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Electrochemical Sensors Based on Carbon Allotrope Graphene: A Review on Their Environmental Applications

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Anthropogenic activity in terms of urbanization, industrialization, and modern agricultural techniques challenges the natural environment in terms of compromise in air pollution and water quality, which lead to hazardous health impacts on human beings. In this context, it is very essential to monitor the air and water quality to a maximum possible extent with maximum accuracy, which is of utmost significance. A significant effect on human health due to pollutants makes their detection in water and air essential. Even though various techniques of monitoring these pollutants are available, proven advantages of electrochemical techniques attract more attention. Because of this, an attempt is made to review some of the latest advances in electrochemical sensing of environmental contaminants, which include heavy-metal ions and pesticides. Electrochemical sensing has been done by using sensors designed with various materials. However, sensors designed with carbon and its allotropes such as carbon nanotubes, graphene derivatives, carbon nanodots, active carbon, screen-printed carbon electrode, and others are reviewed. Even though these sensors are capable of being used in medical analysis, food safety, soil quality, drug detection, *etc.*, the review paper highlights only applications related to environmental monitoring. This review is mainly meant to come up with an understanding of the present-day progress in electrochemical applications based on carbon and its allied materials towards environmental pollutants. This review highlights some of the synthesis techniques of graphene (an allotrope of carbon) and sensor designing along with their performance. This review has established the compatibility in the published literature that graphene and related materials play a significant role in electrochemical sensing of pollutants.

Антропогенна діяльність з точки зору урбанізації, індустріалізації та сучасних сільськогосподарських технологій кидає виклик природньому середовищу з точки зору компромісу в забрудненні повітря та якості води, що призводить до небезпечних наслідків для здоров'я людей. У цьому контексті дуже важливо стежити за якістю повітря та води в максимально можливій мірі з максимальною точністю, що має першорядне значення. Значний вплив на здоров'я людини через забруднювальні речовини робить виявлення їх у воді та повітрі необхідним. Незважаючи на те, що є різні методи моніторинґу цих забруднювачів, доведені переваги електрохемічних методів привертають все більше уваги. Через це робиться спроба переглянути деякі з останніх досягнень в області електрохемічного зондування забруднювачів навколишнього середовища, до яких відносяться йони важких металів і пестициди. Електрохемічне зондування було зроблено за допомогою датчиків, розроблених з різних матеріялів. Однак розглядаються датчики, розроблені з вуглецем та його алотропами, такими як вуглецеві нанотрубки, графенові похідні, вуглецеві наноточки, активний вуглець, виконана методом трафаретного друку вуглецева електрода та інші. Незважаючи на те, що ці датчики можуть бути використані в медичній аналізі, задля нешкідливости харчових продуктів, якости ґрунту, виявлення ліків тощо, дана оглядова стаття висвітлює лише програми, пов'язані з моніторинґом навколишнього середовища. Цей огляд в основному має на меті одержати розуміння сучасного проґресу в електрохемічних застосуваннях на основі вуглецю та суміжних з ним матеріялів щодо забруднювачів навколишнього середовища. У цьому огляді висвітлюються деякі методи синтези графенових матеріялів (алотропної форми вуглецю) та проєктування датчиків, а також їхня продуктивність. Цей огляд встановив сумісність в опублікованій літературі стосовно того, що графенові та споріднені матеріяли відіграють значну роль в електрохемічному зондуванні забруднювальних речовин.

Key words: electrochemical sensing, heavy metal ions, carbon allotropes.

Ключові слова: електрохемічне зондування, йони важких металів, алотропи вуглецю.

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1. INTRODUCTION

Quality of air and water is a predominant factor for human existence in terms of health. An increase in population, rapid urbanization, industrialization, and new agricultural techniques degrades both air and water quality contributing to environmental challenges. Compromised monitoring and unhygienic treatment of waste result in the deposition of pollutants directly or indirectly into an ecosystem. In addition to this, the lack of implementation in government laws regarding pollution control and reduced groundwater have further intensified water scarcity as well as pollution [1–4]. Heavy metals (HM) like mercury, cadmium, lead, and pesticides, emerging pollutants, *etc.* are the pollutants of worry. A biogeochemical mechanism is once the source of heavy metals while they are due to anthropogenic activity (combustion of fossil fuel, mining, municipal wastewater) in aquatic media. However, the usage of pesticides in modern agricultural techniques also acts as pollutants. In addition, emerging pollutants such as personal care products and troublesome endocrine chemicals also are important [5–8]. The toxic nature of heavy metal ions such as Cu, Pb, Hg, and Cd affect the environment. It is reported that exposure to these metals by human beings through water and food is prone to infection in the immune system [9, 10]. Given this, the protection of ecosystems through environmental analysis and monitoring of contaminants is required [11–13]. It is reported that the present techniques of monitoring these pollutants through hyphenated, spectroscopic, and chromatographic methods even though reliable and sensitive their drawbacks in terms of duration and preparatory methods, and high cost limit their operation [14, 15].

