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Journal of Composites and Compounds

Critical study about recent advanced materials and their electrochemical sensing of organic pollutants

Hicham Meskher [a]*

[a] *Division of Process Engineering, College of Science and Technology, Chadli Bendjedid University, 36000, Algeria*

A B S T R A C T

Because of their unique physical, chemical, and biological characteristics, conductive nanomaterials have a lot of potential for applications in materials science, energy storage, environmental science, biomedicine, sensors/biosensors, and other fields. Recent breakthroughs in the manufacture of carbon materials, conductive polymers, metals, and metal oxide nanoparticles based electrochemical sensors and biosensors for applications in environmental monitoring by detection of catechol (CC) and hydroquinone (HQ) are presented in this review. To achieve this goal, we first introduced recent works that discuss the effects of phenolic compounds and the need for accurate, inexpensive, and quick monitoring, and then we focused on the use of the most important applications of nanomaterials, such as carbon-based materials, metals, and metal oxides nanoparticles, and conductive polymers, to develop sensors to monitor catechol and hydroquinone. Finally, we identified challenges and limits in the field of sensors and biosensors, as well as possibilities and recommendations for developing the field for better future applications. Meanwhile, electrochemical sensors and biosensors for catechol and hydroquinone measurement and monitoring were highlighted and discussed particularly. This review, we feel, will aid in the promotion of nanomaterials for the development of innovative electrical sensors and nanodevices for environmental monitoring.

Peer review under responsibility of UGPH.

A R T I C L E I N F O R M A T I O N

Article history:
Received 19 January 2023
Received in revised form 18 March 2023
Accepted 20 May 2023

Keywords:
Advanced materials
Carbon based materials
Organic pollutant
Electrochemical sensing

Table of contents

(Continued)

* *Corresponding author: Hicham Meskher; E-mail: h.meskher@univ-eltarf.dz*

https://doi.org/10.61186/jcc.5.2.5

1. Introduction

The determination and examination of organic pollution (carbon-based compounds) with analogous chemical properties is an interesting topic in analytical chemistry [1]. This topic is interested in the analyzing of the amount or the kind of the chemical compounds including organic pollutants [2, 3].

Hence, the electroanalytical aspect of the chemical compounds is devoted to the detection and study of organic/inorganic pollutants having comparable electrochemical characteristics. Catechol (CC) and Hydroquinone (HQ) are phenolic compound isomers that are widely employed in a variety of sectors including textiles, paints, plastics, petroleum refineries, cosmetics, antioxidants, insecticides, medicines, and photography [4-7]. Phenolic chemicals are extremely hazardous to human health [6, 8]. Furthermore, United States Environmental Protection Agency and the European Union consider them to be environmental contaminants even at extremely low quantities. A high dose of hydroquinone (e.g., 1 gram or more) might induce weariness, headache, edema, nausea, internal organs, dermatitis, eczema, collapse, and potentially death from respiratory failure in the patient [9-11].

DM de Oliveira et al. (2010) studied the toxic properties stimulated by catechol using human glioblastoma GL-15 cells to get more data about its toxic effects on the human central nervous system. In addition, they reported that it can reduce the glutathione amount and prompted the cell death principally by apoptosis [12]. They also point out that it lowers glutathione levels and induces cell death predominantly through apoptosis. Furthermore, because catechol and hydroquinone have similar structures and properties, they exist concurrently and interact with each other via environmental recognition samples. As a result, breakthroughs in sensitive and quick diagnostic procedures are required for their concurrent analysis. Capillary electrophoresis, gas chromatography, and liquid chromatography are more prevalent procedures that need an isolation step. Electrochemical techniques have the advantages of being simple to operate with precision equipment and saving time, and depending on the features of the isomers of dihydroxybenzene, electrochemical processes may be appropriate alternatives, as many reports have been referenced in the literature [13-15].

To detect CC effectively, sensitive, easy and fast analytical methods for quantitative and qualitative CC monitoring are strongly needed [16]. Hence, various analytical methods for detecting CC have been developed and applied over the years, including gas chromatography/mass spectrometry [17], chemiluminescence [18]synchronous fluorescence [19], electrochemical methods [20], high-performance liquid chromatography (HPLC) [21]. Although these analytical methods exhibited effective detection of CC, they involve many disadvantages. Some of them are expensive [17,18] or need training personnel because these analytical tools require complicated processes [19]. Others require too long sensing and response time [21], have low sensitivity and specificity or need a sample of pretreatment [22]. One of the most promising and widely used methods for CC detection is electrochemical sensing due to its prominent characteristics including simplicity, short analysis time, wide linear range, high selectivity, high sensitivity, and low cost [23].

