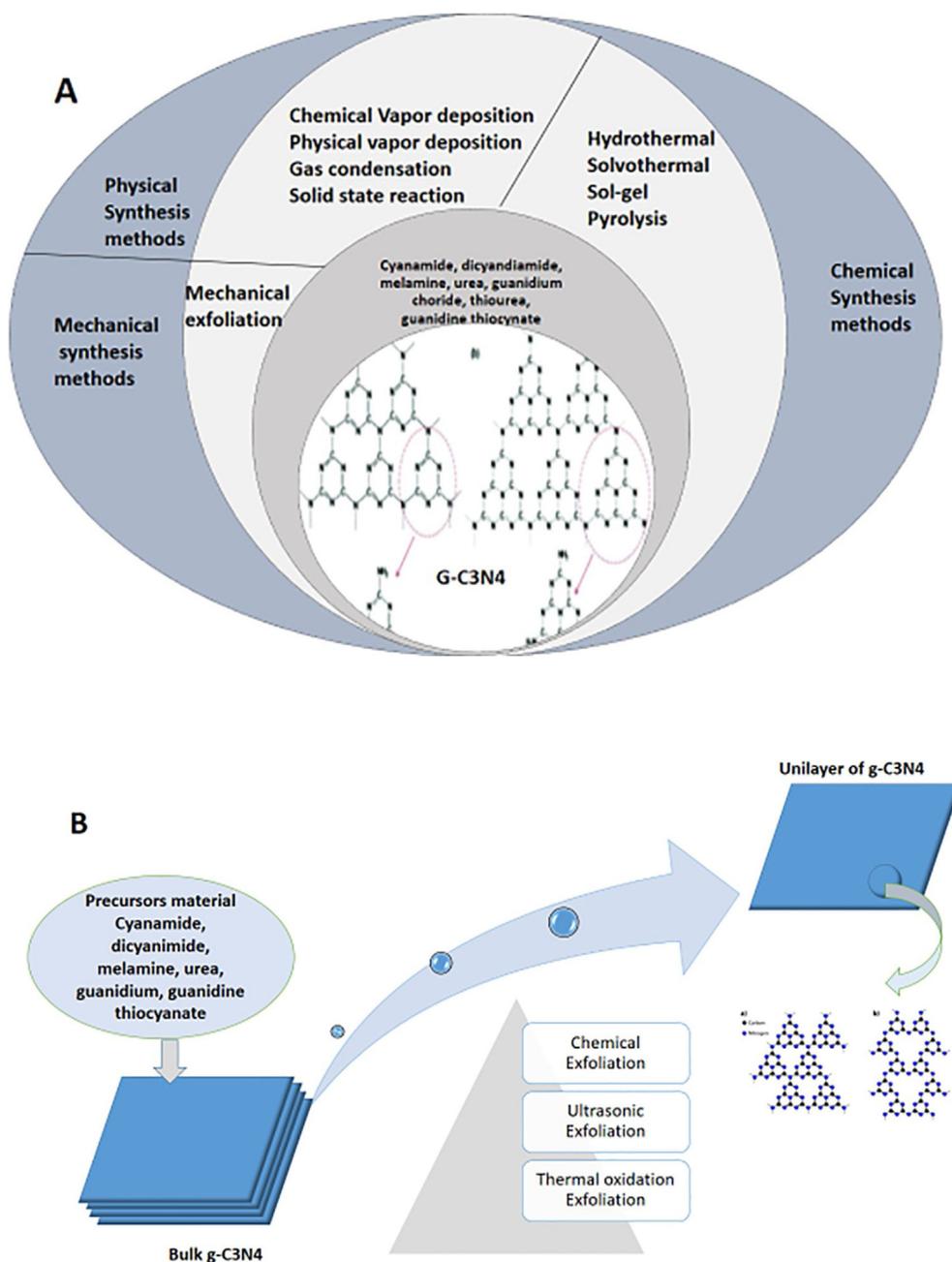


Fig. 1. Electrochemical sensing application areas of graphene and graphene like 2D graphitic carbon nitride.



**Fig. 2.** (A) shows mechanical, physical and chemical methods that have been used in synthesizing 2D  $g\text{-C}_3\text{N}_4$ . Materials, (B) Exfoliation methods that produce ultrathin sheets of graphitic carbon nitride.

xanthene dyes, indigotine dyes, and quinolone dyes [55]. The azo dyes are the major synthetic dyes as they account for more than half of global dye production [56]. The main chemical feature of the azo dyes is the presence of an azo group ( $-\text{N}=\text{N}-$ ) and aromatic rings. Excessive intake of the azo food dyes however can be harmful to human health; for example, Sunset yellow and Tartazine are food colorants which can cause harmful effects such as allergies, asthma, migraine and cancers [57,58] as they contain an azo functional group. The maximum limit level for Tartazine and Sunset yellow is 100 ppm and 50 ppm respectively if analyzed individually and 100 ppm when combined [59].

In monitoring these substance levels in food products and beverages, various analytical methods have been developed for the detection of azo food colorants. Among these are, high performance liquid chromatography–mass spectrometry (HPLC–MS) ([8], capillary electrophoresis [60], surface-enhanced raman

spectroscopy (SERS) sensor [61], fluorimetry [62] and thin layer chromatography [63]. These methods involve complex steps in their application hence tiresome and time-consuming. In recent times, electrochemistry analytical methods involving use of bare or modified electrodes have been used in the detection of food additives such as tartrazine and sunset yellow [8,64,65] due to their convenience, rapid response, higher sensitivity and selectivity [66].

Graphene Oxide (GO) is a 2D material which is similar to graphene [67] and possesses multiple oxygen functional groups [68]. Its carbon atoms can be linked to the hydroxyl or epoxy groups, whereby, carboxyl and carbonyl groups can be used to modify the surface boundary. Fascinating properties such as electrical conductivity, mechanical strength, and high specific surface area has made GO useful in developing chemically modified electrodes [69]. Reduced graphene Oxide (rGO) has also

found a tremendous interest due to its enhancing properties [70]. Qiu and his fellow researchers developed graphene oxide and multi-walled carbon nanotube nanocomposite-modified GCE for detection of sunset yellow and tartrazine. In this simultaneous determination, the enhanced anodic peak currents represented an excellent analytical performance with low limit of detection of 0.025  $\mu\text{M}$  for sunset yellow and 0.01  $\mu\text{M}$  for tartrazine [8]. Deng and coworkers produced electro-reduced gold nanorods decorated graphene oxide (ERGO-AuNRs) modified electrode for the detection of tartrazine and sunset yellow which showed a wide linear response with the detection limit of 8.6 nM and 2.4 nM, respectively [71]. Other electrochemical sensors based on GO that were developed involved separate determination tartrazine and sunset yellow. Quanguo He and his colleagues produced Copper Oxide-electrochemically reduced GO ( $\text{Cu}_2\text{O}$ -ErGO) nanocomposites glassy carbon modified electrode for sensitive determination of sunset yellow. The  $\text{Cu}_2\text{O}$ -ErGO modified electrode anodic peak current increased for about 25 times compared to a bare GCE. A lower limit of detection of about  $6.0 \times 10^{-9}$  mol/L was obtained and made the  $\text{Cu}_2\text{O}$ -ErGO/GCE to be better than the existing metal-based modified electrodes [7].

Another reported electrochemical sensor for sunset yellow detection based on Au-Pd and reduced GO nanocomposite modified glass carbon electrode (Au-Pd-RGO/GCE) was developed by Wang and others. This Au-Pd-RGO/GCE exhibited greater electrocatalytic performance with a wide range response of 0.686–331.686 mol/L and a low detection limit of 1.5 nmol/L [72]. A sensitive and selective determination of tartrazine based on  $\text{TiO}_2$ -electrochemically reduced GO composite modified electrode was done by He and colleagues. In their study they showed that the modification increased the electrochemically active area of the electrode and there was a significant enhancement of the electrochemical responses of tartrazine with the detection limit of  $8.0 \times 10^{-9}$  mol/L [73]. For more studies which involve the use of

graphene and graphene like 2D materials (Table 1), summarizes sensing tools already developed by researchers that employ graphene, graphene oxide, reduced graphene and graphitic carbon nitride in determination of concentration of tartrazine, sunset yellow, amaranth, allura red and carmine azo food dyes in foods and drinks.

On the other hand graphitic carbon nitride application in detection of these dyes, has been shown by some studies and yet more attention needs to be paid on the use of  $\text{g-C}_3\text{N}_4$  in developing sensors for food dyes detection because it has shown a great promise in the detection of other materials. Karimi and colleagues managed to develop a sensitive sensor for tartrazine ( $\text{g-C}_3\text{N}_4$ /graphite pencil electrode). The  $\text{g-C}_3\text{N}_4$  was prepared from direct pyrolysis of the melamine without modification then used to modify the graphitic pencil electrode hence increased the rate of the electron transfer for the reduction reaction of tartrazine. The voltammetric techniques used was cyclic voltammetry (CV) and differential pulse voltammetry (DPV). DPV results indicated that the sensor was linear to the concentration of tartrazine in dynamic range of  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-5}$  mol/L and the limit of detection was found to be 0.21  $\mu\text{mol/L}$  [74]. The sensor was used in real sample analysis and proved high precision in determining tartrazine trace amounts in saffron fake powder.