In this context, electrochemical techniques play an important role in detecting anthropogenic and natural pollutants with high sensitivity, simple preparation method, low cost, simple operation, short response time, and portable size making them highly potential [16–19]. Analysis of contaminants with basic electrodes endangers certain drawbacks such as slow direct electron transfers and electrode passivation [20, 21]. To overcome these limitations, electrode modification with metal, polymers, nanopolymers with metal oxides, and other carbonaceous materials are preferred. This adjustment helps in the improvement of signal amplification by reducing the over potential of electrochemical reactions [22] support covalent immobilization and ideal biomolecule setting on the electrode surface and allow redox-active sites without any change in the neutrality of enzymes [23].

CNT (carbon nanotubes) and graphene carbon nanomaterials are carbon-based materials. It is reported that nanomaterials derived from graphene are suitable for synthesis techniques that are environment friendly with minimum residual defect and high output [24]. They exhibit high conductivity, large area-to-volume ratio, and rapid electron transfer making them highly potential in various applications. Many reports indicated the role of graphene-derived nanomaterials as electrochemical sensors in energy storage, environmental monitoring, and other applications [25–28].

This paper reported some of the applications during the last five years in electrochemical detection of specific environmental contaminants such as heavy metal ions, pesticides, *etc.* that use platforms derived from graphene.

2. ELECTROCHEMICAL DETECTION

The main principle behind electrochemical detection is to produce electric current through a catalyst coated sensing electrode, when an electrochemical reaction takes place at its surface (Fig. 1).

Electrochemical detection can be taken up by using various techniques such as impedimetric (measurement of impedance) and voltammetry (measurement of current with applied potential) methods. These methods are globally recognized because of their simple operation, high sensitivity, low cost, portable making them highly potential in on-site applications. Voltammetry works on the principle of measuring output current that depends on mass transport by applying voltage in an electrochemical cell. The output current is linearly associated with an appropriate analysis in the sample [29, 30]. This can be further classified into ASV (anodic stripping voltammetry), CV (cyclic voltammetry), and EIS (electrochemical impedance spectroscopy).

ASV is a method of sensing that depends on an earlier stage before the heavy metal ions dissolved in bulk solution drift to an electrode. Based on the applied voltage, heavy metal ions generate elemental metal through electro reduction [31, 32]. For an applied voltage, applied electrons are released by dissolving elemental metals. This produces intense current by diffusing trivalent or divalent cations even for low metal concentrations. It is noteworthy that concentration and stripping current are interrelated [33]. ASV

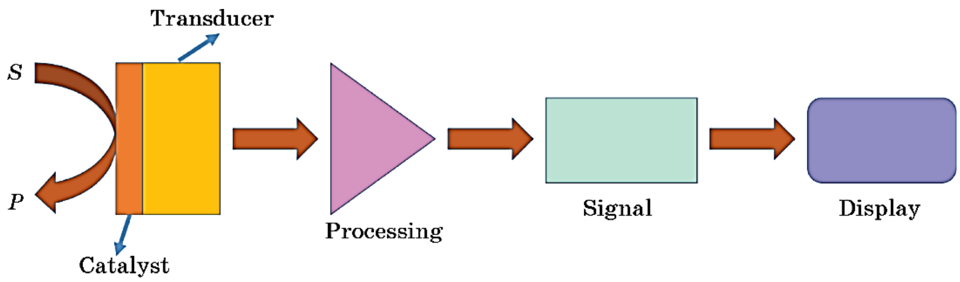

Fig. 1. Electrochemical sensor.

technique has a high capability of sense. An *r*GO/MnO_2 nanocomposite doped with nitrogen was fabricated and applied for GCE modification. On applying this technique for the detection of Hg, the enhanced sensor was reported to have high sensitivity and low detection limit [15]. Many such reports were published with *r*GO/Fe_3O_4 showing enhanced performance and low detection limit [34, 35].

3. DESIGNING OF PLATFORMS FOR ELECTROCHEMICAL SENSORS

Sensor platforms are meant for high selectivity, sensitivity, durability and low response time, cheap and consume low power. In this regard, major efforts based on sensing technique, the material used has been considered by researchers. Keeping this in view, sensor designing, synthesis of graphene derivative platforms, and their functionalization were discussed.

