# Review Article
# Carbon allotropes as sensors for environmental monitoring

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Environmental pollutants are a major global concern as they threaten human safety and economic stability. As a result, on-site, low-cost and reliable monitoring is becoming essential. Carbon allotropes have proven their high potential in sensing applications due to their outstanding properties, especially in nanoscale. This article summarizes some of the recent advances in sensing of environmental pollutants using carbon allotropes, especially in the form of carbon nanomaterials. It also provides a critical perspective of the challenges and promising approaches for future applications.

## Introduction

The versatility of the carbon atom lies in the diversity of its chemical bond that can range from $sp^3$, $sp^2$ to $sp^1$ and combinations of them, to yield crystalline or amorphous solids. Over the past two decades, most of the attention in the electrochemical applications of carbon has turned toward carbon nanomaterials (CNMs), with a huge diversity in structure and allotropic forms. These materials can be classified based on their dimensions into zero-dimensional nanoparticles (NPs) such as quantum dots and fullerenes, one-dimensional (1D) structures like carbon nanotubes (CNTs) and carbon nanofibers, two-dimensional (2D) layered materials such as graphene and three-dimensional (3D) structures such as graphene-CNTs hybrids and foams [1,2]. The electrochemical activities of the different allotropes strongly depend on the hybridization state and the structure, as illustrated in Figure 1 for the heterogeneous electron transfer (HET) rates between the electrode surface to the electrolyte, $Fe[(CN)_6]^{4-/3-}$, benchmark redox pair.

Compared with other nanomaterials such as metal NPs [8], metal oxide nanowires (NWs) [9] and transition metal dichalcogenides [10], CNMs exhibit favorable features such as large surface area to volume geometry, high chemical stability, low cost, wide potential windows, relatively inert electrochemistry and rich surface chemistry for a variety of redox reactions [11••]. As a result, CNMs are used in sensors for detection of a wide range of pollutants/contaminants, such as heavy metals, toxins, pathogens, pesticides and other small organic molecules [11,21–23].

CNM-based electrochemical sensors are promising alternatives to current gold standard methods of gas chromatography/mass spectrometry [24] and atomic absorption spectroscopy [25] for obtaining *in situ* and real-time information of pollutants, because of the simplicity of the instrumentation, quick test process and minimal sample preparation. The general components in the electrochemical sensing of pollutants with CNMs are illustrated in Figure 2. The CNMs act as the transducer to convert the chemical input signal to an electrical output. The CNMs can be used in their pristine form or combined with modifiers that play distinct roles in the sensing mechanism, such as improvement of selectivity, conductivity, surface area or catalytic activity.

CNM-based sensors can be broadly classified into electrochemical and electrical sensors based on the configuration and circuit elements. The former includes voltammetric, amperometic and impedimetric devices, and the latter comprises field-effect transistors (FET) and chemiresistors. Traditionally, an electrochemical sensor consists of three electrodes—working electrode (WE), reference electrode (RE) and counter electrode (CE)—immersed in an electrolyte. A redox reaction occurs on the surface of the WE, while the complementary reaction occurs in the CE and the potential is measured with respect to the RE. On the other hand, FET-based sensors consist of a source