## 2.2. Electrochemical detection of toxic chemical substances in the environment

Two-dimensional (2D) nanomaterials including  $\text{g-C}_3\text{N}_4$  are promising in developing sensors for monitoring environmental pollutants due to their special physical and chemical behaviors [81]. Heavy metals, inorganic/organic compounds, toxic gases, pesticides, antibiotics and other harmful chemical residues cause environmental pollution worldwide which poses a threat to human health and natural environment [82,83]. Hazardous

**Table 1**  
Analytical techniques involving the use of Graphene, graphene derivatives and graphene like 2D materials graphitic carbon nitride in detection of azo dyes; tartrazine, sunset yellow, amaranth, allura red and carmine.

| Food Colorants | Method  | Material/Electrode Used                             | Linear Range   | Limit of Detection          | References |
|----------------|---|---|--|-----------------------------|------------|
| Amaranth       | CV and EIS  | $\text{MnO}_2\text{NRs-ErGO /GCE}$                  | 0.02–10 $\mu\text{M}$ ,<br>10–400 $\mu\text{M}$                                    | 1.0 nM                      | [75]       |
| Sunset Yellow  | EIS   | GO/MWCNTs   | 0.09–8.0 $\mu\text{M}$ ,   | 0.025 $\mu\text{M}$         | [8]        |
| Tartrazine     | EIS   | GO/MWCNTs   | 0.09–8.0 $\mu\text{M}$ ,   | 0.01 $\mu\text{M}$          |            |
| Sunset Yellow  | CV and second-derivative linear sweep voltammetry | $\text{Cu}_2\text{O-ErGO/GCE}$                      | $2.0 \times 10^{-8}$ mol/L– $2.0 \times 10^{-5}$ mol/L                             | $6.0 \times 10^{-9}$ mol/L  | [7]        |
| Amaranth       | SWV   | CNT/GO-IL/GCE                                       | $2.0 \times 10^{-5}$ – $1.0 \times 10^{-4}$ mol/L                                  | 0.1 nM.                     | [76]       |
| Sunset Yellow  | CV  | Au/RGO/GCE  | $5.0 \times 10^{-10}$ – $4.0 \times 10^{-6}$ M                                     | 2 nM                        | [65]       |
| Tartrazine     | CV and second-derivative linear scan voltammetry  | $\text{TiO}_2\text{-ErGO-GCE}$                      | 0.002–109.14 $\mu\text{M}$ ,<br>$2.0 \times 10^{-8}$ – $2.0 \times 10^{-5}$ mol/L, | $8.0 \times 10^{-9}$ mol/L  | [73]       |
| Sunset Yellow  | CV  | ERGO-AuNRs  | 0.01–3.0 $\mu\text{M}$   | 2.4 nM                      | [71]       |
| Tartrazine     | CV  | ERGO-AuNRs  | 0.03–6.0 $\mu\text{M}$   | 8.6 nM                      |            |
| Sunset Yellow  | CV and DPV  | Au-Pd-RGO/GCE                                       | 0.686–331.686 $\mu\text{M}$  | 1.5 nM,                     | [72]       |
| Amaranth       | DPV   | $\text{Fe}_3\text{O}_4/\text{rGO}$                  | 0.05–50 $\mu\text{M}$  | 50 nM                       | [77]       |
| Sunset Yellow  | CV  | CTAB-GO/MWNT/GCE                                    | $1 \times 10^{-7}$ – $2 \times 10^{-5}$ M  | $1 \times 10^{-8}$ M        | [4]        |
| Tartrazine     | CV  | CTAB-GO/MWNT/GCE                                    | $3 \times 10^{-8}$ – $6 \times 10^{-7}$ M  | $5 \times 10^{-9}$ M        |            |
| Sunset Yellow  | CV  | ILRGO-Au/GCE  | $4.0 \times 10^{-9}$ – $1.0 \times 10^{-6}$ M                                      | $5.2 \times 10^{-10}$ M     | [66]       |
| Tartrazine     | CV  | ILRGO-Au/GCE  | $7.0 \times 10^{-9}$ – $1.5 \times 10^{-6}$ M                                      | $8.3 \times 10^{-10}$ M     |            |
| Allura red     | CV  | IL-GO-MWCNT-GCE                                     | $8.0 \times 10^{-10}$ – $5.0 \times 10^{-7}$ mol/L                                 | $5.0 \times 10^{-10}$ mol/L | [78]       |
|                | SWSV  |   | $5.0 \times 10^{-9}$ – $4.5 \times 10^{-7}$ mol/L                                  | $3.0 \times 10^{-9}$ mol/L  |            |
| Tartrazine     | CV  | IL-GO-MWCNT/GCE                                     | $1.0 \times 10^{-8}$ – $1.0 \times 10^{-6}$ mol/L                                  | $7.0 \times 10^{-9}$ mol/L  |            |
|                | SWSV  |   | $2.0 \times 10^{-8}$ – $1.3 \times 10^{-7}$ mol/L                                  | $1.0 \times 10^{-8}$ mol/L  |            |
| Allura red     | SWV   | IRGO/Au/GCE   | 0.0006–0.2 $\mu\text{mol/L}$   | 0.00043 $\mu\text{mol/L}$   | [79]       |
| Tartrazine     | CV and DPV  | $\text{g-C}_3\text{N}_4$ /graphite pencil electrode | $1.0 \times 10^{-7}$ – $1.0 \times 10^{-5}$ mol/L                                  | 0.21 $\mu\text{mol/L}$      | [74]       |
| Allura red     | CV and DPV  | PDDA-Gr-Ni/GCE                                      | 0.05–10.0 $\mu\text{mol/L}$  | 8.0 nmol/L                  | [80]       |

materials in the environment for instance in air, soil and water need to be monitored to safeguard the public and environment. Generally, different analytical techniques have been developed for assessing these chemical substances. These include conventional ones such as HPLC [84], and novel recent different electrochemical ones such as PEC [10,85,86] and ECL [87,88] sensors just to highlight a few, which apply nanomaterials to improve sensitivity, selectivity as well as reducing cost and time needed. In addition, different world regulatory authorities have set the maximum limits of some substances. For the case of pesticides the Council of the European Union set the total maximum admissible concentration of pesticides to be 0.5  $\mu\text{g/L}$  [89]. The World Health Organization (WHO) established limit levels of metal ions. To mention a few heavy metals such as  $\text{Pb}^{+2}$  10 ppb,  $\text{Hg}^{+2}$  6 ppb and  $\text{Cu}^{+2}$  2000 ppb for drinking water.

### 2.2.1. Detection of antibiotic drug residues in the environment

Antibiotics in the environment can find their way in water sources and food through the soil when they are used or disposed incorrectly. In the environment they can also interfere with the ecosystem. When human become exposed, they can get health problems such as hypersensitivity, disturbance of normal flora in the human body and development of resistant bacteria which can become hard to treat. Some sensors have been developed in the detection of environmental antibiotics.

Li and coworkers developed a photoelectrochemical aptamer sensor for kanamycin detection based on GO/water-dispersible graphite-like carbon nitride ( $\text{GO/w-g-C}_3\text{N}_4$ ) metal-free nanocomposites. F-doped  $\text{SnO}_2$  (FTO) was modified by the  $\text{GO/w-g-C}_3\text{N}_4$ . Water-dispersible graphite-like carbon nitride ( $\text{w-g-C}_3\text{N}_4$ ) and aptamer were used as visible light-active material and biorecognition element respectively. The doping of GO not only enhanced the response but also provided a platform for immobilizing the kanamycin binding DNA aptamer on the surface of the sensor via  $\pi$ - $\pi$  stacking interaction. Fig. 3 illustrates on the fabrication of the FTO electrode with  $\text{GO/w-g-C}_3\text{N}_4$  and selective identification of kanamycin by aptamer schematically. The resulting sensor showed good response from the  $\text{GO/w-g-C}_3\text{N}_4$  hybrid which was observed to be linearly proportional to the concentration of kanamycin in the range from 1 nM to 230 nM and LOD was 0.2 nM. This study exhibited promising output in the  $\text{w-g-C}_3\text{N}_4$  further application in aptamer sensors [10].

Furthermore, in antibiotic detection is a study by Jiang and coworkers in this year 2019 [90]. They have developed a novel sensitive PEC sensor for the detection of chloramphenicol (CAP) antibiotic in honeycomb samples with support of aptamer. By using facile one-pot hydrothermal route, they fabricated  $\text{MoS}_2/\text{nitrogen doped graphene hydrogels (MoS}_2/\text{NGH)}$  p-n heterojunction. The construction of the p-n heterojunction led to an improved photocurrent intensity by the fast transfer and separation rate of photogenerated electron-hole, in turn a good PEC response was revealed by the  $\text{MoS}_2/\text{NGH}$  heterojunction. This novel sensor not only indicated wide linearity in the concentration range from 32.3 ng/L to 96.9 ng/L but also a low detection limit of 3.23 ng/L. In testing real honey samples, the sensor produced promising results for its application.

Another recent study among many on antibiotic detection [91], involved the use of simple electrostatic interaction strategy to design and produce a p-n heterojunction based on p-type  $\text{BiFeO}_3$  nanoparticles coupled n-typed ultrathin  $\text{g-C}_3\text{N}_4$  nanosheets ( $\text{BiFeO}_3/\text{utg-C}_3\text{N}_4$ ). This heterojunction was advantageous due to the ability of narrowing photoactive materials band gap which improved visible light utilization as well as facilitation of the charge separation rate which boosted PEC performance of  $\text{BiFeO}_3/\text{utg-C}_3\text{N}_4$ . An on-off PEC aptasensor was produced which proved to be highly sensitive and selective towards ampicillin (AMP) determination owing to the superior PEC properties of  $\text{BiFeO}_3/\text{utg-C}_3\text{N}_4$ . The resulted PEC aptasensor showed not only excellent response with a wide linearity ranging from  $1 \times 10^{-12}$  mol/L to  $1 \times 10^{-6}$  mol/L but also low LOD of  $3.3 \times 10^{-13}$  mol/L. The sensor was tested in real samples and exhibited good feasibility in analysis of ampicillin from food and environment samples. Other novel recent electrochemical sensors involving different techniques such as PEC [92], ECL [93] and fluorescent [94] which employ graphene and graphene like 2D materials have been produced for rapid, simple selective and sensitive determination of antibiotics.

