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Magesa, Felista

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

Felista Magesa[a,b], Yiyong Wu[a], Yaling Tian[a], John-Mary Vianney[b], Joram Buza[b], Quanguo He[a,*], Yimin Tan[a,*]

[a] School of Life Sciences and Chemistry, Hunan University of Technology, Zhuzhou, 412007, China
[b] School of Life Sciences and Bioengineering, Nelson Mandela African Institution of Science and Technology, Arusha, 447, Tanzania

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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.

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

* Corresponding authors.
E-mail addresses: magesaf@nm-aist.ac.tz (F. Magesa), wyy5082010@163.com (Y. Wu), tianyaling0212@163.com (Y. Tian), john-mary.vianney@nm-aist.ac.tz (J.-M. Vianney), joram.buza@nm-aist.ac.tz (J. Buza), hequanguo@126.com (Q. He), csfutanyimin@126.com (Y. Tan).

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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_3N_4, 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_3N_4. 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_3N_4 has found its use in fluorescent sensors [22,31,41–43], voltammetric and amperometric electrochemical sensors. In addition ultrasensitive 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_3N_4 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_3N_4, 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_4 (4.5–5 MPa) at temperature 220 °C. Lotsch and Schnick did tricyanomelaminate salts thermal decomposition at > 450 °C and observed graphitic like materials [50]. Furthermore, exfoliation method is used in obtaining ultrathin unilamellar g-C_3N_4 nanosheets. The recent development in exfoliation of 2D g-C_3N_4 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_3N_4 nanosheets with >2 nm thick, ultrasonic exfoliation produces g-C_3N_4 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,

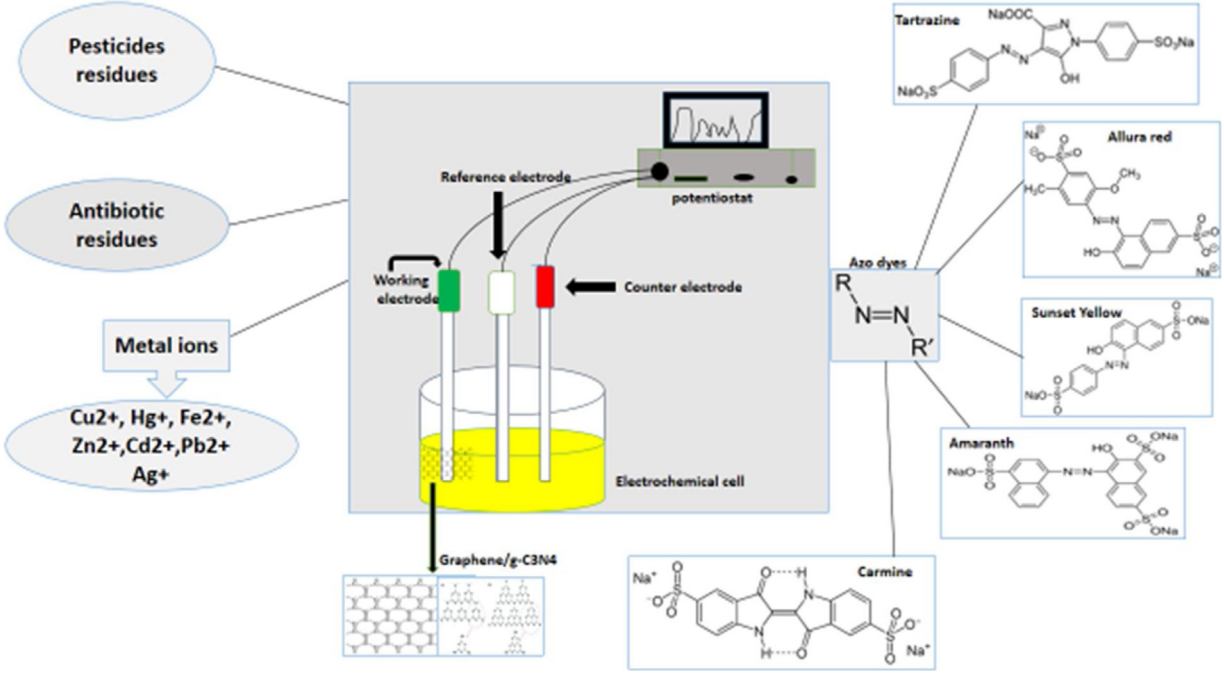

Fig. 1. Electrochemical sensing application areas of graphene and graphene like 2D graphitic carbon nitride.