Modified electrodes have been frequently employed in electrochemical analysis for sensitive and selective compound detection [23]. Glassy carbon electrodes (GCE) offers various benefits over conventional solid electrodes, including biocompatibility with test samples and a quick and simple technique of production from inexpensive materials [24]. They have a repeatable and renewable surface with little residual current during analysis. GCE also has a cheap production cost, porous surfaces, and once it is modified, it may be utilized to reduce fouling in electrochemical sensor electrodes when working with phenolic compounds such as CC and HQ [25, 26]. However, the GCE modified with nanomaterials has lately gained prominence. Increase the electrochemical characteristics of the substances under consideration. The key benefits of utilizing modified GCE with nanoparticles on large electrodes or unmodified GCE include effective surface area, enhanced sensitivity and selectivity, and efficient mass transfer via electron transfer mediation between electrically active species during reactions in solution [27, 28]. Carbon-based nanomaterials (such as carbon nanotubes (CNTs), graphene oxide (GOs), and reduced graphene oxide (rGO)), metals, metal oxides, polymers, and printed polymers are nanoparticles with chemical characteristics, distinctive physical, and electrical components that distinguish them from bulk materials. These distinct features enable them to be employed in a variety of analytical procedures, including the fabrication of new and better sensors. Similar to electrolysis sensors. The nanoparticles cited below have been frequently employed to modify electrodes used in the sensitive and selective detection of CC and HQ and other phenolic compounds using analytical procedures [29, 30].

To resume, the use of nanostructured materials in these electrodes is suggested. Significant increases in compound electrochemical behavior due to high effective surface, stimulating action, and mass transfer. Carbon-based nanomaterials (such as CNTs, GOs, and rGOs), metal oxides, metals, polymers, and printed polymer nanoparticles are all nanoparticles that are utilized to perform the electrocatalytic activity of the electrodes due to their superior electrochemical characteristics. They are employed to improve the detection limit, offer a large electroactive surface area, a catalytic action, high electromagnetic activity, attractive electron transport, sensitivity, and chemical stability [31]. The nanomaterials discussed above have a conductivity effect, which makes them excellent for improving electron transport between analytes and electrodes [32]. These nanoparticles have a wide range of applications, including biomaterials, bioseparation, biomedical and bioengineering applications, and food analysis [33, 34].

The purpose of this chapter is to investigate the electrochemical behavior of various phenolic compounds (Figure 1). Hence, an overview about the advanced methods and technical challenges made for preparing a novel electrochemical sensor for monitoring organic compounds with high analytical performances was presented.

2. Organic pollution in water and its effects

Industrial development has caused a huge increase in the release of potentially toxic compounds into the atmosphere, water bodies, and

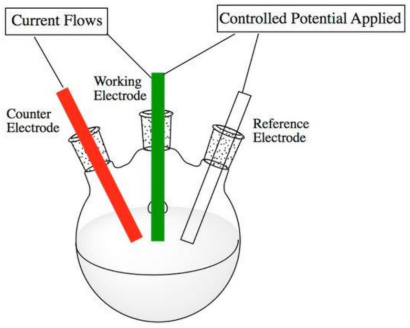


Fig. 1. A typical schematic presentation of a three-electrode system. Reproduced with permission from MDPI [73].

soils. In the last decades, environmental pollutants have been directly connected to the increase in human diseases, particularly those involved with the immune system. The contribution of benzene and its metabolites to this issue is well recognized, making them a public health problem. Catechol (CC) and Hydroquinone (HQ), the major benzene metabolites, are ubiquitous chemicals in the environment due to their widespread application in human and industrial activities. They can be used as a developing agent in photography, dye intermediate, stabilizer in paints, varnishes oils, and motor fuels. In addition, hydroquinone has been used as an antioxidant in the rubber and food industry. From 1950s to 2001 CC and HQ were applied in the commercially available cosmetic skin lightening formulations in European Union countries and since 1960s they were both commercially available as a medical product. They are also present in cosmetic formulations of products for coating finger nails and hair dyes [4-7].