### 2.2.2. Detection of metal ions in the environment

Graphene, graphene derivatives and graphene like 2D  $\text{g-C}_3\text{N}_4$  materials have been utilized in designing sensors for metal ions determination in different samples. Sahoo and co-researchers used reduced graphene oxide/Bi (rGO/Bi) nanocomposites to create a sensor for the detection of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  heavy metal ions. Employing ASV electrochemical technique the results were reported to be 26  $\mu\text{g/L}$ , 17  $\mu\text{g/L}$ , 0.55  $\mu\text{g/L}$ , and 2.8  $\mu\text{g/L}$  for  $\text{Cu}^{2+}$ .

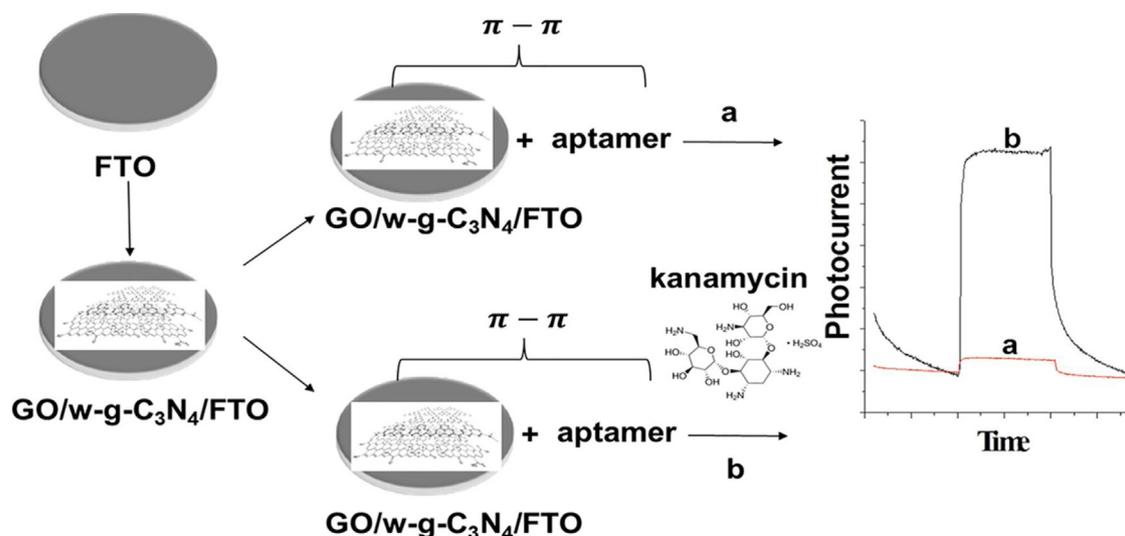


Fig. 3. A Schematic Illustration of Photo Electrochemical Aptasensing Principle Using the on graphene oxide water-dispersible graphite-like carbon nitride F-doped  $\text{SnO}_2$  ( $\text{GO/w-g-C}_3\text{N}_4/\text{FTO}$ ) Electrode [10].

Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> respectively. The detection range was 20–120 mg/L. In testing real samples the sensor exhibited a good response in the determination of Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> levels in ground and lake water. The reported sensor shed new insights in the use of rGO/Bi nanocomposites in ultrasensitive detection of heavy metals, furthermore, on the application in on-site environmental and clinical testing of heavy metals [95].

Other studies have employed the electrochemiluminescent, photoelectrochemical, fluorescent and catalytic properties of g-C<sub>3</sub>N<sub>4</sub> in developing sensors for metal ions detection in the environment. Sadhukhan and Barman modified glassy carbon electrode using g-C<sub>3</sub>N<sub>4</sub> which resulted into an electrochemical sensor for Hg<sup>2+</sup> detection in aqueous solution. The lower detection limit of Hg<sup>2+</sup> was reported to be  $9.1 \times 10^{-11}$  M, which is below the WHO guideline for drinking water ( $10^{-8}$  M). Using the same modified electrode a simultaneous electrochemical detection of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup> was done. The peak currents decreased linearly with metal ions decreased concentration. The LOD was calculated from the calibration curves and found to be  $7 \times 10^{-8}$  M for both Cu<sup>2+</sup> and Pb<sup>2+</sup> [96]. Moreover, in metal ion detection, ECL Behavior of g-C<sub>3</sub>N<sub>4</sub>, with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as the co-reactant and the quenching property of Cu<sup>2+</sup> was used to develop an ECL sensor which showed high selectivity to Cu<sup>2+</sup> determination. The spectral emission of ECL and PL were compared and matched, hence electroexcitation and photoexcitation process produced the same excited states of g-C<sub>3</sub>N<sub>4</sub>. See Fig. 4 below. This sensor exhibited a good response and a linear range of detection being 2.5 to 100 nM with the detection limit of 0.9 nM [87]. Furthermore, the sensor was tested in real samples and it was able to determine the concentration of Cu<sup>2+</sup> in a waste water which was obtained from a local factory. This study provided a less expensive, simple fabrication process for ECL sensor and showed the usability of g-C<sub>3</sub>N<sub>4</sub> ECL properties.

A more sensitive ECL sensor was developed using graphitic carbon nitride/graphene oxide (g-C<sub>3</sub>N<sub>4</sub>/GO) hybrid for ultrasensitive detection of Cu<sup>2+</sup>. GO in this sensor served dual purposes which are enhancing the cathodic ECL signal of g-C<sub>3</sub>N<sub>4</sub> which was approximately 3.8 times and as an immobilization platform for g-C<sub>3</sub>N<sub>4</sub>. The LOD was  $1.0 \times 10^{-11}$  M. The sensor was used to test wastewater samples and exhibited high sensitivity and selectivity [9]. Some other studies on the use of g-C<sub>3</sub>N<sub>4</sub> in the detection of Cu<sup>2+</sup> using different techniques such as fluorescence [41] and photoelectrochemical [53,97] have been done.

Furthermore, discussion on other metal ions detection in different samples, is on a recent study by Ding and co researchers [98]. The aim of the study was producing a sensor for electrochemical determination of Cd<sup>2+</sup> and Pb<sup>2+</sup> individually and simultaneously. In situ chemical polymerization method was used

to prepare poly(2,5-bis(3,4-ethylenedioxythienyl)pyridine)/g-C<sub>3</sub>N<sub>4</sub> (poly(BPE)/g-C<sub>3</sub>N<sub>4</sub>) composites. Then GCE electrode was modified using 10 wt % poly(BPE)/g-C<sub>3</sub>N<sub>4</sub> composite. It was reported that the 10 wt % poly(BPE)/g-C<sub>3</sub>N<sub>4</sub> modified electrode showed wide linearity response and lower detection limit not only in individual concentration determination of Cd<sup>2+</sup> and Pb<sup>2+</sup> but also in the simultaneous concentration determination, Table 2. The response observed is due to the highly ordered tris-triazine structure of g-C<sub>3</sub>N<sub>4</sub> which facilitated the intercalation of metal ions into the g-C<sub>3</sub>N<sub>4</sub> through the nitrogen lone pair electrons. Moreover, the synergistic effect of poly(BPE) and g-C<sub>3</sub>N<sub>4</sub> increased the electrode surface conduction pathway as well as improved the adsorption of metal ions by producing a strong conjugate effect on them. The developed sensor was reported to be feasible in concentration determination of the Cd<sup>2+</sup> and Pb<sup>2+</sup> in real samples.

More recent studies on lead [99,100] and other metals such as mercury, cadmium, zinc [101] and silver [102] have been done. These studies reported sensors which proved to be sensitive and selective in the detection of these toxic metal ions and could be applied in monitoring their concentration in different samples.

### 2.2.3. Detection of pesticides residues in the environment

Pesticides are usually used in agriculture to combat diseases, however their residues can be very harmful to human health and animal safety due to their high biological activity and inherent toxicity. Examples of pesticides commonly used in agriculture include organophosphate pesticides, pentachlorophenol (OP), pymetrozine, thidiazuron, diuron, carbofuran, carbaryl, pirimicarb, diethofencarb, procymidone, folpet, vinclozolin and ditalimfos. When organophosphate pesticides are used improperly or excessively they can slowly enter the food chain and also contaminate water sources [103–105]. The Council of the European Union set the total maximum admissible concentration of pesticides to be 0.5 µg/L [89]. In the determination of these chemicals different conventional methods have been used though they have disadvantages such as time-consuming. The methods include thin layer chromatography [106], chromatography-mass spectrometry [107] and high performance liquid chromatography (HPLC) [84].