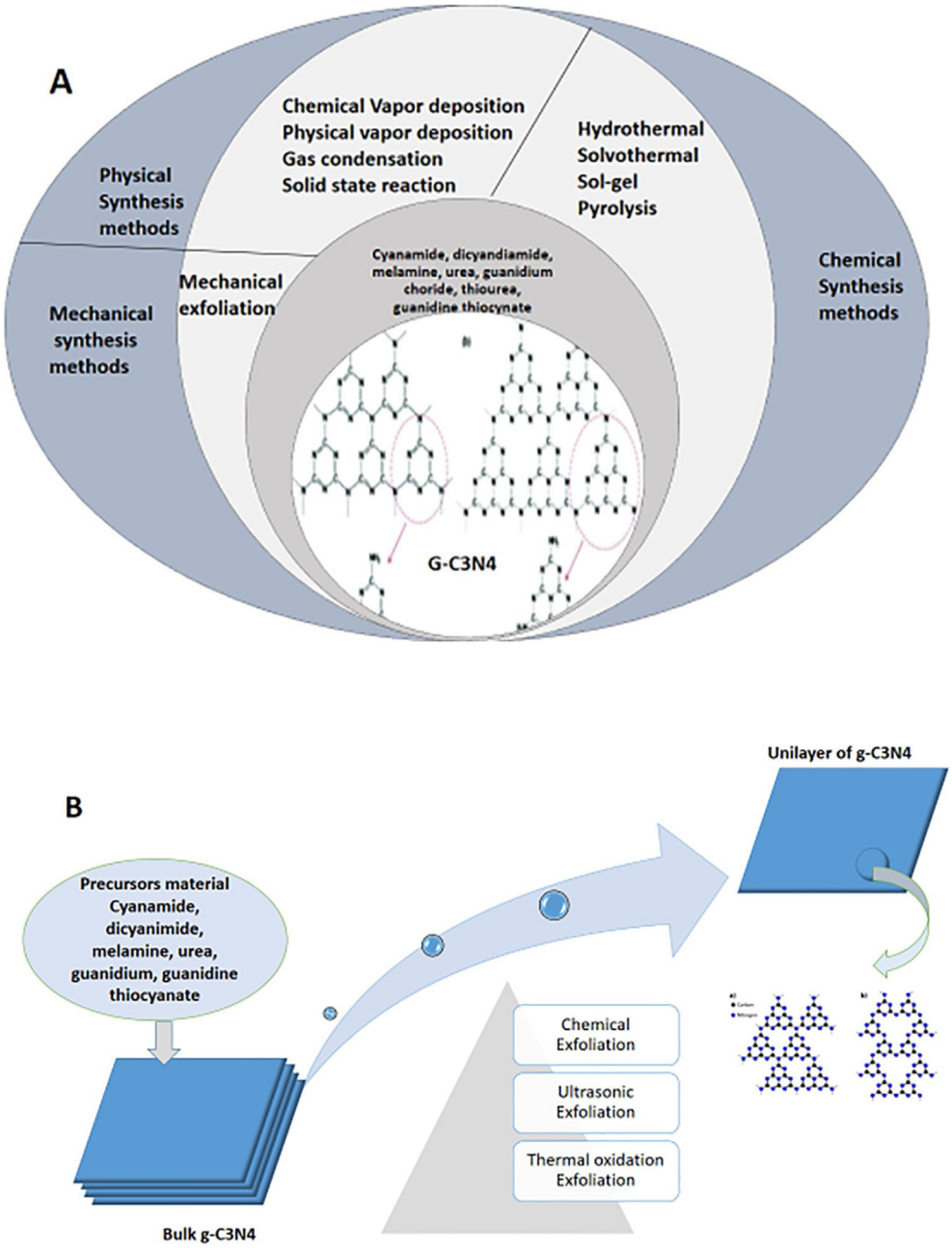

Fig. 2. (A) shows mechanical, physical and chemical methods that have been used in synthesizing 2D g-C_3N_4. Materials, (B) Exfoliation methods that produce ultrathin sheets of graphitic carbon nitride.