**Figure 1**
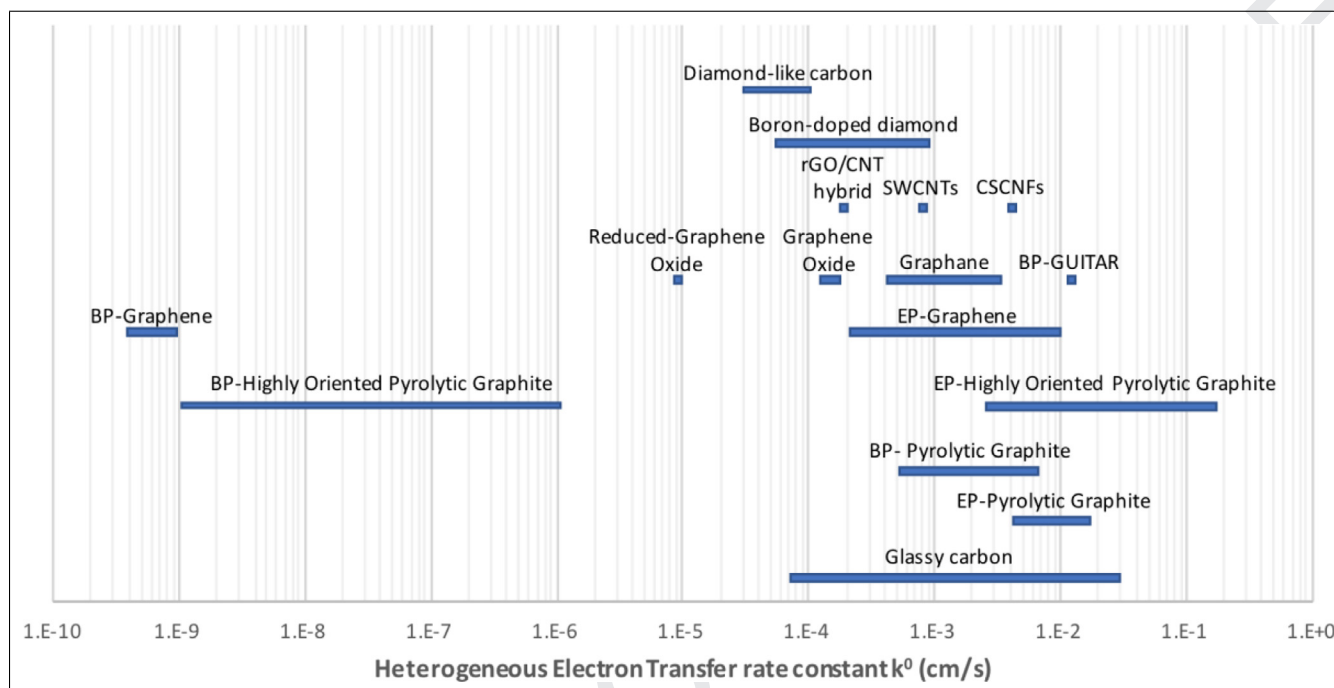


Heterogeneous electron transfer rates for different carbon allotropes in the $Fe[(CN)_6]^{4-/3-}$ benchmark redox pair sensitive to surface structures in the carbonaceous electrodes, such as edge defects and oxygen-containing groups [3–7]. BP and EP stand for basal plane and edge-oriented plane.

(S) and a drain (D) terminal separated by a semiconducting channel, and the current in this channel is modulated by the electric field from the gate (G) terminal. A chemiresistor is a simplified FET without a gate terminal. The modulation of gate voltage in an FET controls the number of charge carriers (holes and electrons) in the channel, thereby affecting its conductance [28]. The FET channel conductance can also be modulated by electrochemical gating under an electrolyte, termed liquid-ion gating [29]. In such electrochemical FET sensor, the concentration of the analyte is quantified based on the channel conductance modulation upon affinity-based binding or adsorption of charged analytes. The advantage of using CNMs as transducer element in FET is that the Debye length, a measure of the field penetration into the bulk, is comparable to the dimensions of these nanostructures, which cause significant modulation of their electronic properties upon exposure to chemicals [30]. This allows for label-free detection of analytes with higher sensitivities and lower limits of detection.

## Recent advances in carbon-based electrochemical sensors for environmental monitoring

Carbon electrodes have been used in electrochemistry since 1962 [31]. After the discovery of fullerene in 1985 [32], many more CNMs have been discovered and designed, most of them being topological distortions or stacking of atomic hexagonal $sp^2$ lattice. Today, the polymorphism of carbon is engineered with more control and understanding than ever before. The recent focus of electrochemical sensing has been primarily for CNMs, most of which are incorporated in a paste [33] or affixed/deposited on the surface of a glassy carbon electrode as a film [19]. Several recent reviews have discussed in detail electrochemical/electrical sensing applications of CNMs, primarily CNT and graphene [1,11,34,35].