Recently, a high demand for rapid and field analytical methods such as electrochemical sensors are being developed to substitute the conventional ones. Sensors employing the use of GO have been developed for pesticides determination. Zhao and co-researchers [108] produced an ultra-sensitive amperometric organophosphate biosensor using electrochemically reduced graphene oxide (ER-GO)-gold nanoparticles (AuNPs)-β-cyclodextrin (β-CD) and Prussian blue-chitosan (PB-CS) electrodeposited on a GCE, fabricated

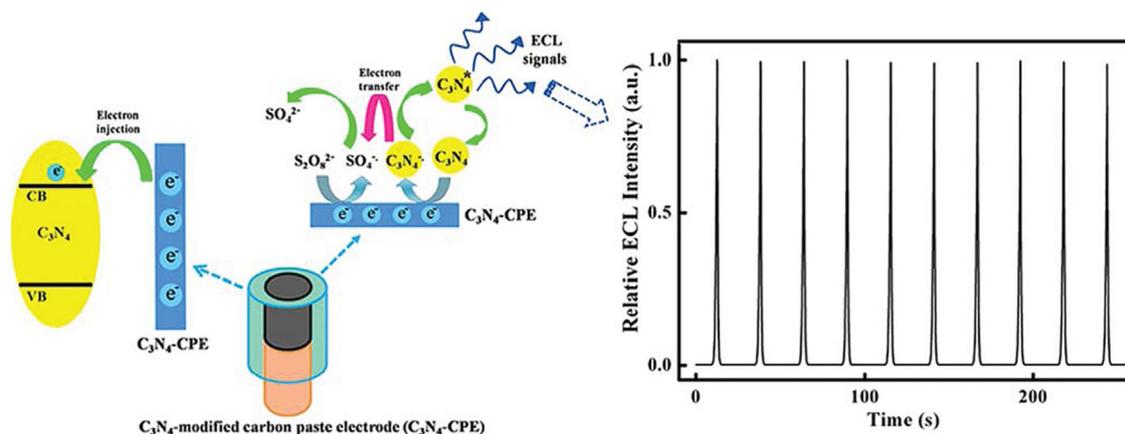


Fig. 4. ECL property of g-C<sub>3</sub>N<sub>4</sub> determination of trace amount of copper [87].

**Table 2**Pb<sup>2+</sup> and Cd<sup>2+</sup> simultaneous and individual concentration determination observations using 10 wt % poly(BPE)/g-C<sub>3</sub>N<sub>4</sub> composite.

| Material   | Electrochemical Technique            | Analyte          | Types of concentration determination | Concentration linear range | Limit of Detection |
|--|--------------------------------------|------------------|--------------------------------------|----------------------------|--------------------|
| Poly(2,5-bis(3,4-ethylenedioxythienyl)pyridine)/g-C <sub>3</sub> N <sub>4</sub> Composites | Differential Pulse Voltammetry (DPV) | Pb <sup>2+</sup> | Simultaneous                         | 0.08–7.2                   | 0.00324            |
|  |                                      | Cd <sup>2+</sup> | Simultaneous                         | 0.12–7.2                   | 0.018              |
|  |                                      | Pb <sup>2+</sup> | Individual                           | 0.1–6.4                    | 0.00327            |
|  |                                      | Cd <sup>2+</sup> | Individual                           | 0.1–6.8                    | 0.0097             |

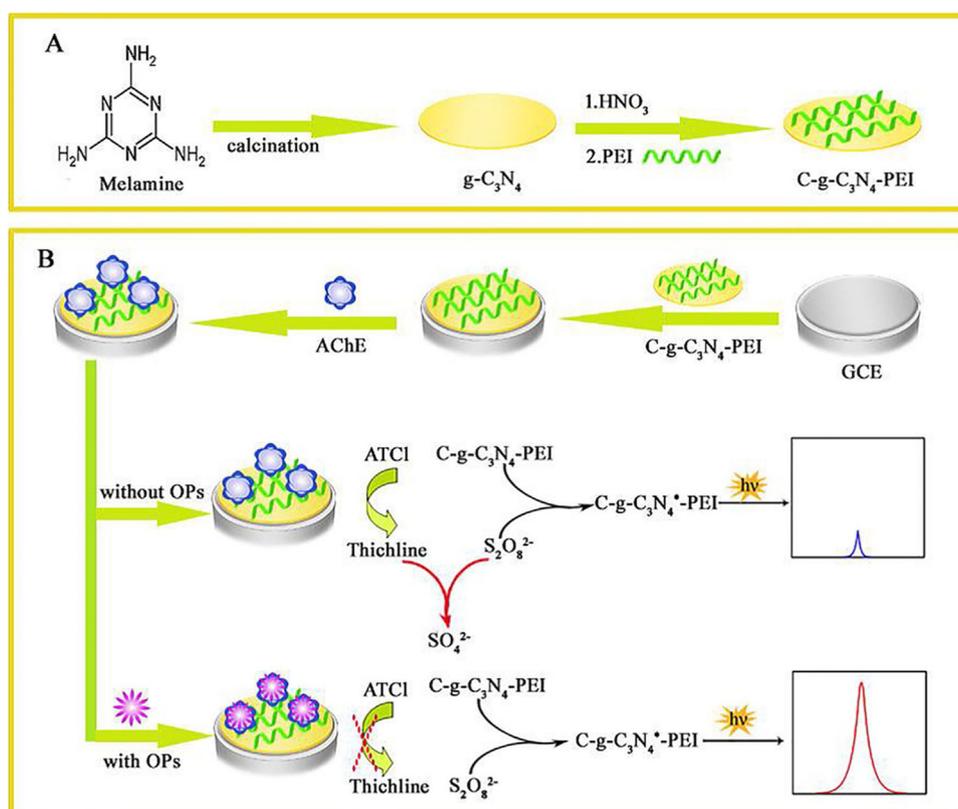
with acetylcholinesterase (AChE). This sensor exhibited selectivity, sensitivity, stability and a good response, with wide linear ranges of  $7.98\text{--}2.00 \times 10^3$  pg/mL and  $4.3\text{--}1.00 \times 10^3$  pg/mL and low detection limits of 4.14 pg/mL and 1.15 pg/mL for malathion and carbaryl respectively, hence can be used in real sample detection. More AChE biosensors for OP pesticides employing the use of GO were reported by Liu [11] and Wu [109] and their co-workers. All the sensors showed applicability in real sample analysis.

More recent studies on Graphene and Graphene like sensors include, a facile electrochemical acetylcholinesterase (AChE) biosensor based on nafion (NA) and Silver (Ag) nanoparticles together with amine functionalized reduced graphene oxide (rGO-NH<sub>2</sub>) [110]. The biosensor NA/Ag-rGO-NH<sub>2</sub>/AChE/GCE proved to be sensitive, stable with good repeatability. It was used to detect malation, methidathion, and chlorpyrifos ethyl with a wide linear range from 0.0063 to 0.077 mg/mL, 0.012 to 0.105 mg/mL, and 0.021 to 0.122 mg/mL, respectively. The LOD were 4.5 ng/mL, 9.5 ng/mL and 14 ng/mL for malation, methidathion, chlorpyrifos ethyl respectively. In the end, the applicability of the biosensor was tested in different tap water samples with different concentration of malation, methidathion and chlorpyrifos ethyl.

A more sensitive Ag-rGO-NH<sub>2</sub>/AChE biosensor was developed by Zhang and others in 2019 [111]. They developed an

amperometric AChE-biosensor using conjugated polymer (furan-2-yl) benzo thiazazole (FBThF) and Ag-rGO-NH<sub>2</sub> nanocomposites. Due to the combined effect of FBThF which was polymerized electrochemically and Ag-rGO-NH<sub>2</sub> which was modified on the membrane surface of the polymer there by providing adhesion for AChE, the resulted novel biosensor exhibited superior catalytic activity and conductivity, as well as excellent biocompatibility. This is shown by the wide linear range of 0.099–9.9 μg/L for malathion, 0.0206–2.06 μg/L for trichlorfon with low LOD of 0.032 μg/L and 0.001 μg/L for malathion and trichlorfon respectively. This sensor is reliable as it was assessed in detection of malathion and trichlorfon in tap water and apple samples, and the results indicated that the biosensor is feasible real sample.

Moreover, non-AChE sensors for pesticides have also been developed. In 2018, Olevoira et al. [112] produced a reduced graphene oxide and b-cyclodextrin (GCE/rGO/b-CD) GCE modified sensor for detection of neonicotinoid insecticides, imidacloprid (IMP), clothianidin (CLT) and thiamethoxam (TMX), in honey, wax and pollen samples. However the sensor exhibited more effectiveness in the determination of neonicotinoid (TMX, CLT and IMP) insecticides in honey samples. The sensor proved to have high sensitivity and conductivity due to the hybrid effect of the high electrical conductivity of the rGO and the inclusion properties



**Fig. 5.** Schematic description of (A) the preparation process of graphitic carbon nitride-poly (ethylenimine) (C-g-C<sub>3</sub>N<sub>4</sub>-PEI), (B) the fabrication of modified biosensor and response mechanism [115].

of b-CD. The LOD for the, IMP, CLT and TMX observed were 8.92  $\mu\text{mol/L}$ , 4.72  $\mu\text{mol/L}$  and 7.45  $\mu\text{mol/L}$  respectively. The sensor is simple to apply in real sample neonicotinoid determination and was tested in honey sample. The results showed that the sensor is sensitive, simple, rapid and can be used as an alternative in detection of neonicotinoid.

To add up on more non AChE biosensors for pesticides determination, another graphene and graphene like material involving biosensor was developed by Islam et al. 2019 [113]. Graphene field effect transistors (graFET) was fabricated on Si/SiO<sub>2</sub> substrate for the detection of chlorpyrifos. Immobilization of anti-chlorpyrifos antibodies on the graphene surface was achieved. The resulted graFET immunosensor indicated good response with a wide linear range of 1 fM to 1  $\mu\text{M}$  in detecting chlorpyrifos with a very low LOD being 1.8 fM in spiked samples. This study provide promising application of the biosensor in determining the concentration of the organophosphates in agricultural products.

Another non-AChE biosensor is a (Forster Resonance Energy Transfer) FRET GO based aptasensor for diazinon which signified the applicability of using aptamers in developing biosensors for pesticides monitoring [114].