On the other hand, CC and HQ can be components of high molecular aromatic compounds (e.g., resin), an intermediate, or appear as a degradation product generated by the transformation of aromatic compounds. Advanced oxidation processes (APOs) of aromatic compounds, particularly of phenol, yield several benzene derivatives, such as hydroquinone, catechol, and resorcinol, as intermediate metabolites of their transformation. The formation of HQ and CC and (and *ρ*-benzoquinone at early stages of phenol oxidation increases the toxicity of phenol wastewaters, showing that these compounds were more toxic and less degradable than

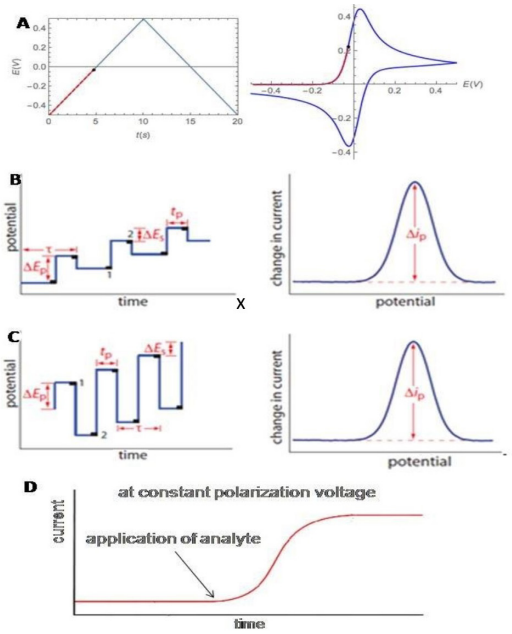


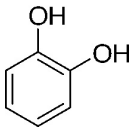
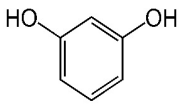
Fig. 2. Electrochemical techniques - parameters andcharacteristic voltammograms: A) cyclic voltammetry, B) differential pulse voltammetry, C) square-wave voltammetry and D) amperometry. Reproduced from Elsevier [77].

the original pollutant [35, 36].

2.1. Effect and toxicity of CC

Catechol (1,2-dihydroxybenzene) is used in a variety of applications such as a reagent for photography, dyeing fur, rubber and plastic production and in the pharmaceutical industry [37]. Substituted catechols, especially chlorinated and methylated catechols, are by-products in pulp and oil mills [38]. Catechol is an intermediary product from the degradation of aromatic compounds and lignin by microorganism [39]. In humans and mammals catechols can occur as metabolites in the degradation of benzene or estrogens or as endogenous compounds, such as neurotransmitter and their precursors [adrenaline, noradrenaline, dopamine and L-DOPA (L-3,4-dihydroxy-phenylanaline) [40, 41].

Table 1.
Some of the physicochemical properties of CC and HQ. Reproduced from Springer [54].

Parameters	CC	HQ
Chemical structure		
Other names	$C_6H_6O_2$ Pyrocatechol, 1.2-benzenedio, 1,2-dihydroxybenzene.	$C_6H_4(OH)_2$ *p*-Benzenediol, 1,4-Benzenediol, dihydroxtbenzene, 1,4-dihydroxybenzene, Quinol.
λmax (nm)	275	289
Boiling point (°C) at 101.3 KPa	245.5	287
Density (g/cm^3)	1.344	1.3
Molecular weight (MW. g/mol)	110.11	110.159
Water solubility (g/l) at 25 °C	430	59
Molecular size (nm)	0.55 x 0.55	-
pKa	9.25, 13	9.9-11.6
Dipole moment (Debye: D)	2.620	0.0
Polarity/Polarizability parameter (n:cm^3)	11.89+- 0.5*10^{-24}	0.21+-0.02
Hydrogen-bonding donor parameter (a_s)	0.85	-
Hydrogen-bondign acceptor parameter (Bm)	0.58	-

Additionally, catechols can be taken up in the form of tabacco smoke (as catechol, catechol semiquinones and polymerized catechols) [42] or as food components (e.g.catechol, dopamine, caffeic acid, tea catechin) [43]. The toxicity of catechols for microorganisms has been demonstrated in the past years [44, 45], and has been suggested to be the reason for the difficulties in cultivating microorganisms on benzene, toluene or chlorobenzene [45, 46]. Despite the fact that catechols are ubiquitous, and their toxicity has been observed in a variety of organisms the modes of action causing the toxicity are hardly understood. In the following review, an overview about the chemical properties of catechols is given, which is required to understand their possible toxic modes of action. The molecular modes of action found for catecholic compounds are summarized and discussed, subsequently. Because basic toxic processes in the context of catechol toxicity are similar in different cell types, ranging from microorganisms to mammals, the information from reactions in different cell types is integrated.