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 (-N = 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 μM for sunset yellow and 0.01 μM 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 (Cu_2O-ErGO) nanocomposites glassy carbon modified electrode for sensitive determination of sunset yellow. The Cu_2O-ErGO modified electrode anodic peak current increased for about 25 times compared to a bare GCE. A lower limit of detection of about 6.0×10^{-9} mol/L was obtained and made the Cu_2O-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 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 8.0×10^{-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 g-C_3N_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 (g-C_3N_4/graphite pencil electrode). The g-C_3N_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 1.0×10^{-7} to 1.0×10^{-5} mol/L and the limit of detection was found to be 0.21 μmol/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 g-C_3N_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	MnO_2NRs-ErGO /GCE)	0.02–10 μM, 10–400 μM	1.0 nM	[75]
Sunset Yellow	EIS	GO/MWCNTs	0.09–8.0 μM,	0.025 uM	[8]
Tartrazine	EIS	GO/MWCNTs	0.09–8.0 μM,	0.01 uM	
Sunset Yellow	CV and second-derivative linear sweep voltammetry	Cu_2O-ErGO/GCE	2.0×10^{-8} mol/L–2.0×10^{-5} mol/L 2.0×10^{-5}–1.0×10^{-4} mol/L	6.0×10^{-9} mol/L	[7]
Amaranth	SWV	CNT/GO-IL/GCE	5.0×10^{-10}–4.0×10^{-6}M	0.1 nM.	[76]
Sunset Yellow	CV	Au/RGO/GCE	0.002–109.14 μ M,	2 nM	[65]
Tartrazine	CV and second-derivative linear scan voltammetry	TiO_2–ErGO–GCE	2.0×10^{-8}–2.0×10^{-5} mol/L,	8.0×10^{-9} mol/L	[73]
Sunset Yellow	CV	ERGO-AuNRs	0.01–3.0 μM	2.4 nM	[71]
Tartrazine	CV	ERGO-AuNRs	0.03–6.0 μM	8.6 nM	
Sunset Yellow	CV and DPV	Au-Pd-RGO/GCE	0.686–331.686 μM	1.5 nM,	[72]
Amaranth	DPV	Fe_3O_4/rGO	0.05–50 μM	50 nM	[77]
Sunset Yellow	CV	CTAB-GO/MWNT/ GCE	1×10^{-7}–2×10^{-5} M	1×10^{-8} M	[4]
Tartrazine	CV	CTAB-GO/MWNT/ GCE	3×10^{-8}–6×10^{-7} M	5×10^{-9} M	
Sunset Yellow	CV	ILRGO-Au/GCE	4.0×10^{-9}–1.0×10^{-6} M	5.2×10^{-10} M	[66]
Tartrazine	CV	ILRGO-Au/GCE	7.0×10^{-9}-– 1.5×10^{-6} M	8.3×10^{-10} M	
Allura red	CV	IL-GO-MWCNT-	8.0×10^{-10}–5.0×10^{-7}mol/L	5.0×10^{-10}mol/L	[78]
	SWSV	GCE	5.0×10^{-9}–4.5×10^{-7} mol/L	3.0×10^{-9} mol/L	
Tartrazine	CV	IL-GO-MWCNT/	1.0×10^{-8}–1.0×10^{-6} mol/L	7.0×10^{-9} mol/L	
	SWSV	GCE	2.0×10^{-8}–1.3×10^{-7} mol/L	1.0×10^{-8} mol/ L	
Allura red	SWV	IRGO/Au/GCE	0.0006–0.2 μmol/L	0.00043 μmol/ L	[79]
Tartrazine	CV and DPV	g-C_3N_4/graphite pencil electrode	1.0×10^{-7}–1.0×10^{-5} mol/L	0.21 μmol/L	[74]
Allura red	CV and DPV	PDDA-Gr-Ni/GCE	0.05–10.0 μmol/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 μg/L [89]. The World Health Organization (WHO) established limit levels of metal ions. To mention a few heavy metals such as Pb^{+2} 10 ppb, Hg^{+2} 6 ppb and 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 (GO/w-g-C_3N_4) metal-free nanocomposites. F-doped SnO_2 (FTO) was modified by the GO/w-g-C_3N_4. Water-dispersible graphite-like carbon nitride (w-g-C_3N_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 π−π stacking interaction. Fig. 3 illustrates on the fabrication of the FTO electrode with GO/w-g-C_3N_4 and selective identification of kanamycin by aptamer schematically. The resulting sensor showed good response from the GO/w-g-C_3N_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 w-g-C_3N_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 MoS_2/nitrogen doped graphene hydrogels (MoS_2/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 MoS_2/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 $BiFeO_3$ nanoparticles coupled n-typed ultrathin g-C_3N_4 nanosheets ($BiFeO_3$/utg-C_3N_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 $BiFeO_3$/utg-C_3N_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 $BiFeO_3$/utg-C_3N_4. The resulted PEC aptasensor showed not only excellent response with a wide linearity ranging from 1×10^{-12} mol/L to 1×10^{-6} mol/L but also low LOD of 3.3×10^{-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 g-C_3N_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 Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} heavy metal ions. Employing ASV electrochemical technique the results were reported to be 26 μg/L, 17 μg/L, 0.55 μg/L, and 2.8 μg/L for Cu^{2+},