Graphene like 2D material g-C<sub>3</sub>N<sub>4</sub> in electrochemical sensing of pesticides has been successfully applied. For example, Wang and co-workers constructed an ultrasensitive ECL biosensor detection based on carboxylated graphitic carbon nitride-poly(ethylenimine) (C-g-C<sub>3</sub>N<sub>4</sub>-PEI) and acetylcholinesterase (AChE) for the determination of OP [115]. In this study ethyl paraoxon was used as a model OP. Covalent bonding between the carboxyl group of C-g-C<sub>3</sub>N<sub>4</sub> and the amine group of PEI resulted in C-g-C<sub>3</sub>N<sub>4</sub>-PEI nanocomposite, Fig. 5(A) shows this bond graphically. The co-reactant of C-g-C<sub>3</sub>N<sub>4</sub>-PEI was K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Hydrolysis of acetylthiocholine (ATCI) under the action of AChE *in situ* produces thiocholine. On the surface of electrode thiocholine consume coreactant K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Due to the fact that organophosphates are AChE inhibitors, the inhibition action of OP on AChE hinders the generation of thiocholine hence reduced consumption of co-reactants, Fig. 5(B) shows schematic representation. This resulted in an increased ECL response. This biosensor applying ECL property of g-C<sub>3</sub>N<sub>4</sub> showed high sensitivity with a wide linear range of 1.0 pM to 5.0  $\mu\text{M}$  and a low detection limit of 0.3 pM. The study paved a way for rapid, simple and sensitive determination of pesticides. In addition, Xia and co-workers produced a sensor using one-step electrochemical reduction technology. They developed an advanced ECL sensor using hybrid g-C<sub>3</sub>N<sub>4</sub>/GR for pentachlorophenol (PCP) detection. The proposed sensor exhibited ultrasensitivity and rapid detection of PCP with low limit of detection being  $1.0 \times 10^{-11}$  mol/L with a wide linear range from  $1.0 \times 10^{-11}$  to  $1.0 \times 10^{-7}$  mol/L [88]. This platform for sensing was tested in the real water sample and showed ideal recovery rates. Their study gives promise in more exploration on the use of GR and g-C<sub>3</sub>N<sub>4</sub> ECL ability in developing sensors for environmental monitoring of pesticides and other related analyses.

### 2.3. Development tendency of electrochemical sensing platforms for contaminants

For a decade now, it can be observed that there is a sharp rise of studies reported on developing graphene and graphene like material based electrochemical sensors for determination of contaminants such as food colorants, metal ions as well as pesticides and antibiotic residues in food product, pharmaceutical products, agricultural products and environment at large. This is due to the fascinating unique physical and chemical properties of these 2D materials. The growth of this hot research area is attributed by day to day development in new nanomaterial synthesis methods from its bulky state or elements to useful one.

For example in 2004, the first synthesis of graphene using mechanical exfoliation is observed. Since then scientists have been able to synthesize graphene and graphene like 2D nanomaterials such as GO, rGO, ERGO, NRGO and g-C<sub>3</sub>N<sub>4</sub>. Till to date, novel advanced methods such as thermal oxidation exfoliation, ultrasonic exfoliation and chemical exfoliation for producing ultrathin 2D graphene like materials have been discovered.

Moreover, the understanding of g-C<sub>3</sub>N<sub>4</sub> properties has increased the horizon of the material application in development of excellent sensing platforms. Many studies have reported as discussed in this report, the feasibility of applying g-C<sub>3</sub>N<sub>4</sub> ECL, PEC, PL, fluorescent and catalytic properties in sensing different contaminants.

Furthermore, graphene and graphene like materials have been combined with other functional nanomaterials to increase conductivity, selectivity, sensitivity and produce novel sensing platforms which are reliable with enhanced performance. One of the combination is with metals such as Ag, Au, Cu<sub>2</sub>O, Fe<sub>3</sub>O<sub>4</sub> and TMDs (e.g MoS, MnO<sub>2</sub>). Another hybrid is with biomolecules such as enzymes, antibodies and aptamers which are used for increasing the recognition ability and signal amplifying of the target material. In addition the graphene like materials can be combined themselves for instance g-C<sub>3</sub>N<sub>4</sub>/GO to enhance the performance activity of the target sensing platform.

However, the above development in the electrochemical sensor for contaminants still needs to grow further. One of the area is on the direct detection of contaminants from the sample. Some samples need pretreatment before being analyzed to avoid non target sample materials to prevent the effectiveness of the sensor. This aspect need novel sensing platforms which can directly be used to test the target analyte without going through the sample pretreatment process. Another aspect is ultrasensitive sensors. Many sensitive sensors have been developed, however there are fewer ultrasensitive sensors developed for determining the ultra-trace concentration of some contaminants, especially in the environment. It is still a challenge in the efficient immobilization of biomolecules on the surfaces of graphene and graphene like materials, hence, more studies should be done to produce robust sensing platforms with improved recognition ability and enhanced detection sensitivity. Another side is on the approach for synthesis of the nanomaterials. In the process of synthesizing the nanomaterials for constructing a novel sensing platform, different materials are needed. Novel synthesis approaches need to utilize environmental friendly materials to come up with green robust sensing platforms.

Graphene and graphene like materials research is still in its initial stage, there is still a huge space for understanding the graphene like nanomaterial properties, green synthesis approaches, functionalization, fabrication and application in construction of green robust sensing platforms.

### 3. Conclusion

Since its discovery in 2004, graphene has shown to be a very interesting and useful material in development of electrochemical sensors. Also its derivatives graphene oxide and reduced graphene oxide have shown great promise in determination of different substance concentrations such as tartrazine, amaranth, allura red, carmine and sunset yellow food dyes, metal ions, pesticide and antimicrobial residues in the environment. Moreover, greater promise has been exhibited by the metal free graphene like 2D material graphitic carbon nitride. Extraordinary properties of graphitic carbon nitride make the material to have a wider application range. More understanding of its properties and application is still needed in the area of food colorants detection, different metal ions determination, pesticides and antimicrobial

residues detection in the environment. Furthermore, the designing of sensors that are selective and which can perform simultaneous detection of dual existing molecules is important. In addition the combination of graphene, graphene oxide, reduced graphene oxide, graphitic carbon and other functional nanomaterial in designing and developing sensors have shown promising results in the sensitivity and selectivity of the developed analytical tools hence more exploration should be done.

### Conflicts of interest

The authors declare no conflict of interest.

### Acknowledgments

This work was supported by the NSFC (61703152), Hunan Provincial Natural Science Foundation (2016JJ4010, 2018JJ3134), Doctoral Program Construction of Hunan University of Technology, Project of Science and Technology Department of Hunan Province (18A273, 18C0522), Project of Science and Technology Plan in Zhuzhou (201706-201806) and Opening Project of Key Discipline of Materials Science in Guangdong (ESI Project GS06021, CNXY2017001, CNXY2017002 and CNXY2017003), The key Project of Department of Education of Guangdong Province (2016GCCX008) and The Project of Engineering Research Center of Foshan (20172010018).