Several studies additionally indicated the toxicity of CC for water flea, zebra fish, trout, rabbit, cat, rat, and mouse and for human cell lines [47]. As mentioned earlier, CC is strongly irritating to the eyes, skin, and respiratory tract, and it has been proven to cause DNA damage, vascular collapse, coma, and death. However, these compounds are considered as the primary pollutants in wastewater due to their high toxicity, high oxygen demand, and low biodegradability [9, 48].

2.2. Effect and Toxicity of HQ

Hydroquinone is an aromatic compound consisting of the benzene ring and two –OH groups at *para* position. It is available in the form of white crystals, but industrial use grades may be light grey or light tan. Contact with air and light causes oxidation and darkening of color. Hydroquinone is soluble in water, methanol, and ether. However, it has less solubility in water than the other two dihydroxybenzenes, which means hydroquinone has less affinity towards hydrophilic solvents. Its octanol/water partition value is also less than that of catechol and resorcinol (Table 1). Hydroquinone can occur naturally in many plant foods, as glucose conjugate, namely, arbutin, for example, in the wheat, pears, coffee, onion, tea and red wine [49, 50].

Dihydroxybenzene and quinones are recognized to induce oxidative stress as well as to nonspecifically bind both DNA and protein [49]. Hydroquinone can form complexes with various di- and trivalente metal ions, such as copper and iron. In the case of copper, the complex formed increased H_2O_2 production by hydroquinone and enhances its autooxidation to benzoquinone [51]. Hydroquinone can be originated during phenol [49] or benzene biotransformation [52]. The benzene is first metabolized by liver cytochrome P-450 monooxygenase to phenol. Further hydroxylation of phenol by cytochrome P- 450 monooxygenase or by human peroxidase resulted in the formation of mainly hydroquinone, which accumulates in the bone marrow [53].

Hydroquinone can also be produced through three chemical processes, involving oxidation, reduction, and alkylation reactions. Firstly, it can be generated by oxidation of phenol; secondly, the oxidation of aniline with manganese dioxide in acidic conditions, followed by reduction with iron dust in aqueous medium; finally, the alkylation of benzene with propylene to originate the *para*-di-isopropylbenzene isomer, besides other isomers, which is oxidized and produces the corresponding dihydroperoxide, that is subsequently treated with an acid to originate hydroquinone [54, 46].

It is known that phenolic compounds are extremely toxic for aquatic organisms at the concentration level of part-per-million and most of them can influence the organolectic properties of shellfish and fish at part-per-billion level [55]. Studies on *Photobacteriumphosphoreum* showed that hydroquinone is one hundred and one thousand times more toxic than catechol and resorcinol, respectively [56]. Meanwhile, it was reported that hydroquinone was the less toxic dihydroxybenzene to the gram-positive bacteria *Bacillus subtilis*; however, it was shown that hydroquinone and catechol mixture exerts a synergistic joint action while the other mixtures have an additive actions [57]. The toxic effect of phenolic compounds on soil microbial activity has been evaluated, showing hydroquinone as the most toxic dihydroxybenzene [44]. The number of cultivable microorganisms decreased with increasing concentration of phenolic compounds. Table 1 highlights key feature properties of CC and HQ.

3. Electrochemistry and electrochemical sensing

Electrochemistry is a field of chemistry that deals with the interaction of electrical and chemical processes [58]. For hundreds of years, scientists have been working on the electrochemical techniques [59, 60]. More sensitive and precise micro- or nano-electrodes have been created and fabricated as a result of the advancement of nanotechnology, bringing the electrochemical technique back to the platform for point-of-care testing [61, 62]. Just before, gas-liquid chromatography, mass spectrometry, nuclear magnetic resonance (NMR), infrared (IR) spectroscopy, and flame element analysis were well-known as examples of laboratory analytical procedures [63, 64]. They are classified as destructive (e.g., mass spectroscopy, flame analysis) or non-destructive (e.g., infrared spectroscopy, electron microscopy, etc.) based on whether the sample is destroyed as a result of the processing phase. These techniques are commercially available, extremely sensitive and accurate, and may be used for a wide range of studies. They are, however, time-consuming and expensive to conduct, need specialized training, and, in some circumstances, significant sample preparation. The equipment used also necessitates a high level of maintenance in order to remain operational and, in most cases, must be used in a clean lab environment [17, 22].