## CNTs

Being nanometer size in diameter, CNTs are 1D carbon allotropes that possess a high surface area to volume ratio, providing is a powerful platform for sensors. Since its discovery in 1991 [36], CNTs have proven its wide-ranging applications in different electrochemical and electrical transducers for the detection of a wide variety of environmental targets. The applications of CNTs-based electrochemical and electrical bio/chemical sensors for bacteria, viruses, heavy metals and toxins in water have been reviewed previously [11,37,38]. Single-walled CNTs (SWCNTs) modified with a variety of materials such as metal and metal oxide NPs, metalloporphyrins, DNA, conducting polymer, etc., for highly sensitive, low power, field-deployable and low cost chemiresistors/FETs for monitoring air pollutants such as volatile organic compounds [21•,39] with an aim to use them as general platform for multiplex sensing and electronic nose/tongue. For example, a sensor array of SWCNTs modified with metalloporphyrins could discriminate among structurally similar aro-

**Figure 2**
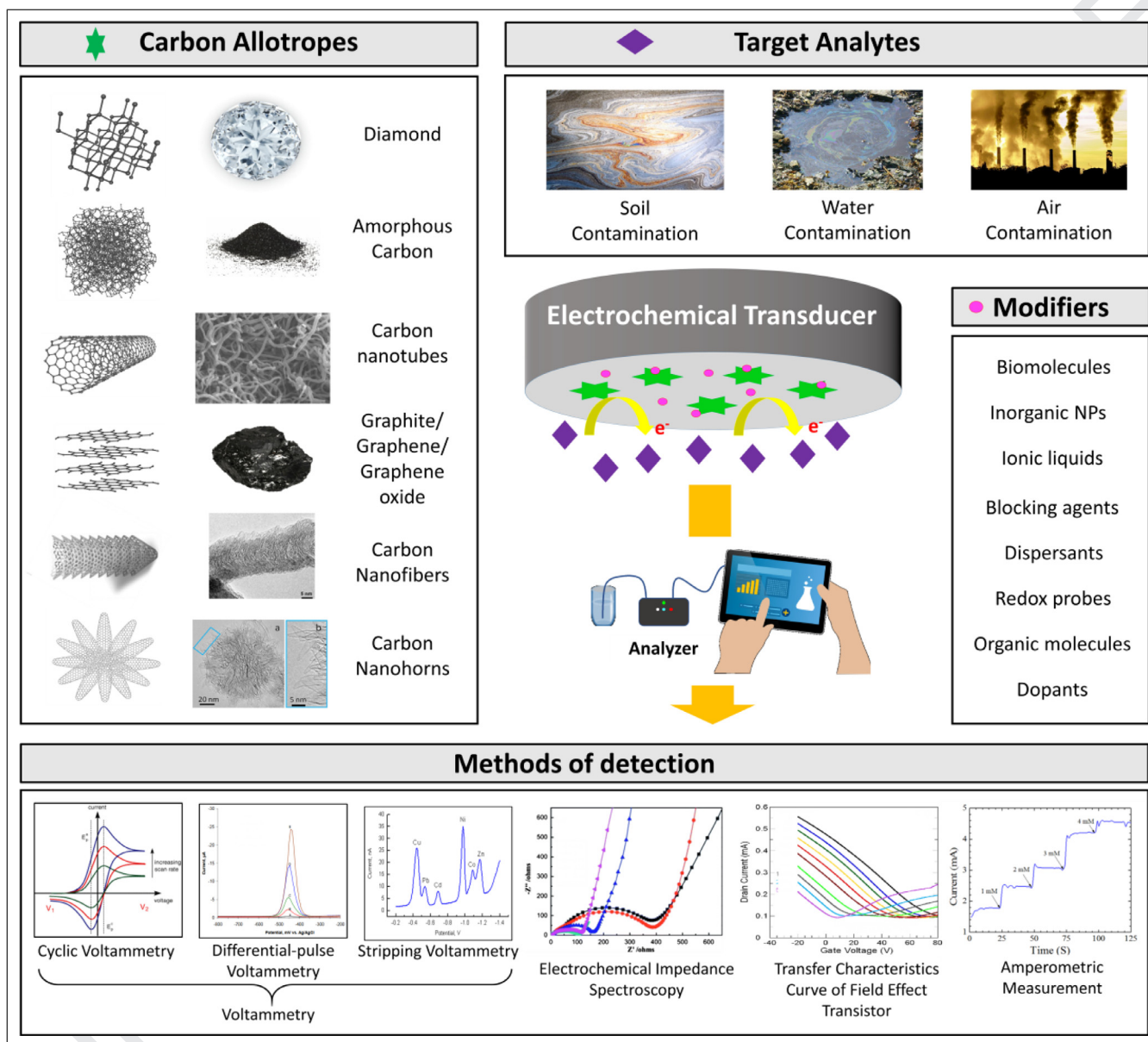