### References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films, *Science* (New York, NY) 306 (5696) (2004) 666–669.
- [2] A.K. Geim, K.S. Novoselov, The rise of graphene, *Nat. Mater.* 6 (3) (2007) 183–191.
- [3] K.S. Novoselov, V.I. Fal'ko, L. Colombo, P.R. Gellert, M.G. Schwab, K. Kim, A roadmap for graphene, *Nature* 490 (7419) (2012) 192–200.
- [4] Y.J. Yang, W. Li, CTAB functionalized graphene oxide/multiwalled carbon nanotube composite modified electrode for the simultaneous determination of ascorbic acid, dopamine, uric acid and nitrite, *Biosens. Bioelectron.* 56 (2014) 300–306.
- [5] Q. He, J. Liu, X. Liu, G. Li, D. Chen, P. Deng, J. Liang, Fabrication of amine-modified magnetite-electrochemically reduced graphene oxide nanocomposite modified glassy carbon electrode for sensitive dopamine determination, *Nanomaterials* 8 (4) (2018) 194.
- [6] Q. He, Y. Wu, Y. Tian, G. Li, J. Liu, P. Deng, D. Chen, Facile electrochemical sensor for nanomolar rutin detection based on magnetite nanoparticles and reduced graphene oxide decorated electrode, *Nanomaterials* 9 (1) (2019) 115.
- [7] Q. He, J. Liu, X. Liu, Y. Xia, G. Li, P. Deng, D. Chen, Novel electrochemical sensors based on cuprous oxide-electrochemically reduced graphene oxide nanocomposites modified electrode toward sensitive detection of sunset yellow, *Molecules* 23 (9) (2018) 2130.
- [8] X. Qiu, L. Lu, J. Leng, Y. Yu, W. Wang, M. Jiang, L. Bai, An enhanced electrochemical platform based on graphene oxide and multi-walled carbon nanotubes nanocomposite for sensitive determination of Sunset Yellow and Tartrazine, *Food Chem.* 190 (2016) 889–895.
- [9] B. Xia, M. Chu, S. Wang, W. Wang, S. Yang, C. Liu, S. Luo, Graphene oxide amplified electrochemiluminescence of graphitic carbon nitride and its application in ultrasensitive sensing for Cu<sup>2+</sup>, *Anal. Chim. Acta* 891 (2015) 113–119.
- [10] R. Li, Y. Liu, L. Cheng, C. Yang, J. Zhang, Photoelectrochemical aptasensing of kanamycin using visible light-activated carbon nitride and graphene oxide nanocomposites, *Anal. Chem.* 86 (19) (2014) 9372–9375.
- [11] T. Liu, H. Su, X. Qu, P. Ju, L. Cui, S. Ai, Acetylcholinesterase biosensor based on 3-carboxyphenylboronic acid/reduced graphene oxide-gold nanocomposites modified electrode for amperometric detection of organophosphorus and carbamate pesticides, *Sens. Actuators B Chem.* 160 (1) (2011) 1255–1261.
- [12] Q. He, Y. Tian, Y. Wu, J. Liu, G. Li, P. Deng, D. Chen, Facile and ultrasensitive determination of 4-nitrophenol based on acetylene black paste and graphene hybrid electrode, *Nanomaterials* 9 (3) (2019) 429.
- [13] J.N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, U. Khan, K. Young, A. Gaucher, S. De, R.J. Smith, Two-dimensional nanosheets produced by liquid exfoliation of layered materials, *Science* (New York, NY) 331 (6017) (2011) 568–571.
- [14] C. Zhu, D. Du, Y. Lin, Graphene and graphene-like 2D materials for optical biosensing and bioimaging: a review, *2D Mater.* 2 (3) (2015) 032004.
- [15] D. Chen, W. Chen, L. Ma, G. Ji, K. Chang, J.Y. Lee, Graphene-like layered metal dichalcogenide/graphene composites: synthesis and applications in energy storage and conversion, *Mater. Today* 17 (4) (2014) 184–193.
- [16] Q. Qu, S. Yang, X. Feng, 2d sandwich-like sheets of iron oxide grown on graphene as high energy anode material for supercapacitors, *Adv. Mater.* 23 (46) (2011) 5574–5580.
- [17] H. Wang, H. Feng, J. Li, Graphene and graphene-like layered transition metal dichalcogenides in energy conversion and storage, *Small* 10 (11) (2014) 2165–2181.
- [18] Q. Tang, Z. Zhou, Z. Chen, Innovation and discovery of graphene-like materials via density-functional theory computations, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 5 (5) (2015) 360–379.
- [19] A. Gupta, T. Sakthivel, S. Seal, Recent development in 2D materials beyond graphene, *Prog. Mater. Sci.* 73 (2015) 44–126.
- [20] Jv Liebig, About some nitrogen compounds, *Ann. Pharm.* 10 (10) (1834).
- [21] A.Y. Liu, M.L. Cohen, Prediction of new low compressibility solids, *Science* (New York, NY) 245 (4920) (1989) 841–842.
- [22] N. Cheng, P. Jiang, Q. Liu, J. Tian, A.M. Asiri, X. Sun, Graphitic carbon nitride nanosheets: one-step, high-yield synthesis and application for Cu<sup>2+</sup> detection, *Analyst* 139 (20) (2014) 5065–5068.
- [23] E. Kroke, M. Schwarz, E. Horath-Bordon, P. Kroll, B. Noll, A.D. Norman, Tri-s-triazine derivatives. Part I. From trichloro-tri-s-triazine to graphitic C 3 N 4 structures, *New J. Chem.* 26 (5) (2002) 508–512.
- [24] J. Liu, H. Wang, M. Antonietti, Graphitic carbon nitride “reloaded”: emerging applications beyond (photo) catalysis, *Chem. Soc. Rev.* 45 (8) (2016) 2308–2326.
- [25] X. Gu, R. Yang, First-principles prediction of phononic thermal conductivity of silicene: a comparison with graphene, *J. Appl. Phys.* 117 (2) (2015) 025102.
- [26] H.L. Lee, Z. Sofer, V. Mazánek, J. Luxa, C.K. Chua, M. Pumera, Graphitic carbon nitride: effects of various precursors on the structural, morphological and electrochemical sensing properties, *Appl. Mater.* Today 8 (2017) 150–162.
- [27] S.-N. Ding, J.-J. Xu, H.-Y. Chen, Enhanced solid-state electrochemiluminescence of CdS nanocrystals composited with carbon nanotubes in H<sub>2</sub>O<sub>2</sub> solution, *Chem. Commun.* 34 (2006) 3631–3633.
- [28] C. Zhu, G. Yang, H. Li, D. Du, Y. Lin, Electrochemical sensors and biosensors based on nanomaterials and nanostructures, *Anal. Chem.* 87 (1) (2014) 230–249.
- [29] J. Dong, Y. Zhao, K. Wang, H. Chen, L. Liu, B. Sun, M. Yang, L. Sun, Y. Wang, X. Yu, Fabrication of graphitic carbon nitride quantum dots and their application for simultaneous fluorescence imaging and pH-responsive drug release, *ChemistrySelect* 3 (44) (2018) 12696–12703.
- [30] Y. Zheng, J. Liu, J. Liang, M. Jaroniec, S.Z. Qiao, Graphitic carbon nitride materials: controllable synthesis and applications in fuel cells and photocatalysis, *Energy Environ. Sci.* 5 (5) (2012) 6717–6731.
- [31] H.-Y. Chen, L.-W. Ruan, X. Jiang, L.-G. Qiu, Trace detection of nitro aromatic explosives by highly fluorescent gC<sub>3</sub>N<sub>4</sub> nanosheets, *Analyst* 140 (2) (2015) 637–643.
- [32] X. Fu, J. Feng, X. Tan, Q. Lu, R. Yuan, S. Chen, Electrochemiluminescence sensor for dopamine with a dual molecular recognition strategy based on graphite-like carbon nitride nanosheets/3, 4, 9, 10-perylenetetracarboxylic acid hybrids, *RSC Adv.* 5 (53) (2015) 42698–42704.
- [33] Y. Liu, Q. Wang, J. Lei, Q. Hao, W. Wang, H. Ju, Anodic electrochemiluminescence of graphitic-phase C<sub>3</sub>N<sub>4</sub> nanosheets for sensitive biosensing, *Talanta* 122 (2014) 130–134.
- [34] L. Chen, X. Zeng, A.R. Ferhan, Y. Chi, D.-H. Kim, G. Chen, Signal-on electrochemiluminescent aptasensors based on target controlled permeable films, *Chem. Commun.* 51 (6) (2015) 1035–1038.
- [35] X. Zhang, H. Wang, H. Wang, Q. Zhang, J. Xie, Y. Tian, J. Wang, Y. Xie, Single-layered graphitic-C<sub>3</sub>N<sub>4</sub> quantum dots for two-photon fluorescence imaging of cellular nucleus, *Adv. Mater.* 26 (26) (2014) 4438–4443.
- [36] H. Dai, S. Zhang, Y. Li, Y. Lin, Excellent graphitic carbon nitride nanosheets-based photoelectrochemical platform motivated by Schottky barrier and LSPR effect and its sensing application, *Analyst* 140 (10) (2015) 3514–3520.
- [37] H. Dai, S. Zhang, G. Xu, Y. Peng, L. Gong, X. Li, Y. Li, Y. Lin, G. Chen, Highly photoactive heterojunction based on g-C<sub>3</sub>N<sub>4</sub> nanosheets decorated with dendritic zinc (II) phthalocyanine through axial coordination and its ultrasensitive enzyme-free sensing of choline, *RSC Adv.* 4 (102) (2014) 58226–58230.
- [38] R. Li, Y. Liu, X. Li, S. Zhang, D. Wu, Y. Zhang, Q. Wei, B. Du, A novel multi-amplification photoelectrochemical immunoassay based on copper (II) enhanced polythiophene sensitized graphitic carbon nitride nanosheet, *Biosens. Bioelectron.* 62 (2014) 315–319.
- [39] L. Xu, J. Xia, L. Wang, H. Ji, J. Qian, H. Xu, K. Wang, H. Li, Graphitic carbon nitride nanorods for photoelectrochemical sensing of trace copper (II) ions, *Eur. J. Inorg. Chem.* 2014 (23) (2014) 3665–3673.
- [40] Y. Dong, Q. Wang, H. Wu, Y. Chen, C.H. Lu, Y. Chi, H.H. Yang, Graphitic carbon nitride materials: sensing, imaging and therapy, *Small* 12 (39) (2016) 5376–5393.
- [41] J. Tian, Q. Liu, A.M. Asiri, A.O. Al-Youbi, X. Sun, Ultrathin graphitic carbon nitride nanosheet: a highly efficient fluorosensor for rapid, ultrasensitive detection of Cu<sup>2+</sup>, *Anal. Chem.* 85 (11) (2013) 5595–5599.
- [42] Y. Zhou, L. Tang, X. Xie, G. Zeng, J. Wang, Y. Deng, G. Yang, C. Zhang, Y. Zhang, J. Chen, Sensitive impedimetric biosensor based on duplex-like DNA scaffolds and ordered mesoporous carbon nitride for silver (I) ion detection, *Analyst* 139 (24) (2014) 6529–6535.

