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Electrochemical Detection of Environmental Pollutants Based on Graphene Derivatives: A Review

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Population-driven socioeconomic urban expansion, industrialization, and intensified modern agricultural practices are interlinked to environmental challenges culminating in compromised water quality due to pollution by toxic, persistent, and bioaccumulative heavy metal ions, pesticides, nitroaromatics, and other emerging pollutants. Considering the detrimental impact of pollutants on human health and ecosystem, their detection in different media including water is paramount. Notably, electrochemical techniques are more appealing owing to their recognized advantages. This research summarizes and evaluates the most recent advances in the electrochemical sensing of environmental pollutants such as heavy metal ions, pesticides, nitroaromatics, and other distinct emerging contaminants. Besides, the review focuses on the application of electrochemical detection of the selected pollutants through analysis of representative reports in the five years from 2016 to 2020. Therefore, the review is intended to contribute insights and guidelines to contemporary progress in specific electrochemical application practices based on graphene derivatives, toward the aforenamed pollutants. Thus, it focused on sensing methods such as cyclic voltammetry, anodic stripping voltammetry, and electrochemical impedance spectroscopy employing different sensing elements incorporating graphene. Moreover, the review also highlighted graphene synthesis pathways, sensor design strategies, and functionalization. Furthermore, the review showed that there is congruence in the literature that functionalized graphene and its derivatives remain as viable modifiers in electrochemical sensing of pollutants. Nonetheless, the study also appraised the absence of literature reports on electrochemical detection of natural organic matter substances like humic acid and fulvic acid using a graphene-based sensor. In reckoning, current challenges related to graphene synthesis and applicability, envisaged opportunities, and future perspectives are outlined.

Keywords: cyclic voltammetry, electrochemical detection, emerging pollutants, functionalization, graphene derivatives, reduced graphene oxide, heavy metal ions, pesticides

INTRODUCTION

Owing to global socioeconomic growth spurred by exponential population rise, water quality has been gradually depreciating. Expansion in the intricately interrelated developmental spheres of urbanization, industrialization, and agriculture has massively contributed to environmental challenges. Furthermore, inadequate treatment of industrial and municipal waste coupled with compromised austerity in regulatory monitoring of effluent has resulted in the deposition of pollutants into the ecosystem. Apart from that, environmental issues including uncapped pollution and diminished groundwater replenishment due to low rainfall have further exacerbated water scarcity and pollution levels (Zhang et al., 2019b; Perreault et al., 2015; Arfin and Rangari 2018; Su et al., 2018; Priya et al., 2018). Among the pollutants which have generated widespread apprehension are heavy metals (HMs) viz mercury, lead, cadmium, pesticides, and emerging chemical pollutants. Even though some HMs are derived from biogeochemical mechanisms, significant HMs in the aquatic media are derived from anthropogenic operations such as fossil fuel combustion, mining processes, incineration, and release of municipal wastewater. Moreover, pesticides have become an integral part of modern extensive agricultural practices and out/indoor domestic health. Meanwhile, personal care products (PCPs) and endocrine disruptive chemicals originating from pharmaceutical and industrial applications are recognized constituents of emerging pollutants (Lingamdinne et al., 2019; Ullah et al., 2018; Sakthinathan and Chen 2015; Sharma and Bhattacharya 2017; Álvarez-Ruiz and Picó 2020).

Inorganic arsenite and HM ions such as mercury, copper, cadmium, and lead have a detrimental impact on the environment besides the health of mankind on account of their toxic nature, persistence in different media, and disposition to biologically accumulate along the trophic system. Human beings become exposed to these metals through consuming contaminated food and portable water. For instance, trivalent arsenic ions are known to cause impairment of major human organs such as the lungs, the liver, and the reproductive system besides weakening the immune system (Molina et al., 2016; Zuo et al., 2019). These pollutants have detrimental effects including damage to body organs and malfunctioning of hormonal systems. Consequently, there is strong motivation to protect ecosystems through environmental analysis and determination of contaminants (Qu et al., 2013; Hou et al., 2018; Liyuan Wang et al., 2013; Lingamdinne and Koduru 2018; Wang et al., 2020). Currently used spectroscopic, chromatographic, and hyphenated techniques are reliable, sensitive, and precise; however, they have inherent shortcomings including prolonging and tedious sample preparatory steps, less economical, utilization of potentially harmful solvents, and the need for trained and certified operators. Inevitably, these approaches become limited for on-site, instantaneous, and *in situ* analysis (Molina et al., 2016; He et al., 2018a; Huang et al., 2019a; Wen et al., 2018).

Conversely, electrochemical (EC) approaches are hugely acclaimed to be versatile in the detection of variant natural and anthropogenic pollutants such as HM ions, pesticides, and other substances of concern owing to numerous merits comparative to the conventional laboratory-centralized means. Specifically, EC methods are accredited for their superior sensitivity and discriminatory ability, lowly detection limits, and cost-effectual status. Moreover, their facileness in operation, rapid analytical response, absence of sample pretreatment, technically miniaturized devices, and portable state make them amenable for on-site analysis (Silwana et al., 2016; Bansod et al., 2017; Smith et al., 2019).

Again, EC methods are acknowledged for their short response time, simple preparation procedures which are used, and high target specificity even when analyte concentration is extremely low especially in complex matrices; thus, there is a diminished impact from potentially interfering chemicals (Theyagarajan et al., 2020a; Jerome and Sundramoorthy 2020).

Using bare electrodes during the analysis of contaminants is prone to some drawbacks including electrode passivation, high overpotential of analyte reactions, and slow direct electron transfer (Hang et al., 2019; Lee et al., 2018; He et al., 2019a). Notwithstanding, there are strategies to mitigate against such limitations, thus improving the sensitivity and preciseness of electrodes. Electrode modification is one such approach using metal (oxide) NPs, polymers, and other carbonaceous materials. Notably, modification serves to decrease the overpotential of EC reactions and preconcentrating capability for some analytes, and it culminates in the generation of an electrode-modifier interface which ensures the formation of bridges and pathways to enable electron shuttling to ultimately improve signal amplification (Salih et al., 2016; Krishnan et al., 2019; Jerome and Sundramoorthy 2020). Besides, electrode modifying facilitates the simultaneous covalent immobilization and effectual anchoring of biomolecules on the electrode surface. It also promotes accessing of embedded redox-active sites by mediators while it preserves the enzyme's original nature and activity (Lawal 2018; Kandaswamy Theyagarajan et al., 2020; Murugan et al., 2020). Among the carbon-based materials are carbon nanotubes and graphenic carbon nanomaterials. For instance, graphene-derived nanomaterials are recognized owing to environmentally friendly synthesis methods; for example, during EC synthesis of graphene, nontoxic solvents are used; comparatively, high yield is obtained and minimum residual defects are formed (Nagarajan and Sundramoorthy 2019). In addition, they have a large specific area-to-volume ratio, conductivity, and fast electron transfer kinetics. Therefore, they have attracted global attention; thus, they are explored in different applications. In particular, graphene-derivatized nanomaterials have become entrenched in applications among others, energy harvesting and storage, and environmental analysis as electrochemical sensors or biosensors (Dideikin and Vul' 2019; Nagarani et al., 2018; Dywili et al., 2019; Li et al., 2015; Gumpu et al., 2017).

This review summarizes and evaluates recent advances in the development and application of EC detection of selected environmental pollutants such as HM ions, pesticides, endocrine disruptors, nitroaromatics, and other pollutants of concern, all based on graphene derivative platforms. Graphene

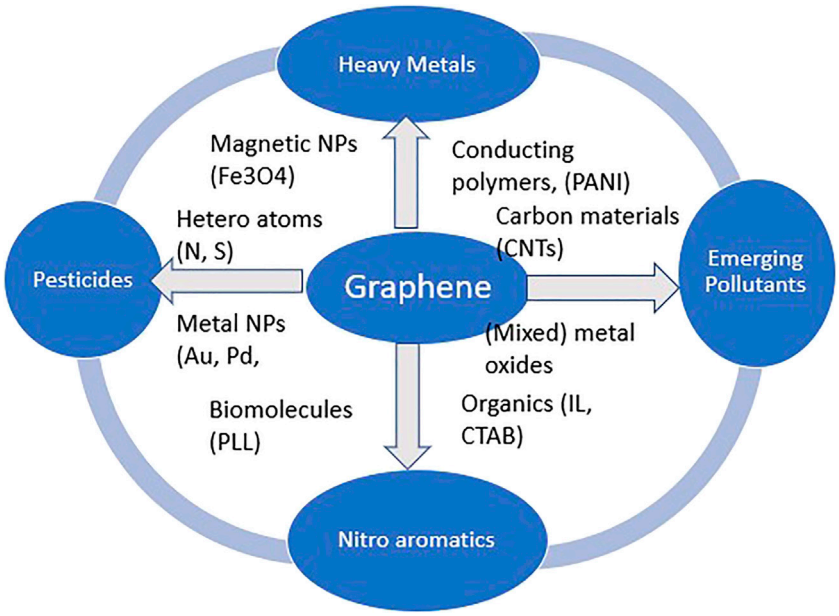

FIGURE 1 | Scheme summarizing the main pollutants reviewed and functionalizing materials associated with graphene in this review.

and its derivative synthesis methods and functionalization are briefly outlined. Ultimately, confronting issues, ensuing opportunities, and prospects are further discussed. The review evaluated representative published reports available through the Internet, on the respective subject in the five years from 2016 to 2020, and in the process, more than 200 reports were examined. The review has been organized into sections which include EC techniques, graphene and its derivatives synthesis approaches, and functionalization of graphene-based materials. Further sections focused on application in EC sensing of diverse environmental pollutants, HM ions, pesticides, emerging contaminants, natural organic matter, nitroaromatic compounds, and other pollutants of interest, all with relevant examples to illustrate contemporary progress. **Figure 1** summarizes the main pollutants and functionalizing materials associated with graphene in this review. The penultimate part is dedicated to challenges, envisaged opportunities, and future perspectives interrelated with the synthesis and application of graphene originating materials.

ELECTROCHEMICAL DETECTION TECHNIQUES

Diverse EC techniques are at the disposal of the scientific research and academic community viz impedimetric and voltammetry. The techniques have gained global recognition owing to their advantages such as high sensitivity, facile operation and procedures, cost-effectiveness, and miniaturizable, portable, and hence potential on-site application. In this part, cyclic voltammetry (CV), anodic stripping voltammetry (ASV), and electrochemical impedance spectroscopy (EIS) are briefly outlined.

Fundamentally, voltammetry pertains to the applying of potential in an EC cell and consequently measuring the resulting current which is controlled by the mass transport. The applied potential progressively changes with the independent time variable while the current response is a function of the potential but has a linear relation with the earmarked analyte concentration in the bulk sample (Yilong et al., 2015; Silwana et al., 2016; Wongkaew et al., 2019; Banerjee et al., 2020). Contemporarily, voltammetry has been used in sync with other innovative strategies including differential pulse, square wave, and anodic stripping with an acclaimed reputation in sensing various analytes.

ASV is a sensing technique which is reliant on a preconcentration stage when the dissolved HM ions drift from the bulky solution to the bare or modified electrode. Depending on an enabling potential difference, the HM ions are electroreduced generating the elemental metal. The neutral metal adsorbates accumulate on the electrode surface leading to the transferring of mobile charges to the surface modifier (Gęca and Korolczuk 2017; Waheed et al., 2018). Uniquely, when a specific anodizing voltage is applied, the elemental metals are dissolved releasing electrons. Simultaneously, the di/trivalent cations diffuse into the electrolyte while generating an intense voltammetric stripping current even in ultralow metal concentration matrices. Significantly, there exists a direct interrelationship between the rate-determining prior concentration step along with the ensuing stripping current (Lee et al., 2017; Waheed et al., 2018; Shtepliuk and Yakimova 2019; Suherman et al., 2017). The basic steps in ASV and relevant data to be extracted are shown in **Figure 2**. ASV stands out as a technique of choice associated with its unique sensing capability features like discriminant selectivity, rapid detection period, and elevated sensitivity.

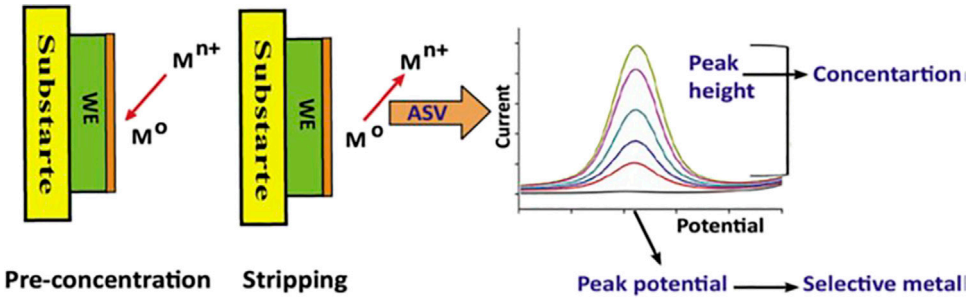

FIGURE 2 | A schematic representation of the basic steps of ASV and the information to be obtained. Reproduced with authorization from (Waheed et al., 2018). Copyright 2018, Elsevier.

Several researchers explored ASV realizing incredible results; typically, Wen et al. fabricated and applied a reduced graphene oxide-manganese dioxide (rGO/MnO_2) nanocomposite doped with nitrogen for GCE modification. Based on CV, EIS, and ASV in the mercuric determination, the enhanced sensor behavior was on account of synergic impact emanating from obtained nanostructured material and doping. Thus, they reported an elevated sensitivity of 72.16 μA μM^{-1} and a low detection limit of 0.0414 nM within a linear range of 0.01–0.2 μM (Wen et al., 2018).

In a different report, Chimezie et al. produced an rGO and *ex situ* synthesized magnetite nanocomposite (rGO/Fe_3O_4) for refashioning a screen-printed carbon electrode (SPCE) surface and investigated quantification of arsenite through DPASV and EIS technologies. Enhanced perfomance of EC sensor was achieved at a linear range of 2–300 μg L^{-1} with low detection limit of 0.10 μg L^{-1} (S/N = 3) compared to reported limit of quantification (0.33 μg L^{-1}). They accounted for the enrichment of performance through synergistically large active surface centers for electron transfer routes (Chimezie et al., 2017).

In other respects, EIS is an accomplished technique undertaken to determine the impedance whose components, frequency-reliant-resistance, and capacitance of the electrode are preceded by perturbating in alternating current mode. Results of experiments are mathematically evaluated with an equivalent electrical circuit (EEC) and reliably provide quantitative electrochemical data on mass transfer hence reaction rates, electrical conductivity, dielectric constant, and direct electron mobility (Jin and Maduraiveeran 2018; Wongkaew et al., 2019). For example, Manavalan et al. fabricated GO-functionalized ZnO nanostars for SPCE modification. They evaluated the altered electrode through CV, DPV, and EIS for methyl parathion (MP) detection (Manavalan et al., 2020). Remarkable sensor behavior was reported giving a low sensing limit of 1.2 nM and superior sensitivity of 16.5 μA μM^{-1} cm^{-2} over a linear range from 0.03 to 670 μM. Furthermore, the amplified EC sensor properties were aftermath due to the combinational collaborative effect of the materials used as indicated by the raised peak currents and lower charge transfer resistance. Meanwhile, the proposed sensor's applicability was assessed in real matrices for MP and it proved a viable candidate. Similarly, Zhou et al. constructed graphene nanoplatelets integrated with a noble metal and Au nanoparticles (GNPs-Au NPs) for refashioning a GCE surface. They investigated the determination of trace level bisphenol A (BPA) using CV, DPV, and EIS strategies and applied the sensor to different water matrices. Their findings demonstrated a low detection capping of 0.027 nM spanning a linear function of 5 × 10^{-3}–100 μM. More so, the improved sensor properties were attributable to increased electrocatalytic behavior due to synergy between the composite materials (Zou et al., 2019).