Application of carbon allotropes for environmental monitoring via electrochemical methods. Transmission electron microscopy (TEM) image of carbon nanohorns is from reference [26], © IOP Publishing. Reproduced with permission. All rights reserved. TEM image of carbon nanofibers is reproduced from Ref. [27] with permission of The Royal Society of Chemistry.

matic hydrocarbons such as benzene, toluene and xylene at concentration as low as 500 ppb at room temperature [40].

**Graphene, graphene oxide and reduced graphene oxide**

Since graphene was first synthesized in 2004 via physical exfoliation by Novoselov [41], it has been widely used as electrochemical and electrical transducer in bio/chemical detection [42–45]. While graphene has excellent electrical properties, it is not easy to synthesize and difficult to dis-

perse. As one of the derivatives of graphene, graphene oxide (GO)/reduced graphene oxide (rGO) is attractive not only because of the appealing parental graphene's properties, but also ease of synthesis and its hydrophilic nature and high dispersibility in many solvents. We reported a high sensitivity detection of $Hg^{2+}$ and $Cr(IV)$ using rGO as the semiconducting channel of a chemiresistor transducer modified with a $Hg^{2+}$ specific aptamer [46] and 1,4-dithiothreitol-functionalized gold NPs [47], respectively. The sensors exhibited fast response and detected as low