- [43] S. Zhang, J. Li, M. Zeng, J. Xu, X. Wang, W. Hu, Polymer nanodots of graphitic carbon nitride as effective fluorescent probes for the detection of Fe<sup>3+</sup> and Cu<sup>2+</sup> ions, *Nanoscale* 6 (8) (2014) 4157–4162.
- [44] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Müller, R. Schlögl, J.M. Carlsson, Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts, *J. Mater. Chem.* 18 (41) (2008) 4893–4908.
- [45] Q. Guo, Y. Xie, X. Wang, S. Lv, T. Hou, X. Liu, Characterization of well-crystallized graphitic carbon nitride nanocrystallites via a benzene-thermal route at low temperatures, *Chem. Phys. Lett.* 380 (1–2) (2003) 84–87.
- [46] H. Montigaud, B. Tanguy, G. Demazeau, I. Alves, S. Courjault, C3N4: dream or reality? Solvothermal synthesis as macroscopic samples of the C3N4 graphitic form, *J. Mater. Sci.* 35 (10) (2000) 2547–2552.
- [47] Y. Gu, L. Chen, L. Shi, J. Ma, Z. Yang, Y. Qian, Synthesis of C<sub>3</sub>N<sub>4</sub> and graphite by reacting cyanuric chloride with calcium cyanamide, *Carbon* 41 (13) (2003) 2674–2676.
- [48] Z. Zhang, K. Leinenweber, M. Bauer, L.A. Garvie, P.F. McMillan, G.H. Wolf, High-pressure bulk synthesis of crystalline C<sub>6</sub>N<sub>9</sub>H<sub>3</sub>·HCl: a novel C<sub>3</sub>N<sub>4</sub> graphitic derivative, *J. Am. Chem. Soc.* 123 (32) (2001) 7788–7796.
- [49] J. Li, C. Cao, H. Zhu, Synthesis and characterization of graphite-like carbon nitride nanobelts and nanotubes, *Nanotechnology* 18 (11) (2007) 115605.
- [50] B.V. Lotsch, W. Schnick, From triazines to heptazines: novel nonmetal tricyanomelaminates as precursors for graphitic carbon nitride materials, *Chem. Mater.* 18 (7) (2006) 1891–1900.
- [51] X. Dong, F. Cheng, Recent development in exfoliated two-dimensional gC<sub>3</sub>N<sub>4</sub> nanosheets for photocatalytic applications, *J. Mater. Chem. A* 3 (47) (2015) 23642–23652.
- [52] P. Niu, L. Zhang, G. Liu, H.M. Cheng, Graphene-like carbon nitride nanosheets for improved photocatalytic activities, *Adv. Funct. Mater.* 22 (22) (2012) 4763–4770.
- [53] J. Xu, L. Zhang, R. Shi, Y. Zhu, Chemical exfoliation of graphitic carbon nitride for efficient heterogeneous photocatalysis, *J. Mater. Chem. A* 1 (46) (2013) 14766–14772.
- [54] M. Chao, X. Ma, Convenient electrochemical determination of sunset yellow and tartrazine in food samples using a poly(L-phenylalanine)-modified glassy carbon electrode, *Food Anal. Methods* 8 (1) (2015) 130–138.
- [55] X.Q. Li, Q.H. Zhang, K. Ma, H.M. Li, Z. Guo, Identification and determination of 34 water-soluble synthetic dyes in foodstuff by high performance liquid chromatography–diode array detection–ion trap time-of-flight tandem mass spectrometry, *Food Chem.* 182 (2015) 316–326.
- [56] J.A. Rodríguez, K.A. Escamilla-Lara, A. Guevara-Lara, J.M. Miranda, M. Páez-Hernández, Application of an activated carbon-based support for magnetic solid phase extraction followed by spectrophotometric determination of tartrazine in commercial beverages, *Int. J. Anal. Chem.* 2015 (2015).
- [57] S.T. Somasundaram, Biodegradation of carcinogenic textile azo dyes using bacterial isolates of mangrove sediment, *J. Coast. Life Med.* 2 (2) (2014) 154–162.
- [58] X. Ye, Y. Du, D. Lu, C. Wang, Fabrication of β-cyclodextrin-coated poly(diallyldimethylammonium chloride)-functionalized graphene composite film modified glassy carbon-rotating disk electrode and its application for simultaneous electrochemical determination colorants of sunset yellow and tartrazine, *Anal. Chim. Acta* 779 (2013) 22–34.
- [59] E. Diaconu, C.P. Ene, Simultaneous determination of tartrazine and sunset yellow in soft drinks by liquid chromatography, *Rev. Chim.* 60 (8) (2009) 745–749.
- [60] L. Zhao, B. Zeng, F. Zhao, Electrochemical determination of tartrazine using a molecularly imprinted polymer–multiwalled carbon nanotubes–ionic liquid supported Pt nanoparticles composite film coated electrode, *Electrochim. Acta* 146 (2014) 611–617.
- [61] Y. Xie, Y. Li, L. Niu, H. Wang, H. Qian, W. Yao, A novel surface-enhanced Raman scattering sensor to detect prohibited colorants in food by graphene/silver nanocomposite, *Talanta* 100 (2012) 32–37.
- [62] Y. Yuan, X. Zhao, M. Qiao, J. Zhu, S. Liu, J. Yang, X. Hu, Determination of sunset yellow in soft drinks based on fluorescence quenching of carbon dots, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* 167 (2016) 106–110.
- [63] F. Soponar, A.C. Moș, C. Sârbu, Quantitative determination of some food dyes using digital processing of images obtained by thin-layer chromatography, *J. Chromatogr. A* 1188 (2) (2008) 295–300.
- [64] T. Gan, J. Sun, Q. Wu, Q. Jing, S. Yu, Graphene decorated with nickel nanoparticles as a sensitive substrate for simultaneous determination of sunset yellow and tartrazine in food samples, *Electroanalysis* 25 (6) (2013) 1505–1512.
- [65] J. Wang, B. Yang, H. Wang, P. Yang, Y. Du, Highly sensitive electrochemical determination of Sunset Yellow based on gold nanoparticles/graphene electrode, *Anal. Chim. Acta* 893 (2015) 41–48.
- [66] M. Wang, J. Zhao, Facile synthesis of Au supported on ionic liquid functionalized reduced graphene oxide for simultaneous determination of sunset yellow and tartrazine in drinks, *Sens. Actuators B Chem.* 216 (2015) 578–585.
- [67] L.J. Cote, F. Kim, J. Huang, Langmuir–Blodgett assembly of graphite oxide single layers, *J. Am. Chem. Soc.* 131 (3) (2008) 1043–1049.
- [68] K.A. Mkhoyan, A.W. Contryman, J. Silcox, D.A. Stewart, G. Eda, C. Mattevi, S. Miller, M. Chhowalla, Atomic and electronic structure of graphene-oxide, *Nano Lett.* 9 (3) (2009) 1058–1063.
- [69] Y. Shao, J. Wang, H. Wu, J. Liu, I.A. Aksay, Y. Lin, Graphene based electrochemical sensors and biosensors: a review, *Electroanalysis: An Int. J. Devoted to Fundam. Pract. Asp. Electroanal.* 22 (10) (2010) 1027–1036.
- [70] A.K. Sundramoorthy, S. Gunasekaran, Applications of graphene in quality assurance and safety of food, *TrAC Trends Anal. Chem.* 60 (2014) 36–53.
- [71] K. Deng, C. Li, X. Li, H. Huang, Simultaneous detection of sunset yellow and tartrazine using the nanohybrid of gold nanorods decorated graphene oxide, *J. Electroanal. Chem.* 780 (2016) 296–302.
- [72] J. Wang, B. Yang, K. Zhang, D. Bin, Y. Shiraiishi, P. Yang, Y. Du, Highly sensitive electrochemical determination of sunset yellow based on the ultrafine Au-Pd and reduced graphene oxide nanocomposites, *J. Colloid Interface Sci.* 481 (2016) 229–235.
- [73] Q. He, J. Liu, X. Liu, G. Li, P. Deng, J. Liang, D. Chen, Sensitive and selective detection of tartrazine based on TiO<sub>2</sub>-electrochemically reduced graphene oxide composite-modified electrodes, *Sensors* 18 (2018) 1911.
- [74] M.A. Karimi, V.H. Aghaei, A. Nezhadali, N. Ajami, Graphitic carbon nitride as a new sensitive material for electrochemical determination of trace amounts of tartrazine in food samples, *Food Anal. Methods* 11 (10) (2018) 2907–2915.
- [75] Q. He, J. Liu, X. Liu, G. Li, P. Deng, J. Liang, Manganese dioxide Nanorods/electrochemically reduced graphene oxide nanocomposites modified electrodes for cost-effective and ultrasensitive detection of Amaranth, *Colloids Surf. B: Biointerfaces* 172 (2018) 565–572.
- [76] M. Wang, Y. Sun, X. Yang, J. Zhao, Sensitive determination of Amaranth in drinks by highly dispersed CNT in graphene oxide “water” with the aid of small amounts of ionic liquid, *Food Chem.* 179 (2015) 318–324.
- [77] Q. Han, X. Wang, Z. Yang, W. Zhu, X. Zhou, H. Jiang, Fe<sub>3</sub>O<sub>4</sub>@ rGO doped molecularly imprinted polymer membrane based on magnetic field directed self-assembly for the determination of amaranth, *Talanta* 123 (2014) 101–108.
- [78] M. Wang, J. Zhao, A facile method used for simultaneous determination of ponceau 4R, allura red and tartrazine in alcoholic beverages, *J. Electrochem. Soc.* 162 (6) (2015) H321–H327.
- [79] M. Cui, M. Wang, B. Xu, X. Shi, D. Han, J. Guo, Determination of allura red using composites of water-dispersible reduced graphene oxide-loaded Au nanoparticles based on ionic liquid, *Int. J. Environ. Anal. Chem.* 96 (12) (2016) 1117–1127.
- [80] L. Yu, M. Shi, X. Yue, L. Qu, Detection of allura red based on the composite of poly(diallyldimethylammonium chloride) functionalized graphene and nickel nanoparticles modified electrode, *Sens. Actuators B: Chem.* 225 (2016) 398–404.
- [81] S. Su, S. Chen, C. Fan, Recent advances in two-dimensional nanomaterials-based electrochemical sensors for environmental analysis, *Green Energy Environ.* 3 (2) (2018) 97–106.
- [82] X. Liu, Y. Tang, L. Wang, J. Zhang, S. Song, C. Fan, S. Wang, Optical detection of mercury (II) in aqueous solutions by using conjugated polymers and label-free oligonucleotides, *Adv. Mater.* 19 (11) (2007) 1471–1474.
- [83] S. Su, W. Wu, J. Gao, J. Lu, C. Fan, Nanomaterials-based sensors for applications in environmental monitoring, *J. Mater. Chem.* 22 (35) (2012) 18101–18110.
- [84] S. Angelino, M. Gennaro, An ion-interaction RP-HPLC method for the determination of the eleven EPA priority pollutant phenols, *Anal. Chim. Acta* 346 (1) (1997) 61–71.
- [85] Y. Luo, Y. Mi, X. Tan, Q. Chen, D. Feng, C. Ai, Ultrathin BiOCl nanosheet modified TiO<sub>2</sub> for the photoelectrochemical sensing of chlorpyrifos, *Anal. Methods* 11 (3) (2019) 375–380.
- [86] P. Yan, D. Jiang, H. Li, J. Bao, L. Xu, J. Qian, C. Chen, J. Xia, BiPO<sub>4</sub> nanocrystal/BiOCl nanosheet heterojunction as the basis for a photoelectrochemical 4-chlorophenol sensor, *Sens. Actuators B: Chem.* 279 (2019) 466–475.
- [87] C. Cheng, Y. Huang, X. Tian, B. Zheng, Y. Li, H. Yuan, D. Xiao, S. Xie, M.M. Choi, Electrogenated chemiluminescence behavior of graphite-like carbon nitride and its application in selective sensing Cu<sup>2+</sup>, *Anal. Chem.* 84 (11) (2012) 4754–4759.
- [88] B. Xia, Q. Yuan, M. Chu, S. Wang, R. Gao, S. Yang, C. Liu, S. Luo, Directly one-step electrochemical synthesis of graphitic carbon nitride/graphene hybrid and its application in ultrasensitive electrochemiluminescence sensing of pentachlorophenol, *Sens. Actuators B: Chem.* 228 (2016) 565–572.
- [89] Directive C: 98/83/EC on the quality of water intended for human consumption, *Off. J. Eur. Commun.* 330 (1998) 42.
- [90] D. Jiang, X. Du, Q. Liu, N. Hao, K. Wang, MoS<sub>2</sub>/nitrogen doped graphene hydrogels pn heterojunction: Efficient charge transfer property for highly sensitive and selective photoelectrochemical analysis of chloramphenicol, *Biosens. Bioelectron.* 126 (2019) 463–469.
- [91] L. Ge, Y. Xu, L. Ding, F. You, Q. Liu, K. Wang, Perovskite-type BiFeO<sub>3</sub>/ultrathin graphite-like carbon nitride nanosheets pn heterojunction: boosted visible-light-driven photoelectrochemical activity for fabricating ampicillin aptasensor, *Biosens. Bioelectron.* 124 (2019) 33–39.
- [92] F. You, M. Zhu, L. Ding, Y. Xu, K. Wang, Design and construction of Z-scheme Bi<sub>2</sub>S<sub>3</sub>/nitrogen-doped graphene quantum dots: boosted photoelectric conversion efficiency for high-performance photoelectrochemical aptasensing of sulfadimethoxine, *Biosens. Bioelectron.* 130 (2019) 230–235.
- [93] D. Huang, X. Liu, C. Lai, G. Zeng, L. Qin, C. Zhang, H. Yi, B. Li, R. Deng, S. Liu, Recent advances in sensors for tetracycline antibiotics and their applications, *TrAC Trends Anal. Chem.* (2018).
- [94] A. Hatami, F. Marahel, A. Sharif, Green synthesis of graphitic carbon nitride nanosheet (g-C<sub>3</sub>N<sub>4</sub>) and using it as a label-free fluorosensor for detection of metronidazole via quenching of the fluorescence, *Talanta* 176 (2018) 518–525.
- [95] P. Sahoo, B. Panigrahy, S. Sahoo, A. Satpati, D. Li, D. Bahadur, In situ synthesis and properties of reduced graphene oxide/Bi nanocomposites: as an