EC SENSOR DESIGN PLATFORMS

Sensor platforms intended to ensure sufficient selectivity and high sensitivity apart from having long-term shelf life and short response time. Additionally, they ought to be economic in terms of low power needs and cost-effective. Numerous efforts that are based on material chemistry, target analyte reactivity, sensing mechanism, and other factors have been pursued by the scientific community. In this section, the following are presented: sensor design strategies, the role of nanosized materials, graphene derivative platform synthesis, and lastly the functionalization using diverse materials like metal (oxides) NPs, polymers, and organic and inorganic materials.

Design Strategies

The detection behavior of a sensor is responsive to the interaction which occurs at the electrode interface with the targeted chemical species. Primarily, any sensor system has key components like the sensing element, recognition element, and transducer (Jin and Maduraiveeran 2018; Peña-Bahamonde et al., 2018). Thus, the sensor components and interface events influence design strategies. Sensor design strategies are premised on the realization that actual environmental, clinical, food, or security-related samples may be complicated matrices and the earmarked analyte may be present in extremely low concentrations. Therefore, the design promotes superior sensitivity and differentiation and upgraded target specificity while ameliorating nonfouling effects. Notably, some acknowledged design strategies that have been applied solely or in combination include analyte affinity enrichment, enhancement of the surface area, increased catalytic effect,

high loading capacity, and amplification of EC signal (Kumar et al., 2019; Hang et al., 2019; Numan et al., 2020; Wongkaew et al., 2019; Moro et al., 2019; Yan et al., 2020a).

The integration of properties of components of sensor configurations has been widely explored with beneficial impact. In one study, Yan et al. constructed a functional sensing configuration deploying Au NPs, ferrocene dendrimer (FcDr), and rGO. The Au NPs/FcDr/rGO nanohybrid was employed to modify GCE and applied in the detection of dichlorvos (Yan, 2020). Remarkably, FcDr is an effectual signaling constituent associated with the strong anchoring on the electrode, electrostatic interaction, and covalent immobilization besides serving as an Fc^{+2}/Fc natural redox probe for EC signal (Yan et al., 2020b). The sensing element components Au NPs have excellent electrical conductivity and improve analyte interaction while rGO nanosheets have a large surface area which is conducive for effective loading and dispersion of metallic NPs onto rGO. Therefore, these components have a synergistic effect stimulating the electron transfer process, hence amplifying the EC signal of the Au NPs/FcDr/rGO/GCE sensor. The proposed sensor attained micromolar detection sensitivity for the pesticide analysis.

Similarly, Malakootian, Hamzeh, and Mahmoudi-Moghaddam investigated the modification of carbon paste electrode (CPE) employing a magnetic $FeNi_3$/CuS/BiOCl NC for concurrent detection of divalent cadmium and lead. The researchers reckoned that the biocompatible and superparamagnetic $FeNi_3$ promotes electrical communication between electroactive species and electrode surface (Malakootian et al., 2020). Meantime, the stable semiconductor BiOCl has high catalytic activity while CuS possesses electrical conductivity qualities like metals. Thus, there was synergistic aftermath that boosted the electron transfer kinetics, ultimately amplifying the sensor signal. Furthermore, through SWASV, the corresponding detection limit of $0.4\,\mu g\,L^{-1}$ and $0.1\,\mu g\,L^{-1}$ for Cd^{+2} and Pb^{+2} was reported while the sensor demonstrated viability when its applicability was evaluated in real samples.

Recently, Kaur assembled a novel NC of ErGO-chitosan (CS)-hemoglobin (Hb) coatings (ErGO-CS/Hb) through a green synthesis method prior to modifying a fluorine-tin oxide (FTO) electrode. The ErGO-CS/Hb configured platform was employed in investigating the quantification of MP via SWV and EIS (Kaur et al., 2020). Notably, the immobilization of Hb onto the ErGO-CS matrix ensued a fast charge transfer rate to the embedded electrode center while safeguarding the nativity of the biomolecule. Evidently, there was magnified pesticide affinity attributed to the delocalized π electron system of rGO which initiated robust π-π stacking interaction with MP. Besides, electrostatic interaction and hydrogen bonding promoted firm binding of the pesticide on the modifier surface. The combination of rGO with CS through amide linkage also improved the dispersion during synthesis, producing a stable nanohybrid. Furthermore, rGO possesses a large surface area, superior electrical conductivity, lower background current, and wide EC potential window while Hb has active redox centers and the hydrophobic biopolymer CS endowed with good film-forming ability was synergistically integrated, manifested in excellent sensitivity and selectivity. So, a limit of detection (LOD) of 79.77 nM and sensitivity of $45.77\ A\ cm^{-2}\ \mu M^{-1}$ were attained.

Likewise, Zeng et al. devised a nanohybrid involving Pd nanoflower-decorated 3D CNT-graphene nanosheets (GNSs) network assembled from CNTs and GNSs for modification of an SPE. The sensing element PdNFs-CNTs-GNSs/SPE was engaged for simultaneous sensing of nitroaromatics, p-nitrophenol (4-NP), 1,3-dinitrobenzene (DNB), 1-chloro-2,4-dinitrobenzene (Cl-DNB), 2,4-dinitrotoulene (DNT), 1,3,5-trinitrobenzene (TNB), and trinitrotoluene (TNT). Initially, 1D CNTs were embedded into 2D GNSs to form a native 3D architectural framework instrumental for prohibiting CNTs and GNSs from agglomerating during synthesis (Zeng et al., 2019). Besides, the 3D structure has a large surface area plus numerous electrochemically active surface sites conducive for high loading of functional NMs on itself confirmed by PdNFs being finely dispersed on the porous CNTs-GNSs scaffold. Effectively, synergism between active PdNFs and CNTs-GNSs porous 3D network facilitates electron channeling between the electrode and redox species, hence fostering electrical communication. Furthermore, the unique configuration had superior electrocatalytic activity toward the reduction of nitroaromatics. The sensor achieved detection limits in the nanomolar level, and the proposed portable sensor system demonstrated potential for prompt, *in situ*, and *point-of-analysis* assessments.

Functional Nanostructures

Nanostructured materials have the potential to considerably boost the surface area-to-volume ratio and they are endowed with numerous active centers and hence influence the analytical performance of a sensor.

Nanopillars are sharp spiked nanostructures with high antibacterial efficacy whenever bacteria come into contact. Their potency mode is piercing the bacterial cell wall, thus rupturing and damaging the microorganism, Thus, nanopillars are favorable modifier candidates where antimicrobial surfaces are needed (Bhadra et al., 2018; Chen et al., 2020; Canalejas-Tejero et al., 2018).

The central bore of nanoneedles is a critical feature which is exploited in the medical field. The bore serves as a conduit where the desired molecules pass through. So, nanoneedles are useful for the delivery of bioactive molecules into cells, loading of drugs, and delivery of drugs to specific points (Shende et al., 2018).

Nanorods are 1D structures with a diameter between 1 and 100 nm and they are amenable for use in the sensing and medical field. For example, Hang et al. constructed a hierarchically vertical fluorinated graphene/ZnO nanorods plus nanoseeds platform which was employed for H_2O_2 determination. The sensor had increased active surface area and inherent self-cleaning and fouling-proof capabilities which enhanced its analytical performance (Hang et al., 2019).

Nanowires (NWs) are "sticks" with a diameter of less than 100 nm and varying lengths. However, when interconnected, NWs form 2D or 3D conductive independent frameworks that are self-supporting but have an excellent specific surface area.

Moreover, NWs have the capability of hosting several structural defects; they are corrosion proof to the reaction conditions and provide the direct charge connectivity between underlying active centers and the electrode surface. Ultimately, NWs improve the electrocatalytic activity and promote signal amplification. For instance, Zhuang et al. designed a sensor premised on 3D nickel oxide NPs, PANI nanowires, and GO. The NiO NP/PANINW/GO matrix was used to modify a GCE and applied for the detection of glucose (Zhuang et al., 2016). The sensing platform exhibited superior electrocatalytic activity while its sensitivity was high (376.22 $\mu A\ \mu M^{-1}\ cm^{-2}$) and LOD was in micromolar level. Similarly, nanotubes also serve as conducting channels linking redox sites with the electrode, besides improving the active surface area which forms the bedrock of EC reactions (Kumar et al., 2019; Cho et al., 2020; Zhang et al., 2018a). Theyagarajan et al. fabricated a sensor employing MWCNTs and a functionalized ionic liquid where the horseradish peroxidase was anchored before modifying a GCE (Theyagarajan et al., 2020b). The sensing configuration was evaluated through detection of H_2O_2 and the corresponding sensitivity and linear range were 55.08 $\mu A\ \mu M^{-1}\ cm^{-2}$ and 0.01–2.07 nM while the LOD was at micromolar level. Furthermore, there were synergism of properties of MWCNTs and functionalized ionic liquid, large surface area, superior electrical conductivity, π–π stacking, covalent immobilization, and accessing of embedded redox sites. Thus, the sensor performance was enhanced.

Graphene Derivative Platforms

The graphene lineage is composed of the pristine precursor graphene and its derivatives inclusive of GO, rGO, and graphene quantum dots (GQDs). Besides, doped graphene is regarded as an offshoot of that family (Zheng et al., 2017; Smith et al., 2019; Thangamuthu et al., 2019). Graphene is a sole layer of an allotrope of carbon with sp^2-hybridized carbon atoms hexagonally arrayed into a two-dimensional (2D) honeycombed entity (Ambrosi et al., 2016; El-Shafai et al., 2018; Beitollahi et al., 2019). For more than a decade, the substantial focus has been directed toward this 2D nanomaterial due to its standout features including excellent chemical inertness and remarkable thermal, optical, mechanical-electrical characteristics (Lee et al., 2019c; Lingamdinne and Koduru 2018; Magesa et al., 2019). Moreover, graphene-derived nanomaterials are conferred with the facility that promotes simple functionalization, superior electron transport capability, and enormous specific surface area-to-volume ratio, besides being biocompatible (Huang et al., 2019b; Kuralay et al., 2016; Kumar et al., 2017; Krishnan et al., 2019). There are diverse pathways for the synthesis of graphene derivatives. Moreover, the derivatives are endowed with peculiar properties which enhance the sensing behavior of composite materials.

Synthesis of Graphene

Conveniently, pristine graphene synthesis processes as depicted in **Figure 3** are segmented as either bottom-up or top to bottom incorporating the Geim-Novoselov pioneered mechanical cleavage of graphite. Notwithstanding that, the technique is roundly recognized as least suitable for scalable commercial graphene production since it is arduous and has inferior reproducibility (Khan et al., 2015; Yin et al., 2015; Molinari and Argurio 2017; Xu et al., 2017; Tiwari et al., 2018). Meanwhile, other respective methods are described in the literature, including defects-generating aqua-chemical exfoliation (Lee et al., 2019b; Lawal 2018), epitaxial forming of graphene on silicon carbide substrate, and chemical vapor deposition (CVD) (Avouris and Dimitrakopoulos 2012; Suvarnaphaet and Pechprasarn 2017; Ahmad et al., 2018), and thermal exfoliation (Mohan et al., 2018; Rowley-Neale et al., 2018). Furthermore, "unzipping" of CNTs is also considered a viable graphene preparation pathway. Comparatively, electrochemical means are preferred owing to their efficacy, rapidness, facile, and environmentally friendly nature (Ambrosi et al., 2016; Sakthinathan et al., 2016). Nonetheless, it has been ascertained that graphene's applicability is hindered by agglomeration arising from the conjunction of π–π restacking, physical defects, multiplex sheet thickness, and inferior aqueous dispersion (Khan et al., 2015; Silwana et al., 2016; Sturala et al., 2018; Beitollahi et al., 2019; Pei et al., 2020). Consequentially, there has been consensus in exploring mitigatory strategies such as the primal conversion of graphene to functionalities-rich GO.

Preparation of Graphene Oxide

The principal approaches for GO synthesis are based on (improved/modified) Hummers method where pyrolytic graphite precursor is subjected to strongly oxidizing and acidic conditions prior to sonication (Zaaba et al., 2017; Lee et al., 2019c; Eigler and Hirsch 2014; Chang and Baek 2017). The resultant GO is hydrophilic owing to the abundant presence of oxygen functionalities. Accordingly, GO is endowed with improved solvent dispersibility and a predisposition for architectural modulation through functionalizing nanomaterials (Bahadir and Sezgintürk 2016; Muthoosamy and Manickam, 2017). Literature sources abound with detailed properties and synthesis protocols of GO (Mohan et al., 2018; Feicht et al., 2019; Smith et al., 2019; Wongkaew et al., 2019; Turkaslan and Mihrace, 2020). Nevertheless, the prevalence of the functional moieties imparts GO with insulating properties. Therefore, in attempts to circumvent such GO limitation and partially restore native pristine graphene qualities, rGO is prepared instead (He et al., 2018b).

Synthesis of Reduced Graphene Oxide

Several methods are at the disposal of researchers for the reduction of GO to rGO to restore certain properties to near pristine graphene. Distinctly, the methods are either thermal or chemical in addition to EC. Significantly, the thermal reduction has concurrent merits of elimination of some oxygen-containing domains, besides stimulating reestablishment of defects through rehybridization of carbon atoms (Dideikin and Vul', 2019; Oliveira and Morais, 2018). Meanwhile, chemical reduction of GO fosters the worthwhile restoration of prototype graphenic structure, although it introduces structural defects. Apart from that, green and soft reduction technologies continue to be

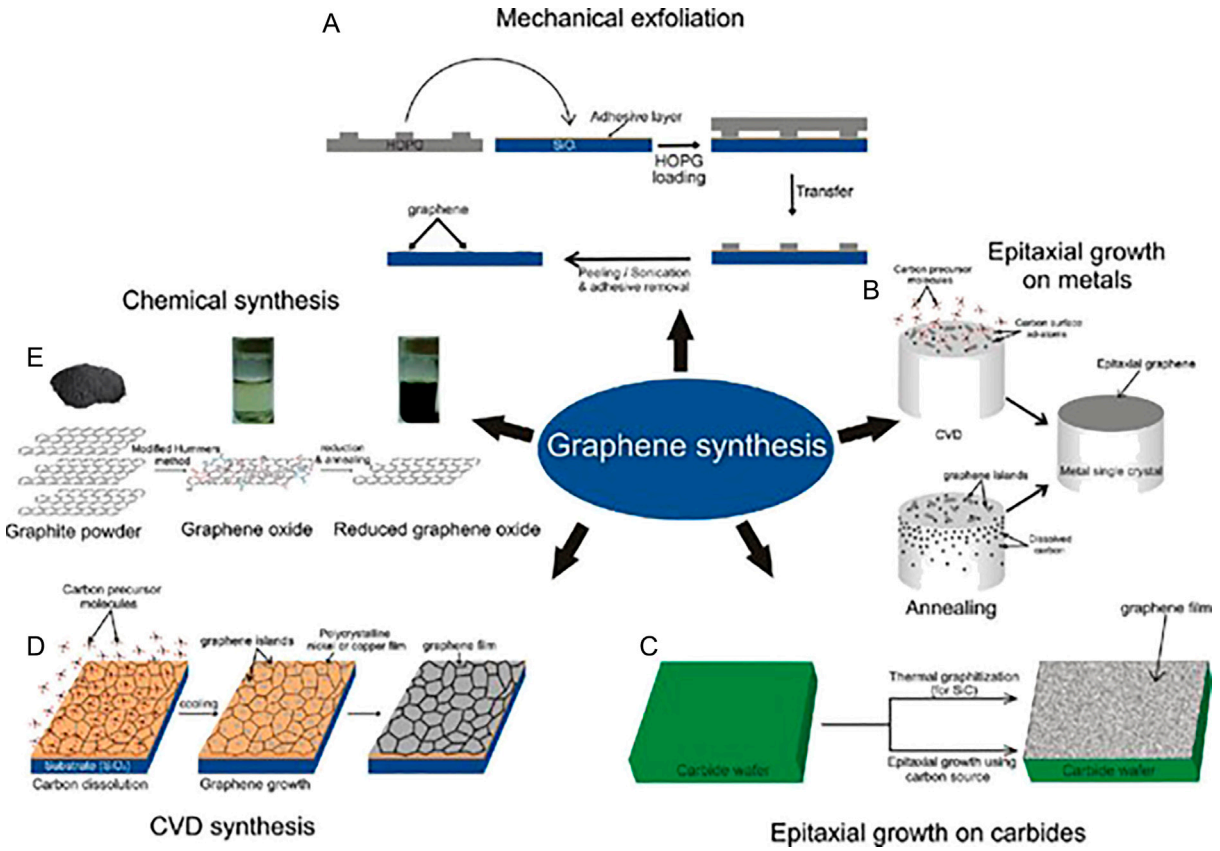

FIGURE 3 | Schematic illustration of different graphene synthesis approaches, **(A)** mechanical exfoliation of graphene flakes, **(B)** epitaxial graphene growth on metal crystal, **(C)** epitaxial growth on carbon sources like silicon carbide wafers, **(D)** CVD method utilizing metal foils to prepare graphene possessing large surface area, and **(E)** chemical synthesis of graphene from graphite oxide. Reproduced with permission from (Jariwala et al., 2011). Copyright 2011, American Scientific Publishers.

attractive. Relatively, thermal reduction is a preferred method while EC reduction is appealing since it promotes tuning of material properties using green route (Cinti and Arduini, 2017; Su et al., 2018). **Figure 4** shows the GO reduction mechanism and the progressive change in oxygen functionalities.