Electrochemical techniques, on the other hand, are gaining popularity in the field of analytical chemistry. These techniques provide the same sensitivity at a cheaper cost, with fewer complicated operating processes and faster on-site detection [65, 66]. For organic pollution detection, many electrochemical systems have been developed. Nanomaterials, in particular, have provided numerous benefits in this field due to their unique electrical, chemical, and mechanical characteristics [67, 68] . As a result, several electrochemical sensors based on nanoparticles have been developed for organic pollution detection [67, 69].

Voltammetry techniques are the most frequently used electrochemical techniques in the detection of organic pollution ions. Voltammetry is a broad term that encompasses all electrochemical systems that rely on measurements of dependent potential current [70-72].

The measurement of a cyclic voltmeter (CV) consists of linearly scanning the voltage in one direction and then inverting the potential of a working electrode. To put it another way, it contains one or more triangular potential waveforms [70]. The basic principle underlying the measurement of a pulse voltmeter is the use of a voltage signal pulse. Different varieties of pulse voltmeters exist by varying the form and amplitude of the pulses [71]. Differential pulse voltammetry (DPV) works by superimposing constant-size pulses on a linear potential slope [74]. When a symmetric square wave waveform is overlaid on a base tray voltage and delivered to the working electrode, square wave voltage (SWV) is measured [75]. A cut-off voltmeter, more precisely an anodic voltmeter (ASV), works in two stages. The first step is to oxide the organic pollution molecule and generate electrons that will be transported on the electrode surface. The pickling stage is the second step, in which the pollution molecule will be reduced. Following the two stages, various variables, such as electrode material, scan rate, matrix material and its concentration, pH of the studied sample are known to impact the analysis [69, 76]

Figure 2 depicts how the possibility for CV, LSV, DPV and SWV to create a signal evolves over time. The combination of several of these approaches improves sensitivity and detection limitations. Differential pulse anode voltmeters (DPASV), square wave anode scanning voltmeters (SWASV), and linear scanning anode voltmeters are included in the kits (SWASV).

3.1. Three-electrode system

A working electrode, a counter electrode, and a reference electrode are often used in a three-electrode electrochemical setup. Between the working and reference electrodes, a voltage is supplied, and the current is measured between the working and meter electrodes [78]. The electrochemical reaction occurs with the transport of electrons at the working electrode. The working electrode material is generally chosen to be redox sensitive. The reference electrode maintains a constant voltage and current over time. Normal hydrogen electrode (NHE), saturated calomel electrode (SCE), and silver-silver chloride electrode are examples of standard reference electrodes [79, 80]. There are certain disadvantages to this sort of bipolar system. Current flowing via the reference electrode depolarizes over time, resulting in a steady drift potential. Because such a tiny voltage difference between the working and reference electrodes can lead to significant measurement error, the three-electrode method is currently utilized by adding a counter electrode that can assist pass the bulk of the current to assure the reference electrode's steady potential [78]. The counter electrode is frequently made of gold or platinum, which is difficult to polarize. The meter electrode is generally the biggest, which aids in current conductivity.

3.2. Types of sensors

The use of chemical sensors is a very interesting topic in environmental monitoring [67, 69, 81]. A sensor typically consists of three components: a sensing element that responds to a certain analysis (target chemical type); a transducer element that transforms this response into a quantifiable signal; and lastly, a measurement element that records the sensor's [82].

Electrochemical sensors are less versatile (they are unique to a single analyzer) than in vitro analytical methods, but they have the benefit of being extremely portable and capable of providing quick (if not real-time) detection of pollution and other target compounds in situ. They also have basic designs that need little or no sample preparation, are simple to install and use, and are yet reasonably priced. However, they are typically restricted in that they are less accurate and more vulnerable to false positives due to chemical species interference from the laboratory analytical process. Depending on the recognition element used to detect the target analyte, portable chemical sensors are classified into three types: biosensors [83], electrochemical sensors [67], and biomimetic sensors [84].