- electroactive material for analysis of heavy metals, *Biosens. Bioelectron.* 43 (2013) 293–296.
- [96] M. Sadhukhan, S. Barman, Bottom-up fabrication of two-dimensional carbon nitride and highly sensitive electrochemical sensors for mercuric ions, *J. Mater. Chem. A* 1 (8) (2013) 2752–2756.
- [97] X. She, H. Xu, Y. Xu, J. Yan, J. Xia, L. Xu, Y. Song, Y. Jiang, Q. Zhang, H. Li, Exfoliated graphene-like carbon nitride in organic solvents: enhanced photocatalytic activity and highly selective and sensitive sensor for the detection of trace amounts of Cu<sup>2+</sup>, *J. Mater. Chem. A* 2 (8) (2014) 2563–2570.
- [98] S. Ding, A. Ali, R. Jamal, L. Xiang, Z. Zhong, T. Abdiryim, An electrochemical sensor of poly (EDOT-pyridine-EDOT)/graphitic carbon nitride composite for simultaneous detection of Cd<sup>2+</sup> and Pb<sup>2+</sup>, *Materials* 11 (5) (2018) 702.
- [99] H. Zhang, Y. Huang, Y. Zheng, J. Zhou, Q. Wu, Z. Zhang, F. Gan, W. Chen, Fluorescence covalent interaction enhanced sensor for lead ion based on novel graphitic carbon nitride nanocones, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* (2019).
- [100] A. Hatamie, P. Jalilian, E. Rezvani, A. Kakavand, A. Simchi, Fast and ultra-sensitive voltammetric detection of lead ions by two-dimensional graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) nanolayers as glassy carbon electrode modifier, *Measurement* 134 (2019) 679–687.
- [101] M. Ramalingam, V.K. Ponnusamy, S.N. Sangilimuthu, A nanocomposite consisting of porous graphitic carbon nitride nanosheets and oxidized multiwalled carbon nanotubes for simultaneous stripping voltammetric determination of cadmium (II), mercury (II), lead (II) and zinc (II), *Microchim. Acta* 186 (2) (2019) 69.
- [102] T. Alizadeh, F. Rafiei, An innovative application of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) nano-sheets as silver ion carrier in a solid state potentiometric sensor, *Mater. Chem. Phys.* 227 (2019) 176–183.
- [103] W. Guan, Z. Li, H. Zhang, H. Hong, N. Rebeyev, Y. Ye, Y. Ma, Amine modified graphene as reversed-dispersive solid phase extraction materials combined with liquid chromatography–tandem mass spectrometry for pesticide multi-residue analysis in oil crops, *J. Chromatogr. A* 1286 (2013) 1–8.
- [104] Z. Li, M. Hou, S. Bai, C. Wang, Z. Wang, Extraction of imide fungicides in water and juice samples using magnetic graphene nanoparticles as adsorbent followed by their determination with gas chromatography and electron capture detection, *Anal. Sci.* 29 (3) (2013) 325–331.
- [105] M. Tankiewicz, J. Fenik, M. Biziuk, Determination of organophosphorus and organonitrogen pesticides in water samples, *TrAC Trends Anal. Chem.* 29 (9) (2010) 1050–1063.
- [106] J. Davies, S. Thuraisingham, The detection and estimation of pentachlorophenol in natural latex by thin-layer chromatography, *J. Chromatogr. A* 35 (1968) 43–46.
- [107] T. Zhou, X. Xiao, G. Li, Microwave accelerated selective Soxhlet extraction for the determination of organophosphorus and carbamate pesticides in ginseng with gas chromatography/mass spectrometry, *Anal. Chem.* 84 (13) (2012) 5816–5822.
- [108] H. Zhao, X. Ji, B. Wang, N. Wang, X. Li, R. Ni, J. Ren, An ultra-sensitive acetylcholinesterase biosensor based on reduced graphene oxide-Au nanoparticles-β-cyclodextrin/Prussian blue-chitosan nanocomposites for organophosphorus pesticides detection, *Biosens. Bioelectron.* 65 (2015) 23–30.
- [109] S. Wu, F. Huang, X. Lan, X. Wang, J. Wang, C. Meng, Electrochemically reduced graphene oxide and Nafion nanocomposite for ultralow potential detection of organophosphate pesticide, *Sens. Actuators B: Chem.* 177 (2013) 724–729.
- [110] M. Guler, V. Turkoglu, Z. Basi, Determination of malation, methidathion, and chlorpyrifos ethyl pesticides using acetylcholinesterase biosensor based on Nafion/Ag@ rGO-NH<sub>2</sub> nanocomposites, *Electrochim. Acta* 240 (2017) 129–135.
- [111] P. Zhang, T. Sun, S. Rong, D. Zeng, H. Yu, Z. Zhang, D. Chang, H. Pan, A sensitive amperometric AChE-biosensor for organophosphate pesticides detection based on conjugated polymer and Ag-rGO-NH<sub>2</sub> nanocomposite, *Bioelectrochemistry* 127 (2019) 163–170.
- [112] A.E.F. Oliveira, G.B. Bettio, A.C. Pereira, An electrochemical sensor based on electropolymerization of β-cyclodextrin and reduced graphene oxide on a glassy carbon electrode for determination of neonicotinoids, *Electroanalysis* 30 (9) (2018) 1918–1928.
- [113] S. Islam, S. Shukla, V.K. Bajpai, Y.-K. Han, Y.S. Huh, A. Ghosh, S. Gandhi, Microfluidic-based graphene field effect transistor for femtomolar detection of chlorpyrifos, *Sci. Rep.* 9 (1) (2019) 276.
- [114] M. Arvand, A.A. Mirroshandel, An efficient fluorescence resonance energy transfer system from quantum dots to graphene oxide nano sheets: application in a photoluminescence aptasensing probe for the sensitive detection of diazinon, *Food Chem.* 280 (2019) 115–122.
- [115] B. Wang, X. Zhong, Y. Chai, R. Yuan, Ultrasensitive electrochemiluminescence biosensor for organophosphate pesticides detection based on carboxylated graphitic carbon nitride-poly (ethylenimine) and acetylcholinesterase, *Electrochim. Acta* 224 (2017) 194–200.