Synthesis of Nitrogen-Doped Graphene

As much as the development of N-doped graphene is concerned, prevalent strategies are variant. Among them are CVD with ammonia gas, nitrogen plasma annealing of graphene, heat conditioning of graphite oxide using melamine, electrically huge energy treatment in ammonia, and hydrothermal tempering involving nitrogen in the form of urea (Lei et al., 2017).

Functionalization

Functionalization with the sole purpose of tuning graphene-based nanomaterial chemicophysical characteristics such as reactivity, electrochemical activity or resistivity, surface energy, and electronic structure has been a subject of research interest for decades. Thus, functionalization has been accomplished either via covalent means or noncovalent interactions. Covalent functionalizing entails the incorporation of variant functionalities onto the graphenic basic structure through attaching by primarily covalent bonds. The incorporation of other entities occurs through the nonmetallic heteroatom replacement of carbon, free radical addition to conjugated bonds, and edge oxygenated moieties reacting with other functional materials. Meanwhile, intermolecular forces viz π-anionic attraction, hydrogen bonding, π–π stacking, van der Waals forces, and hydrophobic interaction are the principal contributors toward noncovalent narrative. A distinctive characteristic of the noncovalent functionalization is that it does not interfere with the graphitic structure while entrenching it with functionalities (Georgakilas et al., 2012; Eigler and Hirsch 2014; Xu et al., 2017; Lawal 2018). Furthermore, graphene is adorned with semiconductor properties despite the absence of bandgap energy. The opening of such a null bandgap is a critical feature of graphene derivatization which enhances target analyte detection (Garg et al., 2014; Talirz et al., 2016; Ould Ne et al., 2017; Sturala et al., 2018). **Figure 5** shows the absence of an energy bandgap in pristine graphene which becomes adjustable due to functionalization. Ultimately, the resultant altered product has inherent hybrid and synergistic properties of the initial components which are advantageous while concurrently overshadowing the individual original limitations. Among

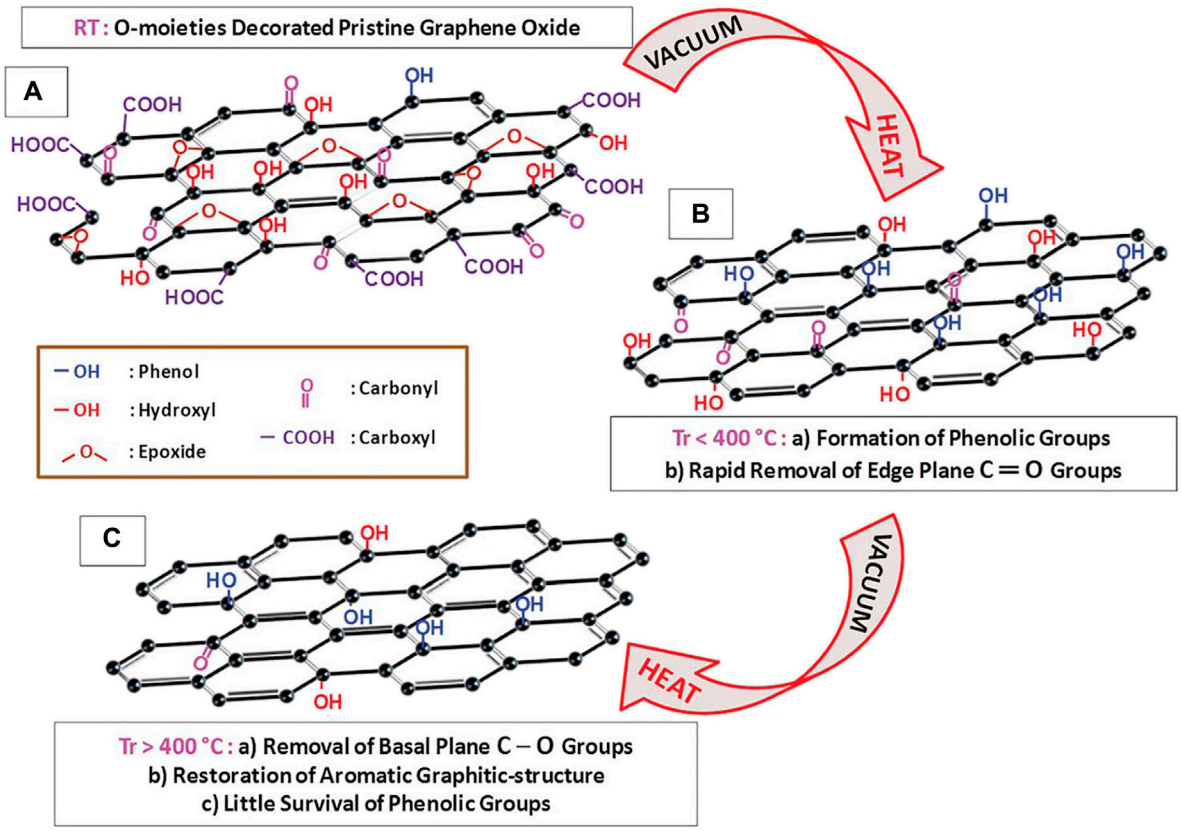

FIGURE 4 | Schematic flowchart of GO reduction pathways. Reproduced with consent from (Khan et al., 2015). Copyright 2015, The Royal Society of Chemistry.

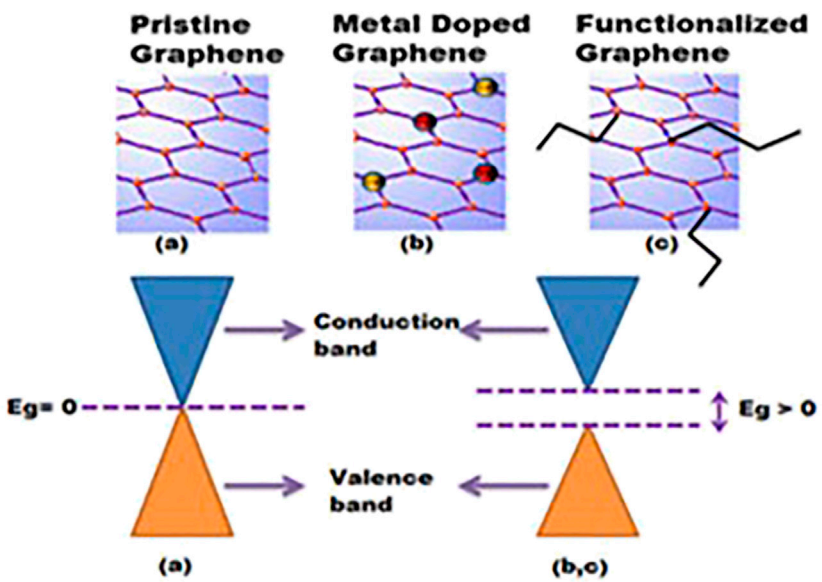

FIGURE 5 | Schematic representation showing **(A)** null bandgap in pristine graphene and **(B)** and **(C)** graphene bandgap opened due to doping and functionalization with different materials. Reproduced with permission from (Garg et al., 2014). Copyright 2014, MDPI.

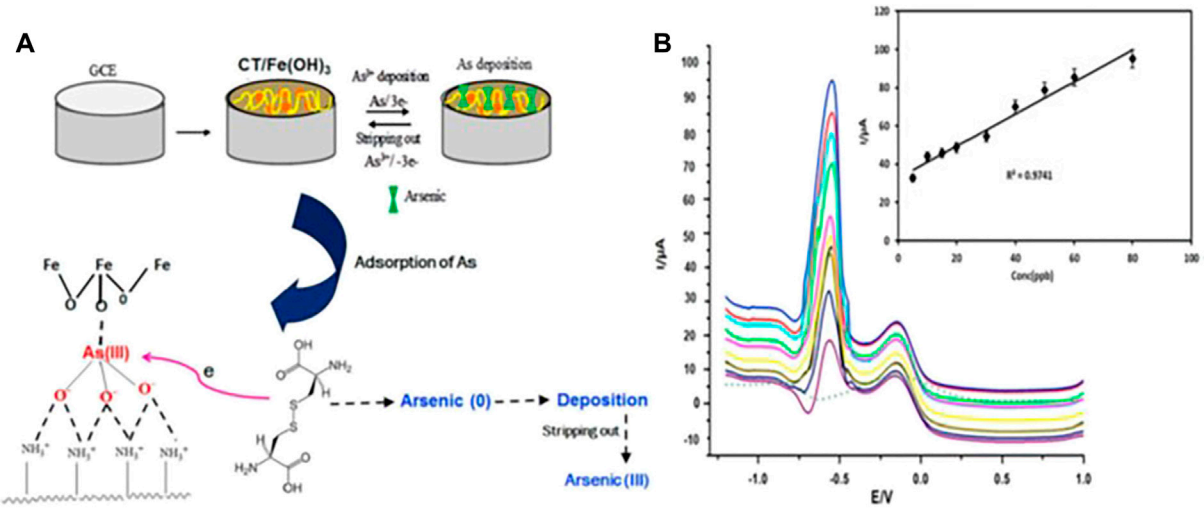

FIGURE 6 | Schematic illustration of **(A)** GC electrode modification by chitosan-$Fe(OH)_3$ composite (CFC) and the As (III) sensing mechanism and **(B)** ASV signal of the CFC modified electrode for various concentrations of As (III) solutions. Reproduced with permission from (Lalmalsawmi et al., 2020). Copyright 2020, Elsevier.

others, these impactful synergies enhance the electrochemical performance of the sensing system.

EC methods have typical drawbacks when utilizing bare electrodes as follows: carbon paste (CP) or glassy carbon (GC) electrodes. Typically, high overpotential and inactivation of the electrode due to the deposition of by-products have been confronted. Notwithstanding, modifying electrode surfaces is an acceptable mitigatory means to counter electrode passivation due to accumulating of reaction by-products and raised overpotential (Hanssen et al., 2016; Campuzano et al., 2019). Electrode surface modification has been accomplished by employing diverse materials. Among them, metal/metal oxide nanoparticles, organic materials including ionic liquids, or carbon nanomaterials especially graphene, SWCNT, or MWCNT have been explored. Other than that, inorganic materials, conducting polymers such as polyaniline (PANI) and heteroatoms doping continue to draw considerable attention of the scientific community owing to numerous merits. Specifically, beneficial synergistic effects that enhance sensor characteristics for the detection of analytes have been realized (Sakthinathan and Chen 2015; Si et al., 2018; Venu et al., 2018). Furthermore, the emanating synergic aftermaths hugely enhance structural morphology and photochemical and electrochemical properties, and the impedance of the electrode surface is diminished while improving preferential accumulation and boosting the electron transport process. Ultimately, the sensor performance regarding sensitivity, selectivity, and stability is improved (Silwana et al., 2016; Bollella et al., 2017; Si et al., 2018). **Figure 6** shows a schematic illustration depicting electrode modification by chitosan-$Fe(OH)_3$ composite (CFC) nanomaterials and the sensing effect.

APPLICATION: ELECTROCHEMICAL DETECTION

Heavy Metal Ions

Uniquely, HM ions can remain in the environment for prolonged timespans since they are not degradable by biological means to form innocuous substances. Furthermore, they are bioavailable and hence have the tendency to be bioaccumulative in the trophic systems and ultimately reach the consumer, the human being. Because of their proclivity to persist in the environment, bioaccumulative disposition, and elevated toxicity (PBT), considerable attention has been directed to HMs based on the detrimental aftermath on ecological systems and the health of the general populace. Even though some HMs such as copper, manganese, nickel, and zinc are an essential trace dietary expectation, exceeding intake levels may have an adverse impact on body functioning. Additionally, when the concentration of some HM ions surpass regulatory limits and there is sufficient exposure to human beings, they may have adverse effects on their health (Stortini et al., 2020). Besides, some HM ions are suspected carcinogens and mutagens. Meanwhile, there have been reports of varying ecological, biota, and human health ramifications due to excessive exposure to some typical metal ions like arsenic, lead, or mercury in parts of the world (Jan et al., 2015; Orr and Bridges 2017; Latif et al., 2018; Pratush 2018; Rehman et al., 2018; Wan et al., 2020). Moreover, their mortal mode is through complications, impairment, or damaging of critical body organs such as liver, reproductive system kidneys, lungs, heart including the central nervous system, and the skin (Zhou et al., 2018; AL-Gahouari et al., 2020; Raril and Manjunatha 2020). Accordingly, for the sake of protecting the environment and for human health safety, timeous detection

(and removal) of harmful HM ions surpassing international guideline levels in the media is of critical importance.

Functionalization applying small organic molecules boosts sensor performance. As such, Raril and Manjunatha constructed a novel polyglycine-modified graphene paste electrode (PGMGPE) for simultaneous EC detection of the divalent ions of mercury and lead. The researchers realized the enhancement of redox signal for the HM ions by the polymer-modified electrode attributable to superior electron transfer kinetics, thus affirming that there was considerable electrode surface property change (Raril and Manjunatha 2020). Thereupon, the PGMGPE was assessed and it demonstrated satisfactory electrocatalytic activity, good stability, and wide linearity response coupled with low corresponding Hg (II) and Pb (II) detection limits of 6.6 and 0.8 μM, respectively. Furthermore, they applied the fabricated EC sensor for the determination of the foregoing HM ions in water and blood serum samples where the recovery was commendable.

Numerous research efforts have been explored exploiting the interlinked microporous nature of three-dimensional nanocomposite structures which improves the effectual surface area and reactive sites for collection/accumulation of targeted substances. Likewise, there is a powerful synergism between graphene and the functional material plus smooth charge carrier movement since the interconnected graphenic network provides unimpeded channels enhancing the sensitivity and selectivity of the modified detection system (Yan et al., 2015; Wang et al., 2015; Guan et al., 2018). Distinctively, Shi et al. (2017a) studied a facile electrode alteration based on a 3D graphene network integrated with bismuth nanoparticles toward multiple HMs sensing. Significantly, wide linear ranges of 1–120 μg L^{-1} for both Cd (II) and Pb (II) with 40–300 μg L^{-1} for Zn accompanied by LOD of 0.05, 0.02, and 4.0 μg L^{-1}, respectively, were proclaimed. They reckoned that the diminished limits, improved sensitivity, selectivity, and other properties of the proposed sensor were associated with the boosted active metal cations binding sites of the porous graphene framework an enhanced path for charge mobilities and bismuth-graphene intensified conductivity synergy. In another study, Xiao et al. (2016) via a self-assembly method constructed a graphitized mesoporous framework and investigated its potential applicability for on-site sensing of HMs contaminants present in aqueous media. The modified bismuth mesoporous graphene framework Nafion bound (Bi/MGF-Nafion) electrode showed enriched properties such as elevated sensitivity (0.437 and 0.210 μA L $μg^{-1}$), 0.3 and 0.1 μg L^{-1} LOD over a broad linear function of 2–70 and 0.5–110 μg L^{-1} for the divalent cadmium and lead correspondingly. Notably, they deduced that the enhancement in properties was linked to the combinational impact of *in situ* coated bismuth with adhesive Nafion and the 3D mesoporosity nature, superior electrical conductivity, and raised active surface area of MGF.