**Figure 3**
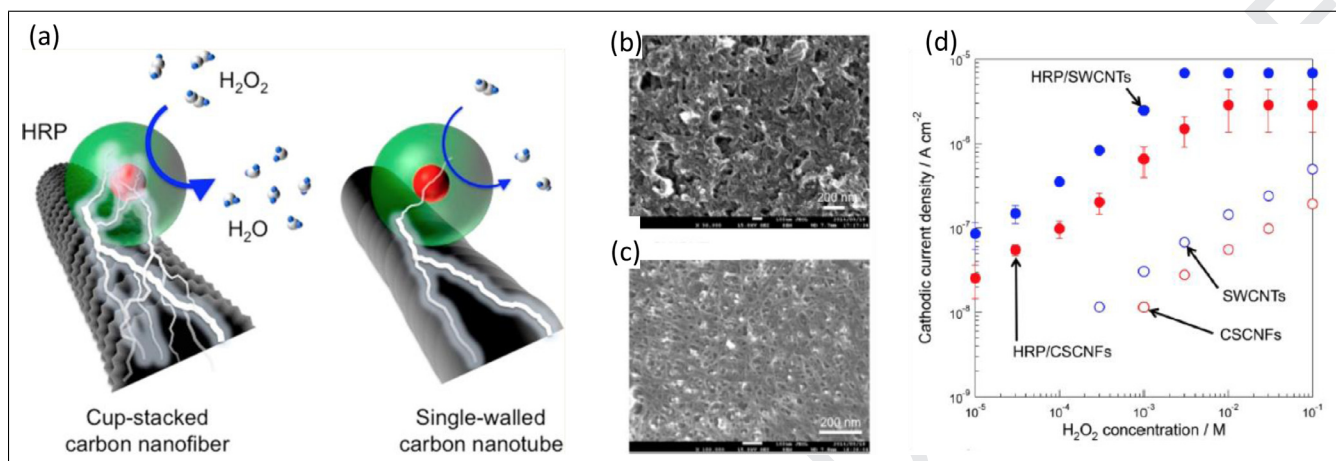


(a) Graphical representation of charge transfer process between $H_2O_2$ and HRP immobilized on CSCNFs and SWCNT. The CNM-HRP sensor allows quantification of cyanide based on the enzyme inhibition by the toxic compound. SEM images of (b) CSCNFs and (c) SWCNTs on glassy carbon. (d) Cathodic current densities of $H_2O_2$ reduction at CSCNF, SWCNT, HRP/CSCNF, and HRP/SWCNT electrodes in 67 mM phosphate buffer (pH 7.4) at +150 mV vs. Ag|AgCl. Reprinted with permission from [4]. Copyright 2016 American Chemical Society.

150 as 0.9 nM Cr(VI) and 0.5 nM $Hg^{2+}$. Similarly, a $Fe_2O_3$
151 NP decorated rGO was suggested for nitrite detection in
152 contaminated water, an environment-unfriendly material,
153 which has a detection limit of as low as 0.015 µM [48].

**Carbon nanohorns**
155 Carbon nanohorns (CNHs) are conical cages that, similar
156 to SWCNTs, are $sp^2$-hybridized, semi-conducting, highly
157 resistant to oxidation, and with equivalent reaction rates.
158 However, they have higher density of defects that fa-
159 cilitates functionalization, they are usually wider, allow-
160 ing free movement of encapsulated molecules [49], and
161 can be mass-produced at room temperature in the ab-
162 sence of potentially toxic metal catalyst. CNHs applica-
163 tions have evolved at a much slower pace than CNTs, be-
164 cause of their aggregation into spherical cluster (Figure 2),
165 which makes dispersion and surface modification diffi-
166 cult. A new approach for separating clusters into individ-
167 ual CNHs was reported recently, which could accelerate
168 their development [50•]. A composite of CNHs and ionic
169 liquid has been used for the amperometric detection of
170 4-aminophenylarsonic acid, a toxic bioaccumulative com-
171 pound. Although the detection limit was not as low as
172 other non-electrochemical methods, the linear dynamic
173 range from 0.5 µM to 3.5 M is much broader, and sam-
174 ple preparation and equipment required are simpler. The
175 sensor showed good accuracy, reproducibility and stabil-
176 ity, coupled with low chemical interference [51].

**Carbon nanofibers**
178 The integration of the versatile biological functions of re-
179 dox enzymes in electrochemical sensing is a technolog-
180 ical breakthrough, but connecting with their redox cen-
181 ter has been challenging. CNTs were first shown effec-

182 tive for overcoming this limitations because of their 1D
183 structure that can penetrate the polypeptide layer [52],
184 and lately, a 1D variant with faster HET rates, the cup-
185 stacked carbon nanofibers (CSCNFs), have gained atten-
186 tion (Figure 3(a)–(c)). The relation of CSCNF and CNT
187 is analogous to that of edge-oriented and basal plane py-
188 rolytic graphite, as the density of edge sites in CSCNF
189 is 1000 times larger than in CNTs. CSCNFs have been
190 modified with horseradish peroxidase (HRP) for ampero-
191 metric detection of cyanide, improving the response and
192 sensitivity toward the analyte. The HRP/CSCNFs elec-
193 trode also provided HET rates that were 1000 times
194 faster than HRP/graphite-casted electrode due to im-
195 proved conductivity. CSCNFs have demonstrated kinetic
196 advantages over CNTs for fast response using enzyme
197 modifiers. However, they exhibited lower cathodic cur-
198 rent (Figure 3(d)), as their diameter is larger and results
199 in lower electrode surface area [4••,53].