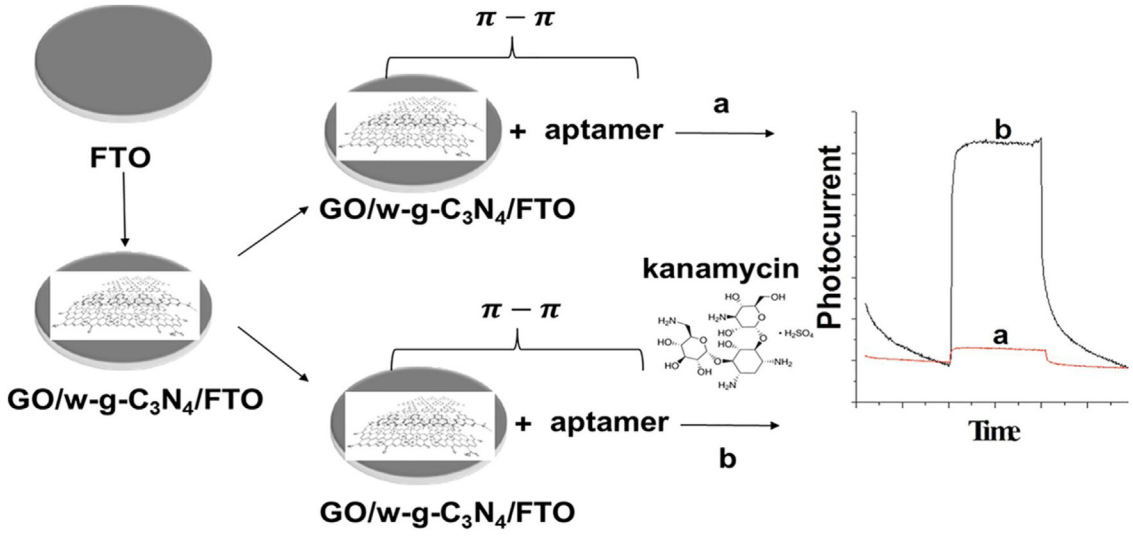

Fig. 3. A Schematic Illustration of Photo Electrochemical Aptasensing Principle Using the on graphene oxide water-dispersible graphite-like carbon nitride F-doped SnO_2 (GO/w-g-C_3N_4/FTO) Electrode [10].

Zn^{2+}, Cd^{2+} and Pb^{2+} respectively. The detection range was 20–120 mg/L. In testing real samples the sensor exhibited a good response in the determination of Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} 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_3N_4 in developing sensors for metal ions detection in the environment. Sadhukhan and Barman modified glassy carbon electrode using g-C_3N_4 which resulted into an electrochemical sensor for Hg^{2+} detection in aqueous solution. The lower detection limit of Hg^{2+} was reported to be 9.1×10^{-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^{2+}, Cu^{2+} and Hg^{2+} was done. The peak currents decreased linearly with metal ions decreased concentration. The LOD was calculated from the calibration curves and found to be 7×10^{-8} M for both Cu^{2+} and Pb^{2+} [96]. Moreover, in metal ion detection, ECL Behavior of g-C_3N_4, with $K_2S_2O_8$ as the co-reactant and the quenching property of Cu^{2+} was used to develop an ECL sensor which showed high selectivity to Cu^{2+} 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_3N_4. 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^{2+} 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_3N_4 ECL properties.