Similarly, Al-Gahouari et al. explored the effects of modifying GCE using a 3D nanohybrid of electrochemically (E) rGO combined with MWCNTs. This was done via covalently functionalizing with an amino acid and L-cysteine (ErGO-MWCNTs-L-cys/GCE) and applied the modified electrode in the monodetermination of lead (Pb^{2+}) ions in water (AL-Gahouari et al., 2020). The authors reported a linearity span of 0.2–40 μg L^{-1} and a calculated sensing limit of 0.1 μg L^{-1} which was recognized to be lower compared to the international standard quantity for portable water. Additionally, by comparison to the bare electrode, the developed sensor system had an upgrade in the electrochemical conductivity, sensitivity, and selectivity which they attributed to synergistic impact among the components ErGO, MWCNTs, and the amino acid. The CV in **Figure 7** validates the proffered deduction while the EIS analysis reveals the combinational effect in lowering the resistance at electrode boundary for electron movement, hence, further affirming that altering electrode surface promoted quick electron relaying by the hybridized material. Correspondingly, Priya et al. designed an HM ion sensor by fashioning the surface of GCE using a nanocomposite material fabricated from GO, the functional group rich amino acid L-cysteine, and a biodegradable but compatible natural biopolymer κ-carrageenan (Priya et al., 2018). They studied the feasibility of the sensing system employing SWASV and hence revealed a broad linearity range of 5–50 nM with comparably low LOD of 0.58 and 1.08 nM and remarkable sensitivity of 1.39 and 1.32 μA nM^{-1} for the divalent Cd and

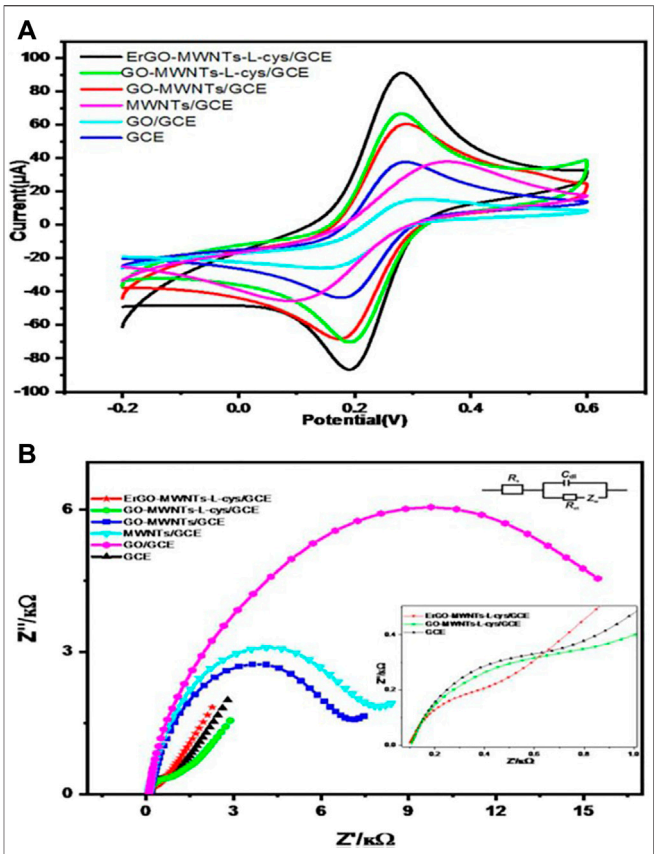

FIGURE 7 | CV and EIS images comparing the behavior of bare GCE as well as differently modified electrodes. Reproduced with permission from (AL-Gahouari et al., 2020). Copyright 2020, Frontiers Media S.A.

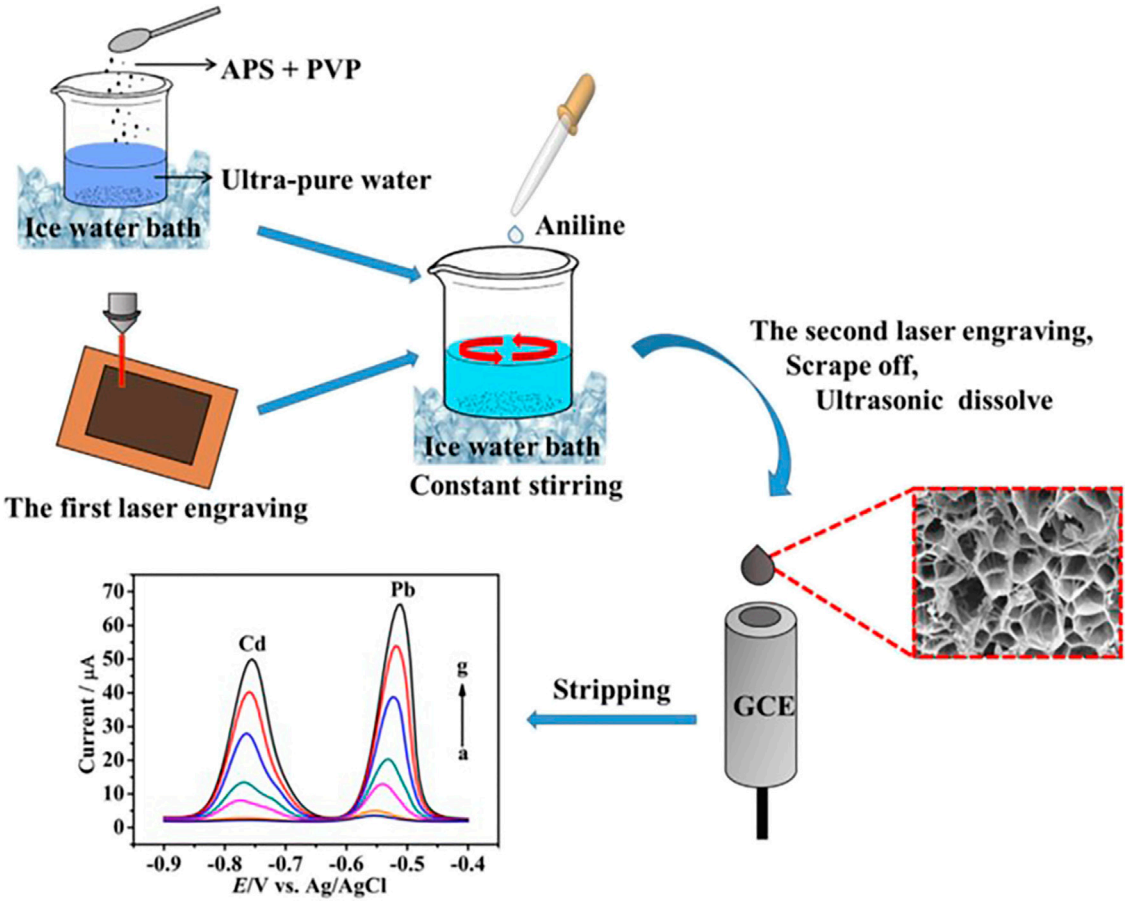

FIGURE 8 | Pictorial schematic of the electrode preparation protocol via N@LEG for the dual EC sensing of Cd (II) and Pb (II). Reproduction was consented from (Lin et al., 2018). Copyright 2018, Elsevier.

Pb, respectively. Furthermore, they ascribed these enhanced characteristics of the modified sensor to the combinational effects of high surface area and functionalized edges of GO, the chelation capacity of the multifunctional amino acid, and the active adsorptive binding of carrageenan toward the HM ions.

Recently, Baghayeri et al. investigated a solvothermally produced graphene-zinc metal-organic framework (G/MOF) platform for arsenic (III) determination. The researchers ascribed the enriched As (III) sensing sensitivity to a fruitful synergistic relationship between the mechanically strong large surface area of graphene and the microporous rich network MOF giving a large active surface area. More significantly, they achieved a detection limit of 0.06 ppb which is more than a hundred times less than the internationally set value while a broad linear span of 0.2–25 ppb was realized demonstrating potential applicability for arsenite detection in real samples (Baghayeri et al., 2020).

Heteroatoms including nitrogen, boron, sulfur, or halogen elements have been incorporated into graphene-derived nanocomposites for modification of electrodes with significant amplifying of properties like electric conduction or electrochemical behavior. Among other contributory factors are the influential dopant-to-carbon electron linkage and the emerging of possible reactive sites for heavy metal ions to accumulate on (Shi et al., 2017b; Guan et al., 2018). Therefore, considerable efforts have been focused on doping of variant nonmetal elements into sensing platforms founded on graphene nanomaterials, exploiting the accruing benefits. For example, Lin et al. designed and investigated a nitrogen-doped laser-engraved graphene electrochemical sensor system using polyaniline, PANI, and polyvinylpyrrolidone, PVP, as the N-doping reagents, for concurrent recognition of lead and cadmium ions employing SWASV (Lin et al., 2018). They attained broad linearity relation in the span from 5 to 380 g L^{-1} and 0.5–380 g L^{-1} for the corresponding Cd (II) and Pb (II) with LOD of 1.08 and 0.16 g L^{-1}. These authors further deduced that there was an integrated effect between the dopant's electron affinity to carbon atoms in the structure and the 3D porous nature of piled graphene layers. Essentially, that raised the effective adsorption surface area, expedited the electron transfer, and ultimately enhanced the electrical conduction, the sensitivity, the response range, and the EC performance of the modified electrode. **Figure 8** shows a representative diagram of the fabrication pathway for the N@LEG electrodes.

Similarly, Lei et al. (2017) designed a nitrogen-doped graphene-modified electrode for joint EC detection of copper (II) and lead (II) ions in aqueous media. Their findings indicated that the proposed sensor showed satisfactory quality with respect to reproducibility plus resistance to interference by chemically similar moieties. Besides, they recorded a calibration detection range of 0.05–2.5 μM with a respective LOD of 11 and 5 nM for copper and lead. Significantly, the researchers accounted for the enriched sensitivity based on the electron interaction between the nitrogen lone pairs and the carbon delocalized π system and increased active sites.

On the other hand, boron as a doping agent is incorporated in a special electrochemical analyte sensing material, boron-doped diamond (BDD) which is hugely acknowledged owing to its reduced background current (bio)chemical stability and wide potential window (Marton et al., 2019). Correspondingly, Pei et al. exploited the uniqueness of BDD and designed a functional independent and innovative electrode based on a BDD substrate, by growing graphene homogenously *in situ* in a vacuum at a raised annealing temperature. The manipulated G/self-standing BDD electrode with minimum defects was studied revealing refined qualities comparative to unaltered GSBDD including a lowly charge transfer resistance (Rct) of the electrode (Pei et al., 2020). They further asserted that the modified electrode attained 0.475 μA L μg^{-1} cm^{-2} sensitivity accompanied by a detection limit of 0.21 μg L^{-1} for lead ions over a spanning linear relation of 1–100 ppb. These boosted properties inclusive of long shelf period were attributed to advantageous collaborative effects of BDD and graphene resulting in increased routes for rapid charge movement. Moreover, this induced an improved active surface area linked to the two-layered graphene manipulation of SBDD, augmented adsorption centers associated with the microporous framework, and upgraded reaction kinetics which is fostered.

Besides nitrogen and boron, fluorine has been recognized as a viable dopant option owing to the higher electronegativity difference with carbon. Such difference potentially prompts increased ionic interaction and spreading of charge densities which stimulate charge transference. Moreover, the presence of the heteroatom causes manipulation of graphene energy gap which ameliorates the conveying of electrons and possible metal-ligand complexing. Subsequently, the synergism promotes the EC performance of the refashioned electrode (Shahzad et al., 2017; Thiruppathi et al., 2017). Accordingly, Thiruppath et al. utilizing CV and SWASV investigated multiple HM ions determination founded on fluorinated GO modified electrode and they reported linear concentration range of 0.6–5.0, 0.3–5.0, and 1.0–6.0 μM for bivalent Cd, Pb, and Hg, respectively. Besides, a recognition limit of 10 nM for both Cd (II) and Pb (II) was submitted and this was confirmation of enrichment of sensor performance shown by peak stripping currents attributable to increased target metal chelation and adsorption centers (Thiruppathi et al., 2017) **Table 1**.

Pesticides

Although pesticides like organochlorine (OCPs) are an integral feature of modern agricultural practices, they have adverse repercussions on human health and the ecosystem owing to their typical characteristics like toxicity. Accordingly, it is paramount to advance environmental protection through monitoring and determinations. Comparably, EC techniques are more appealing credited to their facile status, short response time, cost-effectiveness, and potential on-site application, besides sensitivity and selectivity (Aragay et al., 2012; Koçak et al., 2015; Capoferri et al., 2018; Ren et al., 2019). Because of their predisposition to persist in an ecosystem accompanied by an inclination to be absorbed by aquatic biota consequently, they bioaccumulate and get magnified along the food trophic system. Further, they are lipophilic and cumulatively collected in fatty tissue of organisms; eventually, they may be consumed by human beings through food and water (Fayemi et al., 2016; Hernandez-Vargas et al., 2018; Zamora-Sequeira et al., 2019). OCP such as chlordane, aldrin, lindane, and dieldrin are recognized to be toxic with severe effects on humans and the ecological system. Recent efforts on lindane detection have utilized one-dimensional graphenic carbon in the form of MWCNTs functionalized with either conducting polymer PANI compared to macrosynthetic organic molecule Nylon 6,6 and various metal oxides. The findings of Fayemi et al., based on EC investigations, showed a lowly limit of concentration recognition of 32.0 nM stretching over a linear relationship ranging from 9.90 pM to 5.0 μM. The boosted sensor properties including magnified sensitivity were ascribed to synergy of the integrated properties of the respective nanofibers, MWCNTs, Nylon 6,6, and magnetic material (Fayemi et al., 2016). Even Boke et al. assembled nanocomposites of graphitic carbon nitride (C_3N_4 NTs) and polyoxometalate (POM; $H_3PW_{12}O_{40}$) and developed molecularly imprinted sensors. Through CV and EIS, they realized a linear concentration span from 1.0×10^{-10} to 1.0×10^{-8} M with a recognition limit of 2.0×10^{-11} M for gamma lindane (Pelin Böke et al., 2020).

On the other hand, organophosphate pesticides (OPP) although regulated, excessive use in protecting crops such as vegetables from pests has resulted in contamination of soils and water and eventually food. Furthermore, these pesticides are toxic and reasonably persistent in the ecosystem coupled with being prone to bioaccumulate along the food chain. The major exposure pathways include ingestion of contaminated food and/or water, inhaling sprays, and absorption through the skin while their harmful modal impact is principally nonreversible inhibition of acetylcholinesterase enzyme. Consequently, the neurotransmission activity is hampered with further implications on visual, respiratory, cognitive, sensory, and nervous impairment (Pellicer-Castell et al., 2020; Fu et al., 2019; Zhang et al., 2019c; Sgobbi and Machado 2018; Rajaji et al., 2019; Tian et al., 2018; Heydari et al., 2020). Similarly, carbamates, namely, carbendazim and carbaryl, are used to improve crop production and quality of yields via the elimination of pests. Notwithstanding that, carbamates contaminate ecological systems and are equally harmful to humans and animals on account of their toxicity besides having the same mechanism of disrupting neuronal

transmission with detrimental effects including fatalities (Santana et al., 2019; Oliveira et al., 2020; Rahmani et al., 2018). Even though techniques currently being employed including chromatography are accurate and sensitive, they inherently have drawbacks. Among others, the techniques are laboratory-based, arduous sample preparation; they require certified personnel to operate and inappropriate for local analysis. Therefore, it is paramount to instantaneously detect the presence of different pesticides utilizing cost-effectual, portable, elevated sensitive, and selective devices especially within the aquatic media to enable remedial measures to be instituted when their presence exceeds permissible limits (Govindhan et al., 2014; Capoferri et al., 2018; Hernandez-Vargas et al., 2018; Willner and Vikesland 2018). Remarkably, variant innovative electrochemical technologies have been widely employed in sensing the presence of OCPs as reflected.