**Graphene-CNT heterostructure**
201 A strategy to surpass the intrinsic limitations of carbon
202 allotropes is to combine them as complementary build-
203 ing blocks. For example, graphene has the largest mobil-
204 ity but the slowest HET rates among carbon allotropes
205 (Figure 1), which can be overcome by connecting it with
206 CNTs, that have larger surface area and high electroactive
207 sites density [54]. The individually synthesized nanoma-
208 terials can be hybridized into a composite, using for ex-
209 ample, poly(ionic liquids), that provide strong cation-$\pi$
210 interactions, and have shown multiplex sensing capabil-
211 ities for organic volatiles and temperature. The addition
212 of CNTs resulted in improvement of sensitivity, lower de-
213 tection limit and faster sensor response [55]. An alterna-
214 tive hybridization method to prepare seamless covalently

**Figure 4**
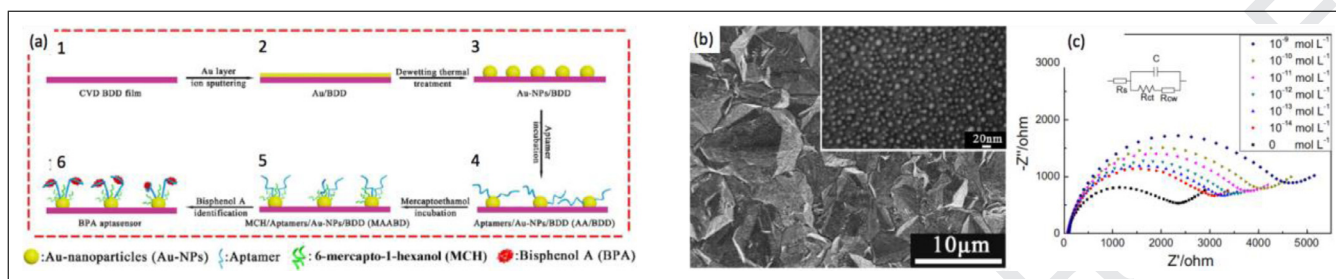


(a) The schematic illustration of the fabrication procedure of the bisphenol-A aptasensor based on BDD coated with Au NPs and modified with aptamer and 6-mercapto-1-hexanol. (b) Boron-doped diamond electrode covered with Au NPs. (c) Impedance spectra (Nyquist plots) of BDD aptasensor incubated with analyte at varying concentrations. The inset in (c) is the equivalent circuit of impedance. Reprinted from [59••] with permission of Elsevier.

bonded structures is *in-situ* growth of CNT on graphene, which provides better orientation control and electrical conductivity through low contact resistance junctions and across a single chemical vapor deposition (CVD)-grown graphene platform. The seamless graphene/CNTs showed higher sensitivity than bare graphene in biosensing applications [19•,56], making it an interesting material to explore for environmental monitoring.

**Diamond**

Diamond is a $sp^3$ hybridized carbon allotrope usually considered not suitable for sensor application due its insulating behavior. However, it provides the advantages of wide potential window and excellent stability in harsh environments over graphite and glassy carbon electrodes [57]. The development of boron-doped diamond (BDD) and nanocrystalline (NCD) diamond has generated interest for sensing applications. In BDD, the substitutional defect of boron causes p-type conductivity to overcome its insulating behavior [58]. A modified BDD electrode has been used for the electrochemical impedance spectroscopy (EIS) detection of currently difficult to detect bisphenol A (Figure 4) at levels as low as $1 \times 10^{-12}$ mol L$^{-1}$, which is lower than any other electrochemical sensor before [59••]. The NCD, on the other hand, has a higher proportion of grain boundaries with $sp^2$ content that provide the conduction paths for electron transportation. A study demonstrated the high-performance of a NCD electrode in an extended-gate FET configuration for electrochemical detection of acetone in water, with high selectivity over other VOC's. It was observed that the smaller the grain in the NCD, the larger the FET response, due to higher conductivity [60].