3.3. Electrochemical sensor

Electrochemical sensors make use of an identifying element known as a matrix, which can be MIPs [85], MOFs [86], carbon compounds [87], or metal oxides nanoparticles (NPs) [88]. Natural recognition elements attach to a specific chemical molecule with great precision [82, 89] and are then converted into a quantifiable outcome.

3.3.1. Background of Electrochemical Sensors

As can be seen in Figure 3, an electrochemical sensor includes a) the identification of elements related to analysis; b) the transducer where a specific reaction occurs interface with recognition elements and results in the appearance of a signal; and c) an electronic system that converts the electronic signal into a meaningful parameter describing the running process [90, 91]. A human operator interface was used to study and show the final data. The following requirements must be met by a high-performance electrochemical sensor for the non-specialized market:

- For the objectives of analysis, the elements of recognition must be highly specific. It is stable under normal storage settings and exhibits acceptable variations between tests.
- The reaction must be unaffected by physical factors such as convection, pH, and temperature.
- The response must be timely, accurate, repeatable, clear, and written on the proper focus range. Untreated samples, such as human blood or urine, must be able to be measured.
- The entire sensor should be low-cost, compact, tiny, portable, and simple to install.

Nanomaterials that function as chemical catalysts are used in the sensor array or sensor recognition element. Its porous structure conducts electricity and serves as an electron transfer agent. The matrix components' electrocatalytic activity allows them to convert the target analyte into a product molecule and transmit the generated electrons to the sensor surface and then to the transducer [90-92]. Nanomaterials such as MIPs [85], MOFs [28], carbon compounds [87], or metal oxides nanoparticles (NPs) [88] must be immobilized and bonded to the surface of a working electrode such as glassy carbon (GCE) electrodes, platinum (Pt) electrodes, and gold (GE) electrodes to alter this interaction. A detecting capability is provided to the working electrode, allowing electrochemical measurements (CV, DPV, SWV, etc.) to be done within the framework of an electrochemical half-cell holding the sample to detect the reduction or oxidation of any analyte.

It was created for this purpose, which is an important element of electrochemical sensor design. Choosing an electrochemical detection approach that allows for easy, quick, and precise measurements of the reaction of interest [87, 93]. Typically, in electrochemical detection, the investigated reaction produces either a detectable current (amperometric) [94], a measurable potential or charge buildup (potentiometric) [95], or a measurable change in the conductive characteristics of a medium (conductivity measurement)between the electrodes [96]. When an electric field is produced between two electrodes immersed in electrolyte solution, current flow is created by migration of ions with opposing charges. Among the three major electrochemical methods, this conversion is the least sensitive. It is hard to differentiate between two ions because conductivity is cumulative. Furthermore, if the ion concentration is too high, it might cause injury to others. The voltage measurement is determined by the difference in output potentials. Activity is transmitted across a membrane put between two solutions with different kinds of charges. Voltage sensors are well suited to detecting low concentrations in tiny volumes. Because it has no chemical effect on the sample, sample volume. Amperometry measures the current generated by the oxidation or reduction of a sample's electrically active species [94, 97]. Since then, this has been the most commonly utilized method. An analyte's inherent characteristic is its oxidation or reduction potential. In general, if the current is measured at a constant voltage, it is referred to as measuring the current; if the current is measured within a regulated potential range, it is referred to as Voltmeter measurement.

4. Analytical characteristics of electrochemical sensor

Any electrochemical sensor has certain static and dynamic attributes. Optimization of these parameters affects the performance of the sensor [98].

4.1. The linear range

Linearity expresses the precision of the response to a group of mea-

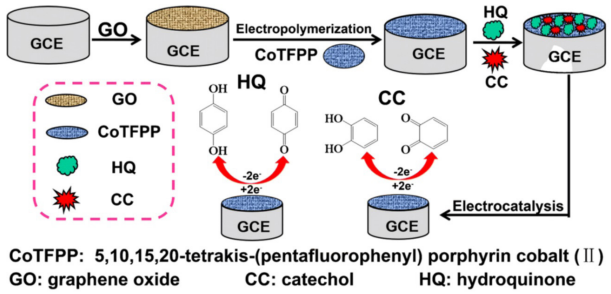


Fig. 3. The fabrication process of the sensor and the catalytic mechanism for the oxidation of catechol and hydroquinone. Reproduced with permission from Springer [92].

surements at different concentrations, where the slope of linearity is the sensitivity of the sensor. linearity good resolution is required because most biosensor applications require not only detection of the analyte, but also measurement of analyte concentrations over a wide operating range [99].