A more sensitive ECL sensor was developed using graphitic carbon nitride/graphene oxide (g-C_3N_4/GO) hybrid for ultrasensitive detection of Cu^{2+}. GO in this sensor served dual purposes which are enhancing the cathodic ECL signal of g-C_3N_4 which was approximately 3.8 times and as an immobilization platform for g-C_3N_4. The LOD was 1.0×10^{-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_3N_4 in the detection of Cu^{2+} 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^{2+} and Pb^{2+} individually and simultaneously. In situ chemical polymerization method was used to prepare poly(2,5-bis(3,4-ethylenedioxythienyl)pyridine)/g-C_3N_4 (poly(BPE)/g-C_3N_4) composites. Then GCE electrode was modified using 10 wt % poly(BPE)/g-C_3N_4 composite. It was reported that the 10 wt % poly(BPE)/g-C_3N_4 modified electrode showed wide linearity response and lower detection limit not only in individual concentration determination of Cd^{2+} and Pb^{2+} but also in the simultaneous concentration determination, Table 2. The response observed is due to the highly ordered tris-triazine structure of g-C_3N_4 which facilitated the intercalation of metal ions into the g-C_3N_4 through the nitrogen lone pair electrons. Moreover, the synergistic effect of poly(BPE) and g-C_3N_4 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^{2+} and Pb^{2+} 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 (ERGO)-gold nanoparticles (AuNPs)-β-cyclodextrin (β-CD) and Prussian blue-chitosan (PB-CS) electrodeposited on a GCE, fabricated

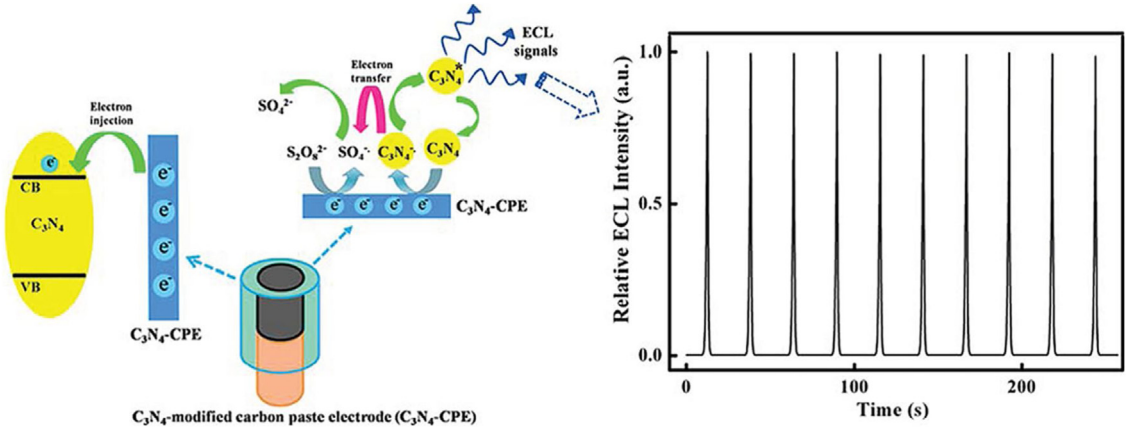

Fig. 4. ECL property of g-C_3N_4 determination of trace amount of copper [87].

Table 2
Pb^{2+} and Cd^{2+} simultaneous and individual concentration determination observations using 10 wt % poly(BPE)/g-C_3N_4 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_3N_4 Composites	Differential Pulse Voltammetry (DPV)	Pb^{2+}	Simultaneous	0.08–7.2	0.00324
		Cd^{2+}		0.12–7.2	0.018
		Pb^{2+}	Individual	0.1–6.4	0.00327
		Cd^{2+}		0.1–6.8	0.0097

with acetylcholinesterase (AChE). This sensor exhibited selectivity, sensitivity, stability and a good response, with wide linear ranges of 7.98-2.00 $\times 10^3$ pg/mL and 4.3-1.00 $\times 10^3$ 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_2) [110]. The biosensor NA/Ag-rGO-NH_2/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_2/AChE biosensor was developed by Zhang and others in 2019 [111]. They developed an amperometric AChE-biosensor using conjugated polymer (furan-2-yl) benzo thiadiazole (FBThF) and Ag-rGO-NH_2 nanocomposites. Due to the combined effect of FBThF which was polymerized electrochemically and Ag-rGO-NH_2 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