Organophosphorus containing pesticides (OPP) specifically malathion, MP, methyl chlorpyrifos, and diazinon are extensively used for the eradication of crops and plant pests in contemporary agricultural practices. Significant amounts of toxic, persistent, and bioaccumulative OPPs ultimately contaminate soil and aqueous media hence have hazardous effects on nontarget species like people. Therefore, detection of such pesticides in food and water with cost-effective, facile, rapid, and portable devices usable in loco is worthwhile (Sgobbi and Machado 2018; Ramachandran and Dhayabaran, 2019; Bolat and Abaci 2018).

Ramachandran and Dhayabaran devised a hybrid chemically polymerized *in situ* composite of MnO_2, polythiophene, and rGO for modifying a GCE intended for sensing MP, an OP categorized pesticide (Ramachandran and Dhayabaran, 2019). Owing to synergistic outcomes among the integrated components including π-π interactive force with MP, enormous effective surface area, satisfactory electrical conductivity, and improved charge transportation, enrichment of EC behavior was realized. The affirmed results were magnified selectiveness, remarkable sensitivity (0.0498 $\mu A\ \mu M^{-1}$), and low LOD of 5.72 nM as well as long shelf span stability thus showing the sensor's potential applicability. In parallel, Tan et al. explored the modification of GCE employing nanohybridized rGO and ionic supramolecular arene for MP determination via EIS, DPV, and other techniques (Tan et al., 2019). Significantly, they reported boosted EC performance of the sensor system including a broad linearity dynamic range of 0.001–150 μM in conjunction with an inferior recognition molarity limit of 0.0003 μM, fast response, specificity, and sensitivity relative to beta-cyclodextrin-functionalized rGO-altered GCE. Additionally, they reckoned that the enrichment in EC properties was ascribable to improved supramolecular preciseness of CP5 toward MP and the synergic outcome of the macrocyclic arene such as fascinating function, complexation host-guest relation based on hydrogen bonds, and π-π interactions. Meanwhile, **Figure 9** shows the comparative development of β-CD-rGO and CP5-rGO and the sensing of MP. Furthermore, a mechanistic sensing route was proposed involving a nitro reduction in a four-electron pathway. Ultimately, the researchers showed the potential viability of the developed system in actual sample analysis.

Pajooheshpour et al. designed an enzyme-free gold-platinum bimetallic nanocluster template on bovine serum albumin (BSA) before integrating it with graphene nanoribbons (Au-Pt@BSA-GNRs). This nanocomposite was used to modify a GCE for the sole purpose of quantification of diazinon (Pajooheshpour et al., 2018). Their CV and SWASV investigation attained a diazinon detection concentration limit of 0.002 μM, over linear function ranges of 0.01–10.0 and 10.0–170 μM. Besides, other properties of the altered electrode such as reproducibility, accuracy, and stability were improved. The refinement in EC properties was attributable to the synergistic impact of the Au-Pt nanoclusters. Effectively, they reduced the analyte transferring distance, generated quantum effects coupled to greatly functionalized protein, BSA, and multiplexed graphene electrical conduction plus vast specific surface area. Also, the fabricated sensor had satisfactory application potential.

In another study on OPP, Yola fabricated hexagonally structured boron nitride quantum dots solely incorporated on GO for manipulation of GCE surface. The innovative BNQDs/GO/GCE manipulated electrode was applied for sensing of MP, diazinon, and chlorpyrifos synchronously (Yola 2019). The researcher asserted improving sensitivity and linear relation span of 1.0×10^{-12} M to 1.0×10^{-8} M and corresponding low LOD for diazinon, chlorpyrifos, and MP were 6.7×10^{-14} M, 3.3×10^{-14} M, and 3.1×10^{-13} M. Remarkably, the magnified EC performance was ascribed to the hybridization synergy of the wide bandgap, electrical conduction, and active surface area of 2D white graphene and novel GO properties.

While exploiting GQDs properties such as superior electron transfer, elevated surface area, and remarkable electric conduction, Mehta et al. attained a comparatively lower parathion low LOD of 46 $pg\ L^{-1}$ within a very broad linearity calibration span of $0.01–10^6\ ng\ L^{-1}$. These results were established when they explored CV and EIS using an SPCE modified electrode with decorated amine-functionalized nanostructured GQDs. Additionally, they submitted that GQDs were homogeneously distributed on the electrode besides acting dually as an electron-donating component and acceptor which enriched the sensor behavior (Mehta et al., 2017).

Rahmani et al. constructed sulfur and nitrogen dually doped (via thiourea) three-dimension graphene decorated with gold nanoparticles composite for electrode modifying hence detection of carbaryl in different matrices. A low LOD of 0.0012 μM was attained within a linear relationship range of 0.004–0.3 μM through EC methods (Rahmani et al., 2018). Moreover, the augmented properties including appropriate lifespan, reproducibility, and satisfactory selectivity were accounted for by the collaborative impact of the hugely porous, enormous particular surface area, and rapid direct electron movement kinetics of 3D graphene evidenced by the amplified anodic peak currents for the altered electrode. Besides, the graphene is interlinked and made functional by the thiourea sulfur and nitrogen atoms relevant for complexation coupled to the excellent electrocatalytic quality of gold nanoparticles. Correspondingly, exploitation of synergistic impacts of noble metal nanoparticles which provide active adsorption centers and excellent electrical conduction, reactivating effect of

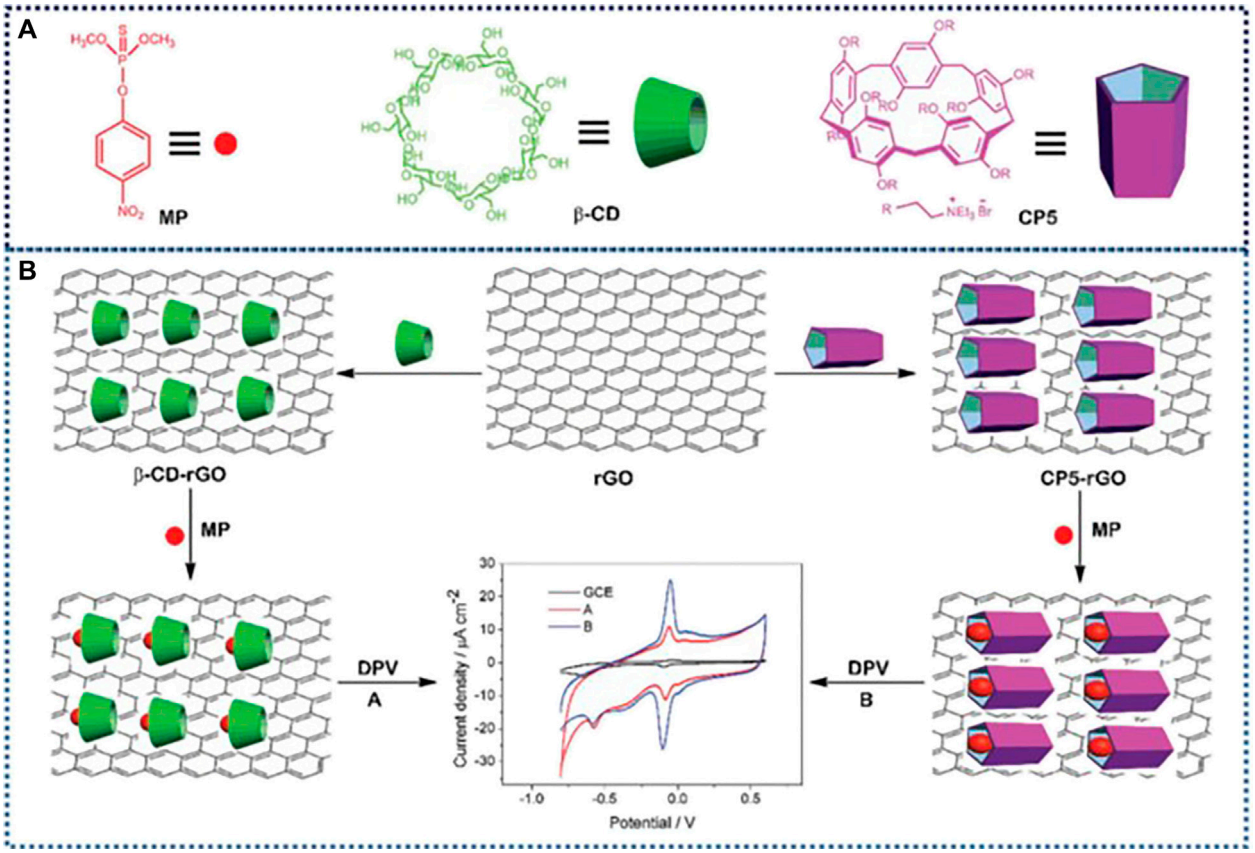

FIGURE 9 | Symbolic diagram of MP, CP5, and β-CD plus the illustrative scheme of CP5-rGO **(A)** and β-CD-rGO **(B)** nanomaterials developed for EC detection route of MP. Reproduction was sanctioned from (Tan et al., 2019). Copyright 2019, The Royal Society of Chemistry.

macromolecule oxime against electrode passivation by the pesticide and doped graphene properties, has been undertaken. Zhang et al. explored the beneficial advantages of the cited materials and fabricated Au NPs-hybridized nitrogen-doped graphene further functionalized with a–SH containing oxime for electrode decoration. They achieved satisfactory sensitivity and reduced dimethoate concentration detection limit of 8.7×10^{-13} M over a broad linearity function range, 1.0×10^{-12} to 4×10^{-8} M, attributable to combinational advantages of the materials (Zhang et al., 2017).

Emerging Pollutants

Emerging pollutants of concern refer to newly discovered compounds, already recognized chemicals that are still being studied to fully establish their ecological and human health implications particularly in conjunction with those recently found. Furthermore, there may be purely present-day issues cropping up on historically known and accepted "harmless" compounds (Su et al., 2018; Borrull et al., 2019; Álvarez-Ruiz and Picó 2020). Even though natural contaminants are present in ecosystems at diminished concentrations, there is the persistent anthropogenic deposition of these compounds, including pharmaceuticals, personal consumer products, industrial chemicals, pesticides, chemical warfare agents, and illicit drugs. Moreover, several of these emerging pollutants have endocrine disruptive characteristics, hence disturbing the natural hormonal functions. Apart from their ecological and human health implications they also causes different cancers and impairment of reproductive cardiovascular functions on human (Azzouz et al., 2019; Jaffrezic-Renault et al., 2020). Notably, triclosan, parabens (alky) phenols, polychlorinated biphenyls (PCBs), perfluorinated compounds, bisphenol A, phthalates, organo/heavy metals, and other chemicals are among the endocrine interfering category generating distress worldwide (Borrull et al., 2019; Karzi et al., 2019; Álvarez-Ruiz and Picó 2020).

While currently used standard techniques for the determination of endocrine interfering chemicals including chromatographic and spectroscopic are reliable and sensitive, they have limitations. Among them are the need for certified personnel to operate the instruments, arduous sample preparation means, and being laboratory-based, thus not applicable for *in situ* analysis. Given the stated reasons, the detection of emerging pollutants including TCS (alkyl) phenols, PCBs, parabens, and other endocrine interfering chemicals in various media inclusive of water, using enormously sensitive, selective, cost-effective, portable, and fast response devices, remains critical even in present time (Zheng et al., 2018; Du et al., 2019; Moyo et al., 2015; Teixeira et al., 2020; Sk et al., 2019; Butmee et al., 2019).

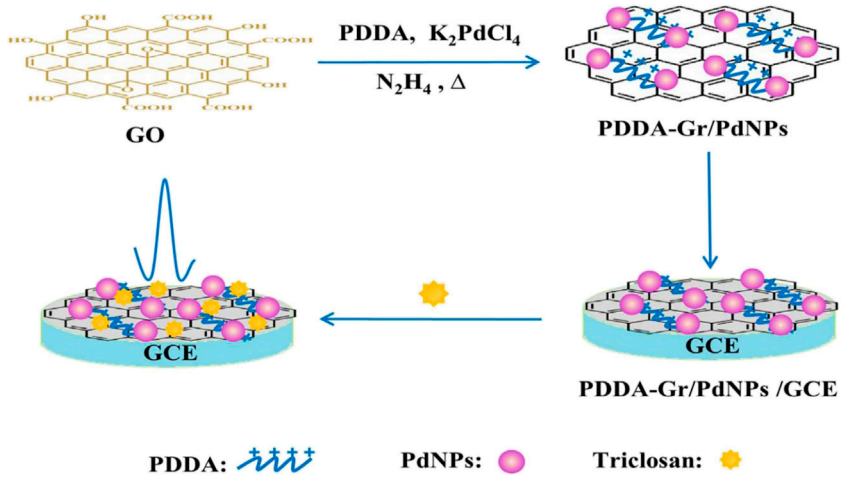

FIGURE 10 | Illustrative scheme of the synthesis method of PDDA-Gr/Pd NPs along with the EC detection of TCS on modified GCE. Reproduced with consent from (Wu et al., 2017). Copyright 2016, Elsevier.

Triclosan

Triclosan (TCS, 5-chloro-2-(2,4-dichlorphenyoxy) phenol) is extensively utilized as a dual preservative and antimicrobial constituent of pharmaceutical, household hygienic goods, and individual care products. Among others are toothpaste, deodorants, soaps, shampoos, lotions, dishwashing detergents, medical disinfectants, and underclothing. Ordinarily, TCS is anthropogenically released into ecological systems and water bodies through wastewater, however ineffectually treated, and it possibly has adverse effects on aquatic biota (Yola et al., 2015; Lehutso et al., 2017; Wu et al., 2017; Zheng et al., 2018; Teixeira et al., 2020). Furthermore, TCS is lipophilic and has been recognized as interfering with endocrine hormonal functioning; hence, it is globally considered a contemporary contaminant to worry about. Apart from that, TCS degradation intermediates and derivatives which include dioxins-like chemicals are potentially harmful owing to their carcinogenic status. Although TCS is regarded as low-level toxic and is regulated by international organizations, its detrimental human impact has been chronicled especially dermal aftermaths as a result of persistent exposure (Jaffrezic-Renault et al., 2020; Du et al., 2019; Moyo et al., 2015; Montaseri and Forbes 2018; Cullinan et al., 2015; Saljooqi et al., 2020).

Wu et al. fabricated nanocomposites consisting of palladium metal NPs, graphene, and a cationic polyelectrolyte poly (diallyl dimethyl ammonium chloride) (PDDA-Gr/Pd NPs) in a facile chemical protocol shown in **Figure 10**. The hybrids were used to refashion the GCE surface and evaluated through CV and DPV for the quantification of TCS. They established a TCS recognition concentration limit of 3.5 nM over a linearity correlation (9.0 nM–20.0 μM), with a remarkable shelf lifetime and satisfactory reproducibility. Particularly, they attributed the enriched sensor performance to the collaborative impact of the constituent material properties such as the good catalytic activity of Pd NPs and superior graphene conductivity and active surface area which enhanced electron transport speed. Besides, the viability of that sensor system was assessed in actual aqueous media samples (Wu et al., 2017).

In a different investigation, Saljooqi et al. fabricated a magnetic iron oxide (Fe_3O_4)-functionalized GO before coating with gold and polypyrrole (Fe_3O_4@Au-PPy/GO) for GCE modification. The modified electrode was used in studying the quantification of TCS through EC techniques such as CV and DPV (Saljooqi, Shamspur, and Mostafavi, 2020). Their findings indicated marked sensitivity, long-term stability in addition to an LOD, and calibration range of 2.5×10^{-9} M and 0.01–1.0 μmol mL^{-1}, respectively. Distinctly, the enhanced performance of this sensor configuration was ascribed to combinational effects of the original properties of the hybrid materials.