4.2. Limit of detection (LOD)

It is defined as the smallest concentration of the analyte to be detected by the sensor. To calculate the limit of detection (LOD), the researchers conventionally use the formula (LOD = 3S / N) to distinguish the signal (S: calculated by the standard deviation SD of the calibration curve) from the noise of the device (N: Noise) [100].

4.3. Selectivity

Selectivity is an important characteristic to consider when choosing a biometric sensor receptor. The receptor can detect a specific target analyte molecule in a sample. It consists of a mixture of spices and unwanted contaminants. To construct a sensor, selectivity is the main consideration when choosing bioreceptors [101, 102].

Sensitivity and selectivity are two additional key elements of electrochemical sensor development [66, 103]. What differs an electrochemical biosensor from a sensor is the immobilization of a biomolecule in the recognition element of the sensor [104]. Immobilization of biomolecules on the working electrode surface such as enzyme [105] and DNA [106] are very efficient approach to enhance current responses and interfaces with a highly precise binding affinity for the targeted analyte [107-109].

4.4. Reproducibility

Reproducibility is the ability of a sensor to generate identical responses for a reproducible experimental setup [110]. It is characterized by precision (similar output when the sample is measured more than once) and precision (the ability of the sensor to generate an average value closer to the actual value when measuring the sample every time). It is the ability of a sensor to produce identical results whenever they are similar. The sample has been measured more than once (44).

4.5. Stability

Stability is the degree to which environmental disturbances are detected in and around the detection system. This is the most important feature in applications where the biosensor requires long incubation steps or continuous monitoring. The response of transducers and electronics can be temperature sensitive, which can affect the stability of the biosensor. Therefore, proper adjustment of the electronics is necessary to ensure a stable response of the sensor [111].

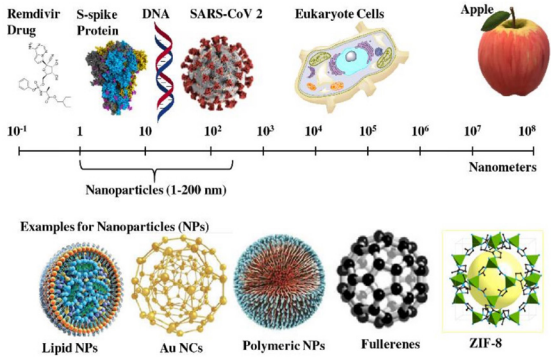


Fig. 4. Illustration of the nanoscale relative to biologically active molecules, and examples of nanomaterials of relevance for biomedical and bio sensing applications. Reproduced with permission from Springer [117].

5. Electrochemical sensors preparation using conductive and semi-conductive nanomaterials

A few years ago, the uses of nanotechnology appeared far-fetched. However, with the discovery of new nanomaterials with novel characteristics, nanoscience research has grown dramatically, and as a result, nanotechnology applications and products have just lately begun to appear. However, nanotechnology applications are starting to emerge, and more research is needed to create novel discoveries and uses for these sorts of materials [112-114]expanding nanomaterials application and reducing costs along with the increase in the global energy consumption.

As highlighted in Figure 4, nanostructured materials with characteristics smaller than 100 nm in particle size, layer thickness, or form are gaining prominence in nanotechnology [115, 116]. The science and technology of nanomaterials and devices, as well as their applications in functionally categorized materials, molecular electronics, nanocomputers, sensors, actuators, and molecular machines, are all included in the topic of nanotechnology [66, 103].

5.1. Carbon Materials

The discovery of atomic-level micro-materials such as fullerenes in the mid-1980s and carbon nanotubes (CNTs) in 1991, as well as graphene, resulted in a significant advancement in nanotechnology [118]. Other materials, including as metal-organic frameworks [119], metals and metal oxides NPs [88], and MIPs [120], have since been developed for application in nanotechnology advancements. Because of the remarkable characteristics of these materials, an intriguing new field of study in nanoscience and nanotechnology has emerged. Furthermore, new characteristics have been identified, and prospective applications for this material are frequently proposed.