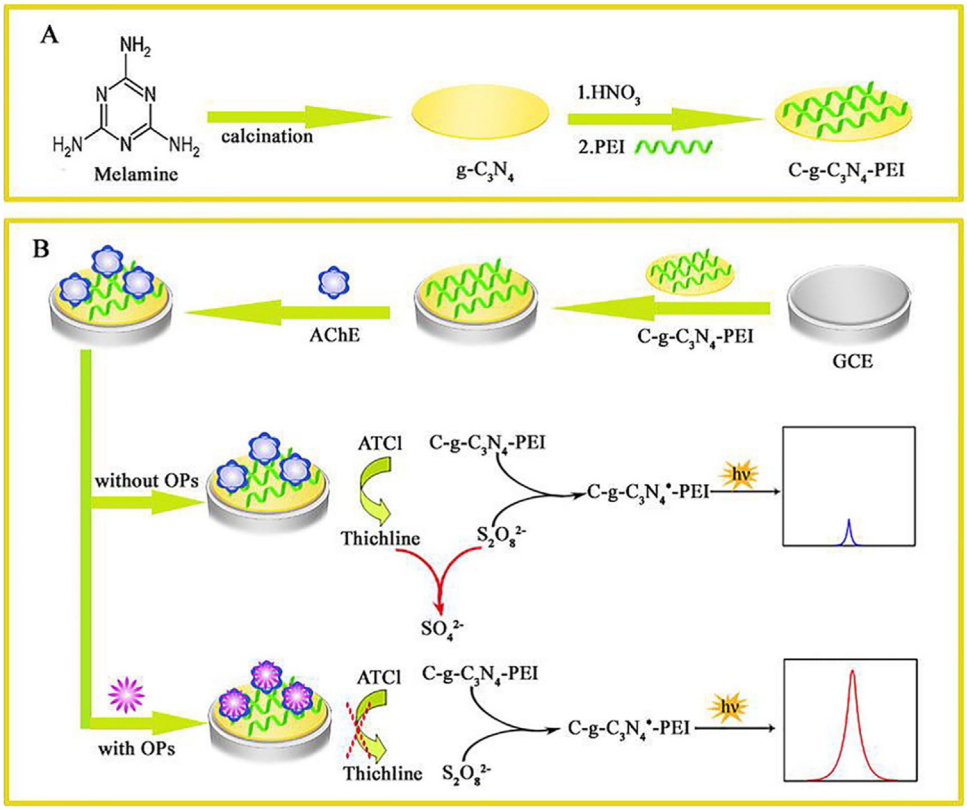

Fig. 5. Schematic description of (A) the preparation process of graphitic carbon nitride-poly (ethylenimine) (C-g-C_3N_4-PEI). (B) the fabrication of modified biosensor and response mechanism [115].

of b-CD. The LOD for the, IMP, CLT and TMX observed were 8.92 μmol/L, 4.72 μmol/L and 7.45 μmol/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_2 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 μM 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_3N_4, 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_3N_4-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_3N_4 and the amine group of PEI resulted in C-g-C_3N_4-PEI nanocomposite, Fig. 5(A) shows this bond graphically. The co-reactant of C-g-C_3N_4-PEI was $K_2S_2O_8$. Hydrolysis of acetylthiocholine (ATCl) under the action of AChE *in situ* produces thiocholine. On the surface of electrode thiocholine consume coreactant $K_2S_2O_8$. Due to the fact that organophosphates are AChE inhibiters, 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_3N_4 showed high sensitivity with a wide linear range of 1.0 pM to 5.0 μM 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_3N_4/GR for pentachlorophenol (PCP) detection. The proposed sensor exhibited ultrasensitivity and rapid detection of PCP with low limit of detection being 1.0×10^{-11} mol/L with a wide linear range from 1.0×10^{-11} to 1.0×10^{-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_3N_4 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_3N_4. 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_3N_4 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_3N_4 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_2O, Fe_3O_4 and TMDs (e.g MoS, MnO_2). 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 foristance g-C_3N_4/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.

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