Meanwhile, Akylidirim assembled a novel NC integrating through a hydrothermal strategy, silver NPs, with graphitic carbon nitride, C_3N_4, GQDs, and an ionic liquid (IL) (Ag NPs/C_3N_4 NTs@GQDs/IL) as electrode modifier (Akyıldırım, 2020). The researcher employed the modified GC electrode in the determination of TCS via CV, DPV, and EIS, subsequently reporting a low LOD of 2.0×10^{-12} M and a linear response spanning from 1.0×10^{-12} to 1.0×10^{-8} M. The Ag NPs/C_3N_4 NTs@GQDs/IL nanohybrid potentially exhibited integral properties emanating from the individual composite materials. These included the large electroactive area and outstanding conductivity of GQDs, the excellent ionic conductivity of IL, electron-conducting pathways of g-C_3N_4, and the electrocatalytic effect of Ag NPs toward TCS and the aftermath was rapid electron mobility.

Parabens

Comparably, another category of chemicals that were initially considered less harmful as they are employed as additives for preservation and antiseptic purposes is parabens. Particularly, they are used in cosmetics, personal care, and pharmaceutical formulations as well as food and beverage preservatives; hence,

they find their way into water sources. Nonetheless, parabens have proven to be disruptive to the human endocrine functional system and dermal problems and may have hazardous environmental implications (Kajornkavinkul et al., 2016; Mendonça et al., 2017; Piovesan et al., 2018; Faradilla Wan Khalid et al., 2019; Muñoz et al., 2020).

Piovesan et al. constructed a nanocomposite integrating rGO and gold nanoparticles in a dispersion of chitosan (Au NPs-rGO-CS) toward modifying the GCE surface. CS served concurrently as GO reductant and nanohybrid stabilizer. They applied the adjusted electrode for the detection of methyl paraben (MeP), an endocrine disruptive constituent of PCPs. The CV and EIS results indicated a wider linear calibration range of 0.03–1.30 μmol L^{-1} with respective limits of quantification and concentration detection of 41.73 and 13.77 μmol L^{-1} and superior sensitivity. Additionally, the upgraded sensor performance as evidenced by the magnified anodic peak currents was attributed to synergic effects of the integrated components (Piovesan et al., 2018).

Mendonca et al. described a solvothermally synthesized ruthenium NPs-functionalized rGO for modifying electrode surface character. The integrated rGO-Ru NPs NC-modified GCE was then evaluated for the quantification of MeP using DPV. Enhanced signal for the altered electrode was observed; hence, an LOD and calibration linear range of 2.40×10^{-7} mol L^{-1} and 5.00×10^{-7} to 3.00×10^{-6} mol L^{-1}, respectively, were reported. This was due to the synergism as a result of the integration of individual material properties which facilitated rapid electron transfer rate and improved conductivity (Mendonça et al., 2017). Analogously, Khalid et al. designed a cellulose nanocrystal (CNC)-functionalized rGO NC for electrode modification, using a facile protocol of sonication and drop-casting (Faradilla Wan Khalid et al., 2019). The CNC-rGO/SPE was employed for MeP determination through CV, DPV, and EIS. In this instance, the acceptable film-forming qualities and antiadsorption ability of CNC were beneficial as well as the outstanding electrical conductivity of rGO. The synergic interaction enhanced sensing by the configured electrode through inhibiting MeP from adsorbing onto the surface of rGO owing to π-π functioning, improved selectivity, and fast charge transfer. An LOD of 1.0×10^{-4} M with a concentration span of 2×10^{-4} to 9×10^{-4} M was attained. The sensor system showed reusability potential and proved to be a viable option in actual product analysis for MeP.

Likewise, Munoz et al. composed different dimensional nanocomposites including rGO decorated with platinum nanoparticles (Pt NPs/rGO) as a surface modifier for GCE. They explored through CV and DPV the detection of MeP and reported magnification of sensor performance such as a low recognition limit of 2.5 μM accompanied by a wider correlation range of 5.0–50 μM and elevated sensitivity of 45 μA μM^{-1}. Meanwhile, they concluded that the platinum-functionalized one dimension CNT was the best sensor platform with LOD and linearity in the nanomolar range (Muñoz et al., 2020). Similarly, Santana and Spinelli exploited the benefits emanating from hybridizing GQDs with a natural polymer CS. They modified GCE and investigated through CV and DPV the determination of TCS and MeP concurrently. Recognition limits of 0.03 μmol L^{-1} plus 0.04 μmol L^{-1} for respective TCS and MeP were achieved over a broad functional span of 0.10–10.0 μmol L^{-1}. Moreover, the enrichment of properties was on account of synergism between GQDs and CS (Santana and Spinelli, 2020).

Bisphenol A

Similarly, bisphenol A, BPA (2,2-bis (4-hydroxyphenyl) propane), is a primary ingredient widely employed for the commercial production of macromolecular products viz polycarbonate polymers and epoxy resins. Furthermore, BPA is thus a useful component of packaging containers employed in the food and beverages industries. However, the presence of BPA in different media including water sources has been substantiated while it is partially treated in the water treatment terrain (Zou et al., 2019; Canevari et al., 2019; Yu et al., 2017). BPA has been recognized for its tendency to accumulate and be magnified along the trophic chain besides its persistence within the ecosystem. Recently, BPA has been acknowledged for its adverse impact on the ecology and health of mankind. Specifically, BPA is an endocrine system disrupting compound which imitates the natural estrogens' hormonal system. Concurrently, the toxic chemical further severely impairs the human nervous function, reproductive system, cardiovascular role apart from being potentially a carcinogen (Sk et al., 2019; Li et al., 2017; Butmee et al., 2019; Pang et al., 2020).

Shi et al. devised a single-step EC reduction of GO in which the formed rGO was used to enfold copper (I) oxide, Cu_2O. The GCE was modified with Cu_2O-rGO nanohybrid and assessed through CV in the determination of BPA (Shi et al., 2017a). When compared to Cu_2O/GCE, rGO/GCE, and the bare electrode, Cu_2O-rGO/GCE had good electrocatalytic performance, as evidenced by the high anodic currents. A diminished LOD and wider linearity function of 5.3×10^{-8} M and 1×10^{-7} to 8×10^{-5} M respectively were reported. Furthermore, the enriched sensor properties were on account of the synergistic impact of rGO possessing high electroactive and superior conductivity plus the marked catalytic activity of the metal oxide which facilitated electron transport. The sensor configuration was evaluated to be a viable candidate for BPA sensing in aqueous media.

Similarly, Canevari et al. fabricated hybridized rGO and carbon NPs material through dispersing GO in alcoholic media with CNPs which simultaneously acted as reductant and attachment link to rGO. The CNPs-rGO hybrids were used in SPCE modification then explored the determination of BPA through DPV and EIS (Canevari et al., 2019). The researchers reported a low LOD of 1×10^{-9} mol L^{-1}, a sensitivity of 189.5 μmol L^{-1}, and a broad linear response spanning from 7.5×10^{-9} to 2.6×10^{-7} mol L^{-1}. The rGO-CNPs-modified electrode showed an elevated electrocatalytic response and reduced charge transfer resistance, thus expediting the unimpeded electron transport from the solution toward the electrode. Significantly, such enriched sensor characteristics were due to the synergy premised on the huge electroactive surface area of CNPs and magnificent electrical conductivity of rGO. Moreover, the sensor design proved to be a potential candidate for BPA sensing in drinking water.

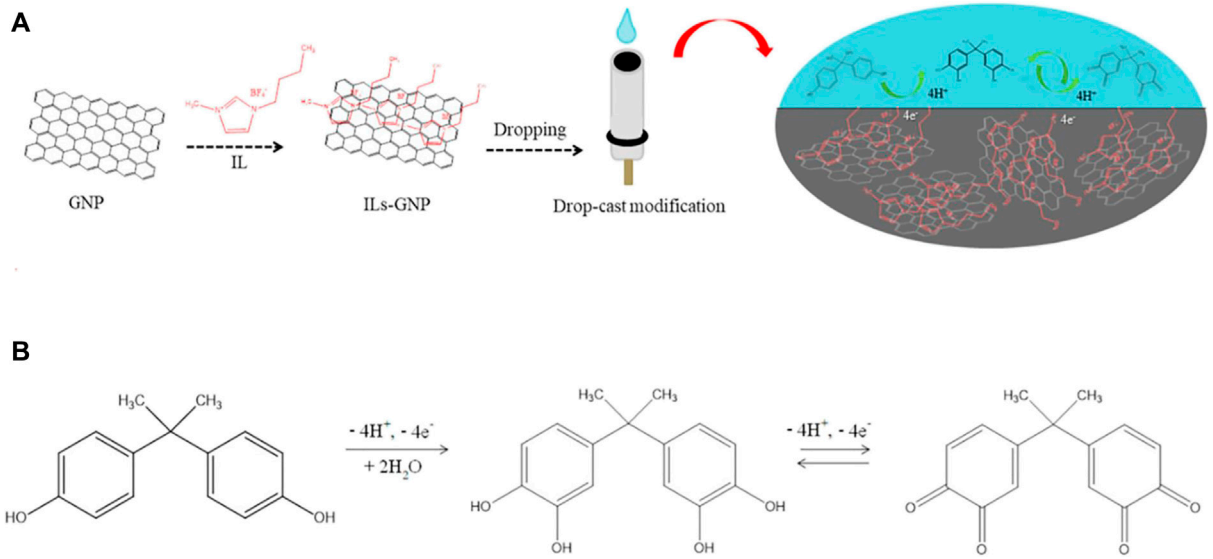

FIGURE 11 | Schematic representation of **(A)** fabrication of IL-GNPs EC sensor and **(B)** EC oxidation detection mechanism of BPA on IL-GNPs/GCPE. Reprinted with approval from (Butmee et al., 2019). Copyright 2018, Elsevier.

Equally, Li et al. assembled a simple GCE modifier integrating reduced graphene oxide, silver metal NPs, and a biopolymer, poly-L-lysine (rGO-Ag NPs/PLL), and then explored the sensor system for BPA detection through CV, DPV, and EIS. Distinctly, a widely varying linear relationship of 1–80 μM with a capped sensing response of 0.54 μM is attained plus satisfactory stability and good specificity. These were attributable to improved electroactive anchoring sites, hydrogen bond linkages, and enhanced electron mobility (Li et al., 2017). Likewise, Butmee et al. fabricated a facile nanocomposite of graphene nanoplatelets functionalized by an ionic liquid (IL-GNPs) as shown in **Figure 11**. The NC was applied for electrode modification prior to investigating BPA sensing using CV, DPV, and EIS techniques. They reported enrichment of properties including a low LOD of 6.4 nM over a linearity function range of 0.02–5.0 μM besides reasonable stability, and enhanced sensitivity was due to synergistic impact owing to elevated ionic conductivity of IL and large surface area of GNPs leading to fast electron mobility (Butmee et al., 2019).

Additionally, **Table 2** shows further findings of recent research utilizing graphene-derived materials toward sensing of pesticides in addition to other emerging pollutants.

Natural Organic Matter

Natural organic matter (NOM) refers to complicated heterogeneous matrices of nonhumic products, humin, humic acid, and fulvic acid other than colloidal matter derived from different hydrological and biogeochemical processes. Moreover, by various means either internal to an ecosystem or exterior like anthropogenic pathways, including microbiological degradation, the formation of natural humic substances principally occurs. Notably, humic acid and fulvic acid have functional component groups viz carboxyl, hydroxyl, phenols, amino acids, among others which influence their behavior in water. Several studies have indicated the variability of NOM in surface waters (Nkambule et al., 2012; Särkkä et al., 2015; Sillanpää et al., 2018; Fakayode et al., 2020).

Significantly, NOM in water is by no means solely toxic nor is it a contaminant. Nonetheless, water's unpalatable organoleptic characteristics inclusive of inferior taste, undesirable color, foul odor, and lack of freshness are attributed to the presence of NOM. Additionally, the organic content is considered responsible for the corresponding and concurrent chemical coagulant expenditure and the regularly undertaken plant backwashing owing to membrane fouling (Moyo et al., 2019; Roosmini et al., 2018; Sarno et al., 2019; Chaukura et al., 2018; Islam et al., 2020). Apart from that, NOM nurtures microbial regrowth and promotes complexation since the terminal functional groups act as ligands which complex with HM ions boosting the bioavailability and toxicity of organometals (Adekunle et al., 2020; Ma et al., 2018; Zhao et al., 2019; Islam et al., 2020). Furthermore, when there is inadequate removal of NOM before either chlorinating or chloramination, it is recognized that the respective chlorine or chlorine dioxide gases react with the organic material forming known mutagenic and carcinogenic disinfectant by-products (DBPs) (Basumallick and Santra 2017; Haarhoff et al., 2010; Nkambule et al., 2009; Ray et al., 2017; Fakayode et al., 2019b; Li et al., 2012; Sillanpää et al., 2018). Besides, the DBPs have other impactful effects, namely, liver damage (Zhang et al., 2019a).

In view of the grave challenges stemming from the variability, indeterminate composition, and the recalcitrant predisposition status of NOM, it is accordingly imperative that innovative technologies be modeled to monitor its prevalence (and removal) to inhibit the formation of DBPs right through the

TABLE 1 | Graphene-based HM ions detection methods, sensing materials, and analytical parameters.