3.1. Sensor Designing

The sensing nature of a sensor is dependent on the reaction between the electrode interface and selected chemical species. Any sensor system essentially consists of a sensing element, recognition element, and transducer [34, 36], which influence the design. The design of a sensor was postulated based on the actual environment and the concentration of an earmarked analyte. It has to promote higher sensitivity and target specific with improved efficiency. It is reported that some of the design strategies include an increase in surface area, analyte enrichment, signal amplification, *etc.* [37–40]. In this context, investigation of modified CPE (carbon paste electrode) engaging magnetic $FeNi_3$/CuS/BiOCl for simultaneous detection of lead and cadmium is of importance. They reported electrical communication between electro-active species and electrode surfaces with the help of superparamagnetic $FeNi_3$ [41]. In a similar way, palladium nanoflower assembled from CNTs and GNSs for modification of an SPE was devised to sense nitro-aromatics, *p*-nitrophenol, *etc.* In this combination, one-dimensional CNTs were embedded into two-dimensional GNSs to form a three-dimensional framework that can curtail agglomeration between CNTs and GNSs during synthesis [42]. This combination was reported as exhibiting superior electrocatalytic activity and capable for reducing nitro-aromatics. This sensor exhibited detection at a nanomolar level and was a high potential for *in situ* assessments. The performance of a sensor can be improved by using nanostructured materials, since they are highly potential in improving surface to volume ratio. In this context, the role of nanopillars, which act as favourable modifiers in case of antimicrobial surfaces [43–45], nanorods of one dimension with diameter between 1 and 100 nm suitable for sensing [20], nanowires of diameter < 100 nm improve signal amplification [46], nanotubes that act as conducting channels between redox sites and electrodes [47, 48] that enhance the performance of sensors, was of significance [49].

3.2. Graphene Derivative Platforms

The graphene family comprises doped graphene, graphene precursors, and its derived associates such as graphene oxide (GO), reduced graphene oxide (*r*GO), and GQD (graphene quantum dots) [50]. Graphene is a carbon allotrope having sp^2-hybridized carbon atoms placed into a two-dimensional hexagonal honeycombed structure [51, 52] with excellent chemical inertness and remarkable electrical, optical, thermal, and mechanical properties [53, 54]. Previous reports indicated that graphene-derived nanomaterials exhibit simple functionalization, large surface area to volume ratio, bio-

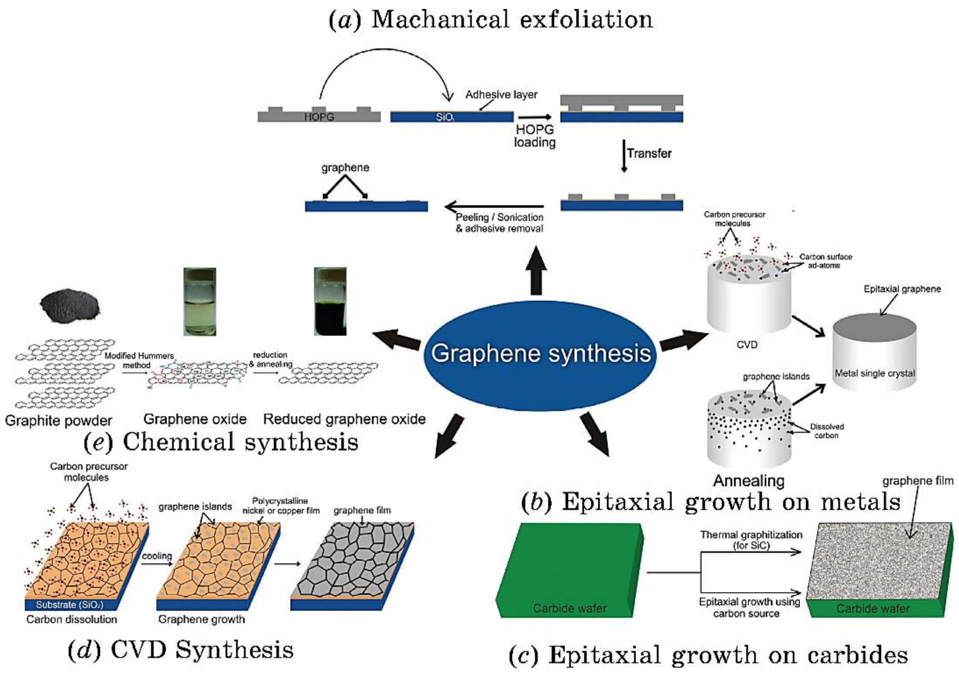

Fig. 2. Electrochemical detection of environmental pollutants based on graphene platforms [79].

compatible nature, and superior electron transport capability [55]. Different methods of synthesizing graphene derivatives exist and they are reported to enhance the sensing behaviour of composite materials (Fig. 2) [56, 57].