**Graphite from the University of Idaho Thermolyzed Asphalt Reaction (GUITAR)**

A primary goal to expand the functionalities of graphitic materials for the development of advanced electrochemical sensors is to achieve faster HET across the basal plane, as it is predominantly exposed and its corrosion resistance is higher than edge-oriented planes (Figure 1). The new graphitic material GUITAR appears to provide the solution. With a $sp^2$ nanocrystalline layered structure and 0.25–1.5 µm thickness, it resembles highly oriented pyrolytic graphite but lacks the step- and edge-defects. Instead, an unusual disorder occurs at the inter-grain regions, increasing the density of states for the fastest HET rates observed at the basal plane in any graphitic material, as shown in Figure 1. At the same time, the lack of gaps for electrolyte intercalation results in a corrosion resistance, competitive with diamond. Since the growth of GUITAR occurs at temperatures as low as 600 °C from a variety of organic precursors in presence of sulfur [3,61•], it is an attractive alternative to graphene that requires high temperature and expensive catalysts, limiting its scaled-up production.

**Graphene variants: graphane and graphyne**

The prediction of graphene before it was experimentally found has inspired the postulation of a new generation of imaginary carbon allotropes. An example is graphyne, a 2D hexagonal network of $sp^1$-hybridized carbon atoms whose stability and electromagnetic properties depend on the number of atoms per side [62]. Density functional theory, of this yet unrealized material, predicts that formaldehyde and $H_2S$ would weakly physisorb on the surface of graphyne nanotubes and induce n-type doping, making them a suitable system for gas sensing [63]. Another proposed variant is graphane, a hydrogenated graphene sheet with an insulating behavior that increases with hydrogenation level due to disruption of the $\pi$-conjugation. CV studies demonstrated that a complex interplay of factors causes GO hydrogenation level to accelerate its HET in Fe[(CN)$_6$]$^{4-/3}$ (Figure 1). However, hydrogenation of graphene can reduce the affinity toward analytes that adsorb by $\pi$–$\pi$ interactions, as demonstrated by differential pulse voltammetry detection of 2,4,6-trinitrotoluene [64–66]. More importantly, graphane could be a fabrication breakthrough for graphene multiplex sensors, as the non-conducting regions can be selectively patterned by existing lithographic processes. Hydrogenation further activates the surface for chemical functionalization, allow-

ing infinite combinations of molecular patterns on a single graphene platform [67]. For example, fluorination increases the electrocatalytic capabilities of the irresponsive graphane in benchmark redox systems studied by CV and LSV [68]. Density functional theory has predicted similar results of $NH_3$ and $H_2S$ having inadequate adsorption energies for detection on pristine graphane, while good adsorption and the derived electronic response on lithiated-graphane [65].

## Future outlook

Electrochemical sensor technology has gained more interest due to many advantages such as more rapid response, on-site mobility, and inexpensive operations and instrumentation. More specifically, carbon-based electrochemical sensors provide the aforementioned benefits, with the added advantages of using inexpensive and non-toxic materials. From a 3D bulk structure in graphite to an atom-thick 2D layer in graphene and 1D in carbon nanotubes, these CNMs, fabricated as a sensing platform, promise a great potential for mass production of miniature and eco-friendly devices. As the phases of synthesis and processing of CNMs are overcome for many varieties like CNTs, rGO, CVD-grown graphene, new challenges arise for interfacing them with substrates, electrodes and other materials to create functional devices. Multiplex detection, portability, high performance, and stability, especially when working with biomolecules, such as enzymes and antibodies, will be key determining factors of success for these devices in commercial settings. An important issue in the future years will be integration of CNM-based electrochemical sensors with user interface with portable long-battery-life devices like cell-phones. Other CNMs that have achieved less development and popularity still hold great promise and is worthwhile to study their applications. These studies should be systematic to compare the electrochemical properties of different carbon allotropes for different systems. At the same time, more real sample studies are necessary to advance and develop strategies to reduce the interference with common coexisting species. Testing of pollutants in real soil, water and air media is the ultimate end of environmental sensing technology; therefore, the experimental approach must expand toward the preparation of this kind of samples. Performing studies with real samples could also directly impact the communities, as specific targets of concern can start being traced in specific areas.

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Q2   [5,6,12–18,20,43,44].

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