S no.	Sensing (nm)	EC technique	Metal ions	Linearity range	LOD	References
1.	rGO/AuNPs/ TPP	DPV	Cd^{+2}	0.05–300 μM	22 nM	Si et al. (2018)
2.	Nitrogen- doped @LEG/PANI/PVP	SWASV	Cd^{+2}	5–380 g L^{-1}	1.08 g L^{-1}	Lin et al. (2018)
			Pb^{+2}	0.5–380 μg L^{-1}	0.16 g L^{-1}	
3.	PG/Gr/PE	CV, DPV	Hg^{+2}		6.6 μM	Raril and Manjunatha (2020)
			Pb^{+2}		0.8 μM	
4.	ErGO/MWCNTs/L-cys	CV, EIS	Pb^{+2}	0.2–40 μg L^{-1}	0.1 μg L^{-1}	AL-Gahouari et al. (2020)
5.	GQDs/Gr	DPASV	Cu^{+2}	0.015–8.775 μM	1.34 nM	Wang et al. (2017)
6.	GO/κ-Car/L-cys	SWASV	Cd^{+2}	5–50 nM	0.58 nM	Priya et al. (2018)
			Pb^{+2}		1.08 nM	
7.	Nitrogen-doped Gr	SWASV, CV, EIS	Cd^{+2}	10 pM-1 nM	8.0 pM	Liu et al. (2016)
			Pb^{+2}	10 pM-1 nM	5.0 pM	
8.	F@SnO_2/T/rGO	CV, DPV	Cu^{+2}	2–1,000 nM	0.3 nM	Cui et al. (2018)
9.	Fluorinated GO	CV	Cd^{+2}	0.6–5.0 μM	10 nM	Thiruppathi et al. (2017)
		SWASV	Pb^{+2}	0.3–5.0 μM	10 nM	
			Hg^{+2}	1.0–6.0 μM		
10.	Nitrogen-doped Gr	SWASV	Cu^{+2}	0.05–2.5 μM	11 nM	Lei et al. (2017)
			Pb^{+2}		5 nM	
11.	CA/rGO	SWV, EIS	Fe^{+3}	1.0×10^{-10}	2.0×10^{-11} M	Göde et al. (2017)
			Cd^{+2}	-1.0×10^{-8} M		
			Pb^{+2}			
12.	SnF-GO-SPCE film	SWASV	Cd^{+2}	0.1–1.5 μM	0.054 μM	Ruengpirasiri et al. (2017)
			Pb^{+2}		0.026 μM	
			Cu^{+2}		0.060 μM	
			Hg^{+2}		0.066 μM	
13.	GO@Fe_3O_4@2-CBT	SWASV	Cd^{+2}		0.02 ng mL^{-1}	Dahaghin et al. (2018)
			Pb^{+2}		0.03 ng mL^{-1}	
14.	rGO/CS/PLL	DPASV, CV, EIS	Cd^{+2}	0.05–10.0 μg L^{-1}	0.01 μg L^{-1}	Guo et al. (2017)
			Pb^{+2}		0.02 μg L^{-1}	
			Cu^{+2}		0.02 μg L^{-1}	
15.	Flower-like NiO/rGO	SWASV	Pb^{+2}		0.01 μM	Sun et al. (2019b)
16.	L-cys/AuNPs/NG	SWV	Pb^{+2}	0.5–80 μg L^{-1}	0.056 μg L^{-1}	Cheng et al. (2016)
		CV				
17.	3DGF/Bi NP film	SWASV	Cd^{+2}	1–120 μg L^{-1}	0.05 μg L^{-1}	Shi et al. (2017b)
		CV EIS	Pb^{+2}	1–120 μg L^{-1}	0.02 μg L^{-1}	
			Zn^{+2}	40–300 μg L^{-1}	4.0 μg L^{-1}	
18.	Fe_3O_4@TiO_2@NG@AU@ETBD	SWV, CV	Pb^{+2}	4×10^{-13}–2×10^{-8} mol L^{-1}	7.5×10^{-13} mol L^{-1}	Liu et al. (2017)
		EIS				
19.	Fe_3O_4/GN//f.GE	SWV, CV	Pb^{+2}	0.001–0.5 nM	0.0123 pM	He et al. (2018b)
		EIS		0.5–1,000 nM		
20.	CS@3DrGO@DNA	EIS	Hg^{+2}	0.1–10 nM	0.016 nM	Zhang et al. (2016)
21.	Bi/Nafion/rGO/AuNPs	CV	Cd^{+2}	1.0–90 μg L^{-1}	0.08 μg L^{-1}	Zhao et al. (2017)
		SWASV	Pb^{+2}		0.12 μg L^{-1}	
22.	N-doped/rGO/MnO_2	SWASV	Hg^{+2}	0.01–0.2 μM	0.0414 nM	Wen et al. (2018)
23.	AuNPs/rGO/DNA	CV	Hg^{+2}	0–2,000 nM	0.04 nM	Zhang et al. (2018b)
24.	PTh-afGQDs	CV, EIS	Hg^{+2}	1 pM–1 μM	0.6 pM	Tian et al. (2020)
25.	IL/GO	SWV	Cd^{+2}	2.4–70 ppb	0.33 ppb	Pandey et al. (2019)
			Pb^{+2}	5–15 ppb	0.42 ppb	
26.	IL-CNT-GF	DPASV, CV, EIS	Cd^{+2}	0.001–1 μM	0.1 nM	Dong et al. (2017)
			Pb^{+2}	0.001–1 μM	0.2 nM	
27.	rGO-Fe_3O_4	DPASV, EIS	As^{+3}	2–300 μg L^{-1}	0.10 μg L^{-1}	Chimezie et al. (2017)
28.	G/Zn MOF	CV, DPV	As^{+3}	0.2–25 ppb	0.06 ppb	Baghayeri et al. (2020)

rGO: reduced graphene oxide; LEG: laser-engraved graphene; PG: polyglycine; TPP: tetraphenylporphyrin; GO: graphene oxide; PANI: polyaniline; PVP: polyvinylpyrrolidone; T: thiazole derivative; Gr: graphene; CA: calixarene; CS: chitosan; GQDs: graphene quantum dots; 2-CBT: benzothiazole-2-carboxaldehyde; PLL: poly-L-lysine; NO-Ur: nitroso-uracil; GE: garlic extract; PTh: polythiophene; IL: ionic liquid; CNT: carbon nanotube; GF: graphene flower; MOF: metal-organic framework.

water purification terrain (Särkkä et al., 2015; Ye et al., 2018; Pavitt and Tratnyek 2019; Adekunle et al., 2020). Lately, electrochemical strategies have been proposed and gained considerable recognition ascribable to being cost-effective, the potential for actual-time, online analysis, elevated sensitivity, and selectivity. Significant reports in the literature show that considerable attention has been focused on the detection of NOM particularly humic and fulvic acids in aquatic environments using spectroscopic techniques. Nevertheless, much of the electrochemical sensing material has been based on either organic macromolecules or (un)functionalized metal (oxides) nanoparticles (Basumallick and Santra 2017; Ma et al., 2018; Fakayode et al., 2019a; Pavitt and Tratnyek 2019; Adekunle et al., 2020; Fakayode et al., 2020).

TABLE 2 | Graphene-based analyte detection techniques, sensing material, emerging organic analytes, and performance parameters.

S no.	Sensing NC	EC technique	Analyte	Linear range	LOD	References
1.	ZnCdTe QD-rGO	CV, DPV	Carbendazim	9.98×10^{-8} to 1.18×10^{-5} mol L^{-1}	9.41×10^{-8} mol L^{-1}	Santana et al. (2019)
2.	3D-rGO-PANI/	CV	Ethion	1.0–70 μg L^{-1}	0.4 μg L^{-1}	Heydari et al. (2020)
3.	MnO_2/PTh/rGO	CV, DPV, EIS	MP	0.50–10 μL	5.72 nM	Ramachandran and Dhayabaran (2019)
4.	CuO-NPs/3D Gr	CV, DPV, EIS	Malathion		0.01 nM	Xie et al. (2018)
5.	rGO/AChE	CV, DPV, EIS	Carbaryl	0,2–1.0 μmol L^{-1}	1.9 nmol L^{-1}	da Silva et al. (2018)
6.	CP5-AuNPs/ GO	DPV	Paraquat	1.0×10^{-8} – 1.0×10^{-5} M	1.0×10^{-8} M	Sun et al. (2019a)
7.	rGO-PDA-Au NPs-Ag NPs-AChE-CS	DPV	MP	0.016–3,040 nM	9.1 pM	Chen et al. (2019)
8.	Apt/rGO-Cu NPs	CV, DPV	Profenofos	0.01–100 nM	0.003 nM	Fu et al. (2019)
			Phorate	1–1,000	0.3	
			Isocarbophos	0.1–1,000	0.03	
			Omethoate	1–500	0.3	
9.	FTO/PA6/PPy/ CrGO	CV, DPV, EIS	Malathion	500–2×10^4 ng mL^{-1}	0.8 ng mL^{-1}	Migliorini et al. (2020)
10.	BNQDs/GO/GCE	CV, EIS	MP	1.0×10^{-12} to 1.0×10^{-8} M	3.1×10^{-13} M	Yola (2019)
			Diazinon		6.7×10^{-14} M	
			Chlorpyrifos		3.3×10^{-14} M	
11.	PrM/rGO	CV, EIS	MP	0.02–1.55; 1.55–114 μM	1.8 nM	Karthik et al. (2018)
12.	g-C_3N_4/GO/Fc-TED	CV, EIS	Metolcarb	0.045–213 μM	8.3 nM	Xiao et al. (2020)
13.	3DG-Au NPs	DPV, CV	Carbaryl	0.004–0.3 μM	0.0012 μM	Rahmani et al. (2018)
14.	Poly (FBThF)/Ag-rGO-NH_2/AChE	CV	Malathion	0.099–9.9 μg L^{-1}	0.032 μg L^{-1}	Zhang et al. (2019c)
			Trichlorfon	0.0206–2.06 μg L^{-1}	0.001 μg L^{-1}	
15.	Au-Pt@BSA-GNRs	SWASV, CV, EIS	Diazinon	0.01–10.0; 10.0–170 μM	0.002 μM	Pajooheshpour et al. (2018)
16.	3DGOS@$CuFeS_2$	CV, DPV	MP	0.073–801.5 μM	4.5 nM	Rajaji et al. (2019)
17.	CP5-rGO	DPV, EIS	MP	0.001–150 μM	0.0003 μM	Tan et al. (2019)
18.	GCE/VS_2QDs-GNP/CMWCNTs/DZBA	CV, DPV, EIS	Diazinon	5.0×10^{-14}–1.0×10^{-8} mol L^{-1}	1.1×10^{-14} mol L^{-1}	Khosropour et al. (2020)
				1.0×10^{-14}–1.0×10^{-8} mol L^{-1}	2.0×10^{-15} mol L^{-1}	
19.	Ab/GQDs	EIS	Parathion	0.01–106 ng L^{-1}	46 pg L^{-1}	Mehta et al. (2017)
20.	Au NPs/FcDr/rGO	CV EIS	Dichlorvos	0.43–218.4 μM	0.21 μM	Yan et al. (2020b)
21.	NG/Au NPs/MNO	CV, DPV	Dimethoate	1.0×10^{-12}–1.0×10^{-8} M	8.7×10^{-13} M	Zhang et al. (2017)
22.	ZnO NSt@GO	CV, DPV, EIS	MP	0.03–670 μM	1.2 nM	Manavalan et al. (2020)
23.	Au-ZrO_2 –GNs	CV, SWV, EIS	MP	1–100 ng mL^{-1}; 100–2,400 ng mL^{-1}	1 ng mL^{-1}	Gao et al. (2019)
24.	AChE-CS/3DG-CuO NFs	CV, SWV, EIS	Malathion	3 pM-46.665 nM	0.92 pM	Bao et al. (2019)
25.	Au NPs/GOAQ	CV, DPV	Paraquat	0.02–24 μM	6 nM	Kong et al. (2019)
26.	FS-rGO	CV DPV	Fenitrothion	0.005–1.0 μM	0.00019 μM	Özcan et al. (2019)
27.	rGO-CNPs	DPV	BPA	7.5×10^{-9}–2.6×10^{-7} mol L^{-1}	1×10^{-9} mol L^{-1}	Canevari et al. (2019)
28.	GNPs-Au NPs	CV, DPV, EIS	BPA	5×10^{-3}–100 μM	0.027 nM	Zou et al. (2019)
29.	IL-GNPs	CV, DPV, EIS	BPA	0.02–5.0 μM	6.4 nM	Butmee et al. (2019)
30.	Au NPs/rGO-MWCNTs	DPV	BPA	5.0×10^{-9}–1.0×10^{-7}; 1.0×10^{-7}–2.0×10^{-5} M	1.0×10^{-9} M	Yu et al. (2017)
31.	rGO-Ag/PLL	CV DPV	BPA	1–80 μM	0.54 μM	Li et al. (2017)
32.	Cu2O-rGO	CV	BPA	0.1–80 μM	0.053 μM	Shi et al. (2017b)
33.	rGO/Ru NPs	DPV	MeP	5.00×10^{-7}–3.00×10^{-7} mol L^{-1}	2.40×10^{-7} mol L^{-1}	Mendonça et al. (2017)
34.	CNC-rGO	CV, DPV	MeP	2×10^{-4} -9x10^{-4} M	1.0×10^{-4} M	Faradillawan Khalid et al. (2019)
35.	Pt-NP@rGO	CV, DPV	MeP	5.0–50 μM	2.5 μM	Muñoz et al. (2020)
36.	Au NPs-rGO-CS	CV, EIS	MeP	0.03–1.30 μmol L^{-1}	13.77 μmol L^{-1}	Piovesan et al. (2018)
37.	Fe_3O_4@Au NPs-PPy/GO	DPV, LSV	TCS	0.01–1.0 μmol mL^{-1}	2.5×10^{-9} M	Saljooqi et al. (2020)
38.	PDDA-Gr/Pd NPs	CV, DPV	TCS	9.0 nM -20.0 μM	3.5 nM	Wu et al. (2017)
39.	Ag NP/C_3N_4 NT@GQDs/IL	CV, DPV	TCS	1.0×10^{-12}–1.0×10^{-8} M	2.0×10^{-12} M	Akyıldırım (2020)
40.	GQDs/CS	CV, DPV	MeP	0.10–10.0 μmol L^{-1}	0.04 μmol L^{-1}	Santana and Spinelli (2020)
			TCS		0.03 μmol L^{-1}	
41.	rGO-ZnO	CV, DPV	Phenol	2–15 μM; 15–40 μM	1.94 μM	Sha et al. (2017)

(Continued on following page)

TABLE 2 | (*Continued*) Graphene-based analyte detection techniques, sensing material, emerging organic analytes, and performance parameters.

S no.	Sensing NC	EC technique	Analyte	Linear range	LOD	References
42.	ZnO/GO	CV, SWV	Phenol	5–155 **μM**	2.2 nM	Arfin and Rangari (2018)
43.	CoTFPP/GO	CV, DPV	CC	1–220 **μM**	0.17 **μM**	Huang et al. (2019b)
			HQ	1–200 **μM**	0.21 **μM**	

MP, methyl parathion; PANI, polyaniline; PTh, polythiophene; AChE, acetyl cholinesterase; PDA, polydopamine; methyl paraben, MeP; TCS, triclosan; BPA, bisphenol A; CS, chitosan; Apt, aptamer; FTO, fluorine-doped tin oxide; PA6, polyamide 6; PPy, polypyrrole; CrGO, chemically reduced graphene oxide; BN, boron nitride; PrM, praseodymium molybdate; g-C_3N_4, graphitic carbon nitride; Fc-TED, ferrocene containing dendrimer; metolcarb, 3-methylphenyl-methylcarbamate; 3DG, 3-dimensional graphene; FBThF, 4,7-di (furan-2-yl) benzo [1,2,5] thiadiazol; BSA, Bovine Serum Albumin; CP5, pillar 5; VS_2QDs, vanadium disulphide quantum dots; GNP, graphene nanoplatelets; CMWCNTs, carboxylated multiwalled carbon nanotubes; DZBA, diazinon-binding aptamer; Ab, antibody; FcDr, ferrocene dendrimer; NG, nitrogen-doped graphene; MNO, 2-(4-mercaptobutoxy)-1-naphthaldehyde oxime; ZnO NSt, zinc oxide nanostars; CuO NFs, copper (II) oxide nanoflowers; GOAQ, graphene oxide 8-aminoquinoline; CoTFPP, cobalt tetrakis(pentafluorophenyl) porphyrin; CC, catechol; HQ, hydroquinone.

Nitroaromatics

Nitroaromatics, namely, nitrophenol compounds are key ingredients in agriculture and industry. Notwithstanding, nitroaromatics compounds find their way into the ecology hence, contributing significantly to environmental pollution due to their elevated toxicity (Qin et al., 2019; Li et al., 2019). Nitroaromatics such as DNT, TNP, TNT, and NB are used in chemical explosives and landmines. Explosives residues are recognized to cause harmful effects to the central nervous, cardiovascular, and respiratory systems among others (Wen et al., 2018; Jigyasa and Kaur Rajput, 2018; Ramachandran and Karunkaran Yesodha, 2019). Therefore, it is crucial to protect the environment through timeous, target-specific, simple, sensitive detection means. EC techniques have gained recognition due to analyte specificity, sensitivity, portability, on-site, and real-time determinations.

He et al. prepared a sensor for EC determination of nitrophenol based on acetylene black paste and graphene hybrid electrode (GR/ABPE). Through CV, respective linear range and LOD of 20 nM to 8.0 and 8.0 μM were reported (He et al., 2019b). Most recently, Hwa et al. fabricated an EC sensor exploiting halloysite nanotubes (HNTs) and Ag NPs decorated on rGO for modification of GCE. The rGO-HNTs-Ag NPs-configured sensor was examined in the sensing of 4-NP through CV and DPV. Significantly, the researchers achieved a linear response in the concentration range 0.1–363.9 μM, with an LOD of 48.6 nM and sensitivity of 35.25 $\mu A \mu M^{-1}$ cm^{-2}. Additionally, the sensor was found viable when evaluated using different sample matrices (Hwa and Ganguly, 2020).

Similarly, Zhang et al. adopted dual heteroatom doping introducing nitrogen and sulfur into graphene nanoribbons prior to base washing (BW) and then modified a GCE. The BW-NS-rGO NRs/GCE sensor was studied through CV, DPV, and EIS in detecting TNT. The sensor platform recorded a wide linear range of 0.0008–5.1 ppm and LOD of 0.1 ppb. The superb sensing performance is attributed to the dual doping of N and S atoms and full exposure of the rich defective active sites of BW-NS-rGO NRs after base washing, and rGO enables target molecules binding besides its high electrical conductivity; thus, signal amplification was realized. The proposed sensing platform was evaluated and exhibited potential for TNT determination in water samples (Zhang et al., 2018b).