Electrochemical methods experience certain drawbacks while using bare electrodes made of carbon paste (CP) or glassy carbon (GC). This includes electrode inactivation due to deposition of byproducts, which can be overcome by modifying electrode surfaces to the possible extent [58]. This modification can be done by using different materials that include carbon nanomaterials especially graphene, single-walled carbon nanotubes (SWCNT), and multi-walled carbon nanotubes (MWCNT).

4. ELECTROCHEMICAL DETECTION OF HEAVY METAL IONS

Heavy metal ions are ions that cannot be degraded through biological means and accumulate in the environment for an extended time. They tend towards being bio accumulative in the ecological system affecting human health. It is a known fact that some of the heavy metal ions like copper, manganese, nickel, and zinc are essential in our regular diet. However, extreme levels of intake affect the impact on body functioning [59]. It is reported that some of the heavy metal ions lead to the incidence of cancer. Also, heavy metal ions such as arsenic, lead, or mercury if exposed more lead to mortality by damaging the liver, kidneys, heart, lungs, skin and nervous system, and the skin [60, 61]. Hence, it is essential to remove heavy metal ions to protect human health and the environment.

The process of adding new properties to material through the addition of small organic molecules enhances the performance of a sensor. In this context, evidenced report on the construction of a PGMGP electrode for electrochemical detection of divalent Hg and Pb ions was of significance (Fig. 3). They reported an increase in redox signal for these ions by the modified electrode with remarkable electrocatalytic activity, stability, and wide linear response [62]. It is also reported that powerful cooperation between graphene and functional material enhances the sensitivity and frequency response of the detection system [63]. A similar study by alteration of facile electrode depending on three-dimensional graphene network integrated with bismuth nanoparticles enhanced sensing of heavy metal ions [64].

A graphitized mesoporous framework was constructed and was tested for sensing heavy metal pollutants in aqueous media [65]. In another report, modified GCE using three-dimensional *r*GO combined with MWCNTs nanohybrid was used in determining Pb^{2+} ions in water [61]. In comparison with bare electrodes, this sensor was

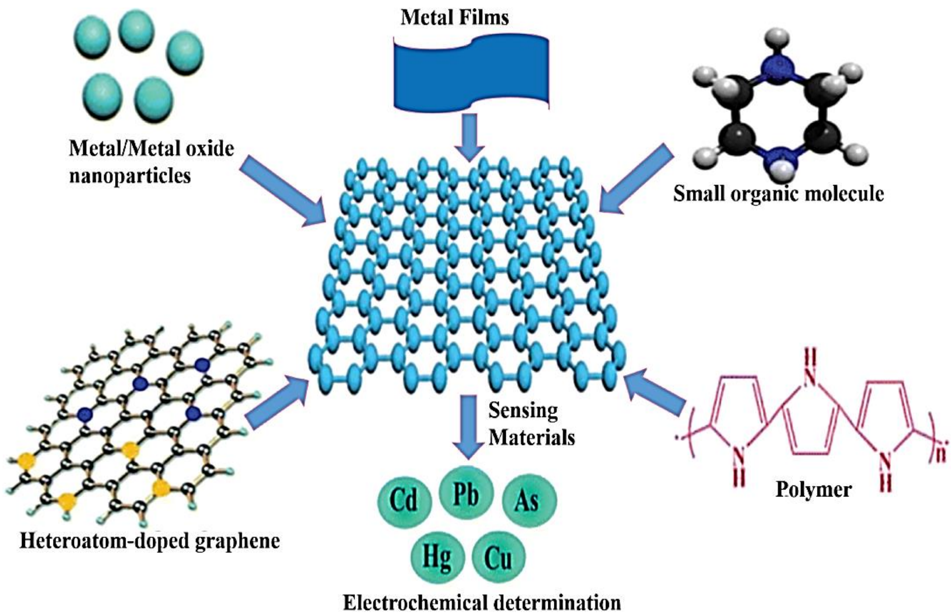

Fig. 3. Graphene-derived nanomaterials as recognition elements for electrochemical determination of heavy metal ions [10, 62].

found to be upgraded in terms of electrochemical conductivity, sensitivity, and selectivity. In another report, thermally produced graphene–zinc MOF for determination of As(III) was reported. This report attributed sensing of As(III) and its sensitivity was due to the strong relation between surface areas of graphene and zinc MOF. The detection limit attained was found to be more than the value set internationally demonstrating the potential for arsenite detection in real samples [66]. Similarly, modified electrodes with nitrogen-doped graphene for simultaneous detection of Cu(II) and Pb(II) ions in aqueous media were reported [67]. Considering all this, it can be inferred that graphene and graphene-derived components play a major role in the electrochemical detection of heavy metal ions.