Li et al. fabricated a core-shell GO@polymerized-Mn-porphyrin (GMPP@AMP) nanocomposite for altering GCE surface and the platform was applied for the determination of NB via CV and DPV. Evidently, there was synergistic impact owing to the prevalence of functionalizing nitrogen-containing moieties, π-π porous conjugated caged metalloporphyrin structure, and GO conductivity expediting the high electron transfer capacity, strong mutual affinity, and increased contact area between NB and the mesoporous polymer enhancing the electrocatalytic activity of the sensor. The reported linear range was 0.04–0.24 mM while LOD was 0.243×10^{-6} M and the evaluated sensor exhibited practical prospects for sensing NB in ecological matrices (Li et al., 2019).

Ramachandran, Nair, and Yesodha explored aromatic nitrogen-doped GQDs synthesized via the hydrothermal

treatment of precursor PANI. The modified GCE (N-GQD/GCE) was employed for the detection of TNP through DPV and an LOD of 0.2 ppb (1 nM) was revealed. They concluded that the enhanced sensitivity and selectivity emanate from rich N-doped aromatic structure of the N-GQD which promoted closer and selective molecular interactions with nitroaromatics through ring stacking, π-π interaction, or hydrogen bonding which improved the electrical conductivity and electron transferability. Again, the sensor also differentiated various nitroaromatic species, TNP, DNT, and NP DNT (Ramachandran and Karunakaran Yesodha, 2019).

Polyphenols

Polyphenols including flavonoids, phenolic acids, tannic acid, and polyphenolic amides are abundantly prevalent in fruits, vegetables, beverages, herbs, and spices among others. Further, notable examples viz garlic acid, curcumin, and catechins are readily available. Polyphenols have diverse acclaimed health benefits; however, some may have potential toxicity. Either way, their detection with facile, sensitive, cost-effective, on-site portable devices is worthwhile (Kokulnathan et al., 2018; Ganesh et al., 2019; Manikandan et al., 2019; Ansari and Arvand 2020; Suvina et al., 2020).

Manikandan et al. (2019) configured a sensor based on fluorine-doped GO and modified a GCE. The F-GO/GCE sensor was applied for the detection of caffeic acid via CV and DPV and then realized concentration range and LOD of 0.5–100.0 and 0.018 μM, respectively. Fluorine has elevated electron affinity which leads to the formation of fluorine dopant-to-graphenic carbon electron linkages and generation of reactive centers, hence improving electrical communication. Moreover, the applicability of the sensor was judged to be a potential quality control means for the determination of polyphenols in food and beverages industry.

Analogously, Kokulnathan et al. constructed a hexamine cobalt (III) coordination complex $[Co(NH_3)_6]^{+3}$ grafted onto a rGO NC-modified GCE. The rGO/$[Co(NH_3)_6]^{+3}$ chelate was produced through a sonochemical process. The platform was employed via CV, DPV, and EIS for the determination of a flavonoid, morin (MR) (Kokulnathan et al., 2018). They revealed a wide linear range, LOD, and sensitivity of 0.008–72.35 μM, 1.0 nM, and 4.326 μA μM^{-1} cm^{-2} correspondingly. Notably, the cobalt hexamine complex has excellent electrocatalytic activity attributed to its heterogeneous electron transferability which enhanced the sensor's analytical performance.

Recently, Ansari and Arvand developed a magnetic bar carbon paste electrode (MBCPE) modified using cobalt ferrite magnetic electrospun nanofibers (NFs) and GO and reconnoitred the determination of rutin, a flavonoid. They applied CV and DPV to investigate the behavior of rutin on the modified MBCPE (Ansari and Arvand, 2020). Significantly, they reported two linear ranges viz 0.001–0.1 nM and 1.0–100 nM besides an extremely low LOD of 0.94 pM. Likewise, they ascribed the enriched sensor characteristics to the spinel ferrite's superior electrical conductivity due to swinging of electrons between different valence states of the metals and availing surface redox-active sites for adsorption.

Catechol (CT) has varied health advantages and is regarded as a principal fragment of tea catechins. However, CT is recognized to have potential toxic and carcinogenic characteristics; thus, its determination has been pursued. Suvina et al. (2020) devised an original CT sensor based on lanthanum cobaltite anchored on graphene nanosheets (LaCo/GNSs) and modified a GCE prior to monophenol determination through CV and EIS. The sensor configuration attained LOD of 1.0 nM, sensitivity of 5.68 μA μM^{-1} cm^{-2}, and broad linear range of 0.009–132 μM. Distinctly, the sensor components LaCo and GNSs impacted the sensor analytical performance as LaCo has a nanostructured framework with great biochemical compatibility, superior electrical conductivity, large surface area, rapid electron transfer, and short channels. Conversely, graphene is known for its delocalized π electron system, excellent electron communication, numerous structural defects, and high surface area-to-volume ratio. These properties were synergistically integrated attaining increased surface area, increased analyte affinity, and signal amplification.

Nitrates and Sulfates

Nitrates are key ingredients of fertilizers which are a backbone of intense farming practices. They are also available as a constituent of the natural nitrogen cycle; however, transcend fertilizer applications cause an imbalance. Consequently, excess nitrates are leached into ecological systems including soil and water sources. Distinctively, excessive exposure to nitrates may pose potential risks to human health on account of potential toxicity. Moreover, nitrates also affect ecological balance in water sources leading to adverse aftermaths on aquatic biota due to eutrophication. On the other hand, sulfates are also valuable constituents of contemporary industrial and agricultural practices. Despite that, they invariably contribute to environmental pollution. Therefore, it is critical to enforce environmental protection and safeguard human health, through EC detection techniques which are more appealing attributable to their simplicity, rapid response, high sensitivity, target specificity, portability, and potential actual on-site analysis (Mahmud et al., 2020; Jiang et al., 2020; Li et al., 2020).

Bagheri et al. developed a sensor based on Cu NPs, MWCNTs, and electrochemically prepared rGO where the Cu NPs were deposited on the MWCNTs-rGO matrix to create a platform. The Cu NP/MWCNTs/rGO nanohybrid was utilized in modifying a GCE and then used for concurrent determination of nitrates and nitrites via CV (Bagheri et al., 2017). The authors deduced that the well-dispersed Cu metal on MWCNT-rGO composite contributed to the improvement of the electrochemical activity and the active redox sites. Ultimately, the sensor had high sensitivity and differentiation, while a low LOD of 0.1 μM and a wide linear range of $1–10^{-3}$ μM were achieved. Additionally, the sensor was evaluated proving to be a potential candidate for nitrates/nitrites analysis in samples.

Correspondingly, Wang, Kim, and Cui prepared a nitrate sensor utilizing polyelectrolytes, positively charged poly(diallyl dimethyl ammonium chloride) (PDDA), and negatively charged poly(sodium 4-styrene sulphonate) (PSS) with self-assembled Cu NPs and graphene NSs (Wang et al., 2018). They modified an

electrode surface and then applied the sensor for detection of nitrates through CV attaining sensitivity of 0.2 μA μM^{-1} and detection limit of 7.89 μM. Furthermore, it was considered that the polyelectrolytes stimulated anchoring the graphene onto the glass substrate and the resultant 3D network actuated enhancement of reactive surface area and ultimately the sensor performance. Again, the practicality of the proposed sensor was examined demonstrating promising viability for the determination of nitrates in real water samples.

Yu et al. (2016) designed a sensor based on the electrooxidation of a complex heteropoly blue with poly-$_L$-lysine-functionalized graphene. The platform was employed in modifying GCE prior to investigating the determination of sulfate ions through SW. The determination was undertaken indirectly in the presence of a surfactant cetyltrimethylammonium bromide (CTAB) due to high overpotential. A wide linear range and LOD of 0.8–1,000 and 0.26 μM, respectively, were reported. More so, there was synergism among the blue complex, the surfactant, and graphene which resulted in signal enhancement.

CHALLENGES AND OPPORTUNITIES

Although significant research on graphene synthesis has been undertaken, inherent impediments still exist. Presently, graphene-based nanomaterial preparation methods have prospects for improvement in terms of reproducibility and possible upscaling. The goal remains to synthesize functionalizable graphene-based nanomaterials which would attain preciseness and sensitivity expeditiously though produced through cost-effective means. Furthermore, the fabricated material needs to have prolonged stability and durability under ambient and environmental conditions with the potential to be used again. On the other hand, numerous nanomaterial sensors have been designed, explored, and evaluated at laboratory status but methods for upscaling of nanomaterials to massive production at low cost with satisfactory reproducibility continue to be challenging. Thus, facile but cost-effective graphene-based material synthesis approaches to enable bigger scale production are still an area to pursue (Molina et al., 2016; Nag et al., 2018; Tiwari et al., 2018; Wongkaew et al., 2019).

Utilizing graphene-based material in electrode modulation continues to have drawbacks such as fouling and nonspecific interaction, hence generating other signals. Besides that, agglomeration results in the manifestation of defects particularly when composites are formed integrating organic polymers. Another distinct challenge is the applications in real original matrices which need to be explored further to establish the influence of sample matrix (Sturala et al., 2018; Krishnan et al., 2019; Smith et al., 2019). Currently, the wholesome effects of graphene-derivatized nanomaterials on ecological systems are yet to be fully understood. Moreover, the extent of these graphene-based nanomaterials' impact on human health is being studied. Besides, understanding the toxicity and persistence, it is prudent to prevent deposition of nanoparticle materials into aquatic media while toxicological impact and scientific knowledge gaps of nanographene and its derivatives on the environment are being reduced. Therefore, the question of the fate and dilemma of bioavailability of nanomaterials to aquatic flora and fauna in the environment needs to be interrogated further (Sharma et al., 2020; Lai et al., 2018; Huang et al., 2019a; Song et al., 2016). Apart from that, the absence of international regulatory framework and proclaimed definitions to guide the evaluation of nanomaterials toxicity on the environment, aquatic biota, and humankind retards progress on assessment. Consequently, there is a need for consensus in establishing such guidelines (Huang et al., 2019b; Song et al., 2016).

Windows of opportunities are present given that it is imperative to continuously improve protocols for graphene synthesis to achieve bulky graphene production. Besides, controlled synthesis is desirable to produce crystals of specific chemicophysical characteristics to prevent restacking of graphene and provide outstanding templates for large-scale preparation. Additionally, modification of graphene surface to mitigate against fouling and nonspecific interactions, improve reusability of materials, and enhance reproducibility and repeatability of synthesis processes requires further studying. Moreover, the assessment of selectivity, stability, and sensitivity of graphene-based nanohybrids in unpleasant conditions and complicated environmental matrices of multiplex analytes presents research possibilities. Beyond this, more research to assure the global population of the biocompatibility, zero environmental persistence, and nontoxicity status of graphene-based NMs is valuable. As such, the perpetual application of graphitic materials would hinge on research to evaluate and repress toxicity, thus guaranteeing the absence of any potential health risk to both humans and the ecosystem (Wang et al., 2020; Peña-Bahamonde et al., 2018; Lee et al., 2019a; Tiwari et al., 2018; Lawal 2018; Cinti and Arduini 2017; Willner and Vikesland 2018).

Critical method refinement for NMs development from 2D to 3D graphenic structures and utilization of 3D printing technology remains very attractive since electrical and electronic characteristics are greatly enhanced with diverse possibilities in applications. Furthermore, there is potential in miniaturization of graphene sensors and fabrication of flexible graphene sensor devices for point of analysis of pollutants. Besides, further exploration of applications of GQDs motivated by their superior properties should be rewarding for the scientific community (Molina et al., 2016; Sturala et al., 2018; Su et al., 2018; Zuo et al., 2019). Therefore, the functionalization of graphene-derived NMs with diverse materials continues to be appealing. Hence, further understanding of the interaction between analytes and hybridized graphene derivatives would be generated. Apart from that, the potential EC detection mechanisms for DBPs-inducing NOM, emerging contaminants of concern, and hazardous pesticides enlist exploration. Moreover, various innovative research initiatives coupling functionalized graphene-derived nanomaterials to different technological dimensions to develop improved and cost-effective devices for point of assessment of contaminants of concern are worthwhile.

CONCLUSION AND FUTURE RECKONING

This review evaluated recent electrochemical detection of HM ions, pesticides, and emerging pollutants utilizing different electrodes modified with graphene-derived nanocomposite materials. Apart from that, the review summarized the graphene-based materials methods of synthesis and their functionalization. Likewise, the immediate challenges being encountered in the synthesis and application of graphene nanomaterials have been outlined, thus pointing to envisaged opportunities for future research. Among others, massive scale production of graphene nanomaterials remains a dilemma, while the aspects of reproducibility as well as long-term stability of fabricated sensor systems are daunting. Meanwhile, the totality of the impact of nanosized materials including graphene and its offshoots on human health and environment is yet to be fully documented and international guidelines on ecotoxicity need to be established. Virtually, graphene-derived materials including rGO, 3D graphene, GQDs, and doped graphene remain appealing for nanocomposite synthesis and electrode modification. Enhanced sensor configurations culminate in the development of portable sensor devices with the potential for *point of analysis* and online monitoring of HM ions and organic and emerging pollutants in protecting different media especially food, water, and the environment.

AUTHOR CONTRIBUTIONS

The manuscript was written by CK, while TN, BM, NH, and AA reviewed and edited the manuscript apart from the supervisory functions. Furthermore, TN is the corresponding author on behalf of the authorship. All authors read and approved the final manuscript.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships or otherwise that could be perceived as a potential conflict of interest.

GLOSSARY

AApt aptamer
Ab antibody
AChE acetyl cholinesterase
ASV anodic stripping voltammetry
BN boron nitride
BPA bisphenol
BSA bovine serum albumin
CA calixarene
2-CBT benzothiazole-2-carboxaldehyde
CC catechol
Cl-DNB 1-chloro-2,4-dinitrobenzene
CMWCNTs carboxylated multiwalled carbon nanotubes
CNT carbon nanotube
CrGO chemically reduced graphene oxide
CoTFPP cobalt tetrakis(pentafluorophenyl) porphyrin
CP5 pillar 5
CS chitosan
CuO NFs copper (II) oxide nanoflowers
3DG 3-dimensional graphene
DNB 1,3-dinitrobenzene
DNT 2,4-dinitrotoulene
DPV differential pulse voltammetry
DZBA diazinon-binding aptamer
EC electrochemical;
FBThF 4,7-di (furan-2-yl) benzo [1,2,5] thiadiazol
Fc-TED ferrocene containing dendrimer
FcDr ferrocene dendrimer
FTO fluorine-doped tin oxide
g-C3N4 graphitic carbon nitride
GE garlic extract
GF graphene flower
GNP graphene nanoplatelets
GOAQ graphene oxide 8-aminoquinoline
GO graphene oxiderreduced graphene oxide
GO graphene oxiderreduced graphene oxide
GQDs graphene quantum dots
Gr graphene
HM heavy metals
HQ hydroquinone
IL ionic liquid
LEG laser-engraved graphene
metolcarb 3-methylphenyl-methylcarbamate
MeP methyl paraben
MNO 2-(4-mercaptobutoxy)-1-naphthaldehyde oxime
MOF metal-organic framework
MP methyl parathion
NB nitrobenzene
NC nanocomposite
NG nitrogen-doped graphene
NO-Ur nitroso-uracil
4-NP p-nitrophenol
PA6 polyamide
PANI polyaniline
PCPs personal care products
PDA polydopamine
PG polyglycine
PLL poly-l-lysine
6PPy polypyrrole
PrM praseodymium molybdate
PTh polythiophene
PVP polyvinylpyrrolidone
SWV square wave voltammetry
T thiazole derivative
TCS triclosan
TNB 1,3,5-trinitrobenzene
TNT trinitrotoluene
TNP trinitrophenol
TPP tetraphenylporphyrin
VS2QDs vanadium disulphide quantum dots
ZnO NSt zinc oxide nanostars