5. ELECTROCHEMICAL DETECTION OF PESTICIDES

Even though pesticides are essential in modern agricultural techniques, their toxic nature, adverse effect on human health and the ecosystem are of prime concern. Hence, it is very important to monitor them for environmental protection. In this context, electrochemical techniques due to their short response time and low cost make them play a vital role in detecting these pesticides (Fig. 4)

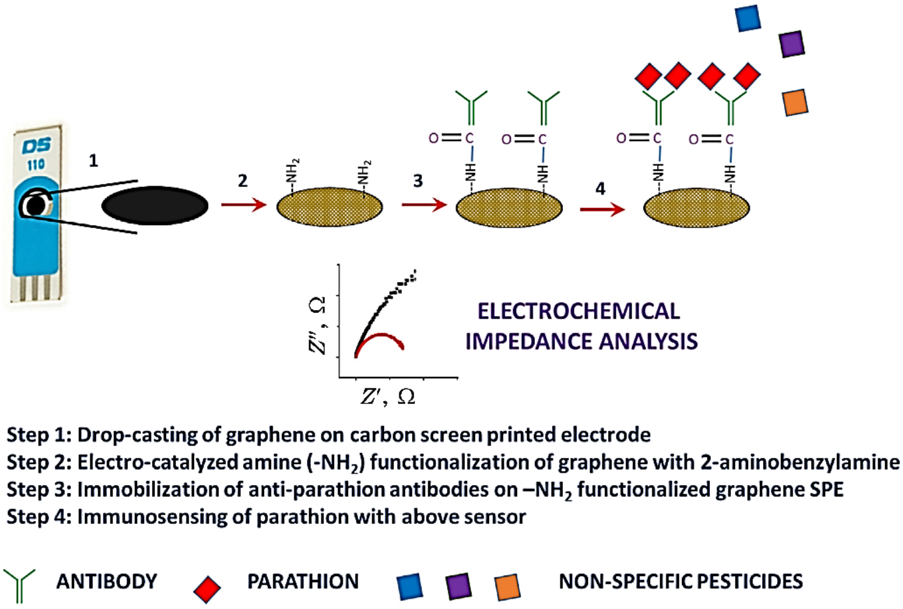

Fig. 4. Detection of pesticides in food using graphene on carbon screen-printed electrode [81].

[68, 69]. As they persist in an ecosystem and being lipophilic, the chances of consumption by humans through food and water are more [70, 71]. Lindane was one of the pesticides found to be toxic that severely affect humankind and the ecological system. Detection of lindane was reported to utilize 1*D* graphitic carbon in the form of MWCNTs, which boosted sensor properties with magnified sensitivity [72]. Similarly, graphitic carbon nitride and polyoxometalate nanocomposites were assembled to develop molecularly imprinted sensors to detect lindane [73].

6. CHALLENGES AND OPPORTUNITIES

Even though significant research on the synthesis of graphene was taken up, barriers still exist. There is a scope for improving the synthesis methods in terms of upgrading sensitivity, cost-effective means, stability, and durability in the surrounding environment. Even though many nanomaterial sensors are being designed, massive production of nanomaterials at low cost with good performance continues to be a challenging task. Hence, low cost and simplified synthesis of graphene-based materials force us to pursue in that direction [74, 75]. At the same time, graphene-based materials in the modulation of electrodes have certain drawbacks that include the generation of unwanted signals. In addition, agglomeration leads to the presentation of defects with composites of organic polymers [76]. At present, the complete effect of graphene-derived nanomaterials on ecological systems was not known. Moreover, the impact of graphene-based nanomaterials on human health is being studied. Apart from knowing toxicity, it is wise to prevent the deposition of nanoparticle materials into aquatic media [77]. Also, need for formulating proper guidelines is suggested in evaluating the toxicity of nanomaterials on the environment and human health [78].

7. CONCLUSIONS

This review evaluated the recent electrochemical detection of HM ions and pesticides 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. Virtually, graphene-derived materials including *r*GO, 3*D* 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.

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