Carbon nanoparticles, polymers, and metal oxides study now spans numerous fields, with the objective of better understanding and utilizing these interesting materials. Other areas of research have been devoted to fundamental sciences in order to change the structure and surface of these nanomaterials. These materials characteristics have opened new vistas in chemistry, physics, engineering, medicine, and materials science [121, 103].

5.1.1. Carbon nanotubes (CNTs)

The discovery of fullerenes at Buckminster Fuller in 1985 marked the beginning of a new era in carbon chemistry and the development of novel materials. Sumi Ijima of Japan discovered carbon nanotubes (CNTs) in 1991 [118]

Carbon nanotubes have gotten a lot of interest since they were dis-

covered because of their field emission and electron transport capabilities, as well as their superior mechanical and chemical properties. As a result, there is a rising possibility for carbon nanotubes to be used as field-emitting devices [122], nano-transistors [123], microscopy tips [124]the flexible deformation during the tip manipulation modifies the original shape of these nanotubes, which could affect its electrical properties and reduce the accuracy of AFM nanomanipulation. Thus, we developed a protocol for searching the synergistic parameter combinations to push single-wall carbon nanotubes (SWCNTs, or components of composite materials [125]. Single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) are the two kinds of carbon nanotubes [126]. As can been in Figure 5, SWCNTs are cylindrical nanostructures formed by rolling a single sheet of graphite into a tube. As a consequence, SWCNTs can be compared to molecular threads, with each atom on the surface [127, 128]. MWCNTs are made up of a collection of such nanotubes that are piled concentrically like tree trunk rings. The figure below presents single walled carbon nanotube (SWCNT) and multi walled carbon nanotube (MWCNT) [129].

Carbon nanotubes are one of the most common nanotechnology construction materials. Carbon nanotubes look to be an outstanding material, with tensile strength 100 times that of steel, thermal conductivity greater than the finest diamond, and electrical conductivity equivalent to copper but with much higher current carrying capacity. Much more crucial.

5.1.1.1. Structure and properties

Some properties of CNTs are stated below.

Electricity: The structural characteristics of the nanotube reveal how twisted it is. Carbon nanotubes have the property of being extremely conductive and hence metallic. Its conductivity has been demonstrated to be a function of its symmetry, degree of torsion, and diameter [130, 131].

Mechanical: The tiny diameter of carbon nanotubes has a large effect on mechanical characteristics when compared to graphite fibers of typical micron size. The ability to connect high elasticity and strength with high toughness, which is not present in graphite fibers, is perhaps the most noteworthy consequence. These characteristics of carbon nanotubes open the way for the creation of a new generation of high-performance composites. The nanotube as a whole is highly flexible because to its length [132].

Chemical: The large specific surface area and -rehybridization enable particle adsorption, doping, and charge transfer on nanotubes, as well as electronic property modification [133].

Thermal and thermoelectric: The heat conductivity of nanotubes is quite high. As a result, nanotube reinforcements in polymeric materials are predicted to improve the thermal and thermomechanical characteristics of these compounds substantially [134].

5.1.1.2. Synthesis and purification

Arc vacuum, laser ablation, and chemical vapor deposition (CVD) are three well-established techniques for constructing carbon nanotubes (Table 2).

However, in order for carbon nanotubes to be employed in new technologies, these highly crystalline materials must be mass-produced at a reasonable cost on a huge scale. CVD catalytic technology, namely the floating catalyst technique, is the best way for producing high number of carbon nanotubes in this context. This approach is more regulated and cost-effective than arc unloading and other procedures [135-139].

5.1.1.3. Carbon nanotube in electrochemical sensors

As highlighted in, Carbon nanotubes have an extremely high electrical, thermal, and mechanical conductivity. It opens up a slew of new opportunities in materials research, electronics, chemical processing, energy management, and a variety of other fields [87, 140, 133].

5.1.2. Graphene

Graphene is an atomically thin two-dimensional (2D) honeycomb sheet of sp^2 carbon atoms [147, 148] (Figure 6). It has been demonstrated to have several desired qualities, including strong mechanical strength [149, 132], electrical conductivity [150], and molecular barrier capabilities [151]. As a result of these factors, several research attempts have been made to combine graphene into various nanomaterials and nanocomposites such as carbon nanotubes, polymers, metals, and metal oxides to manufacture and develop electrochemical sensors and biosensors [152-154].

5.1.2.1. Synthesis and preparation

When it comes to the production of graphene and its derivatives, the intended structure and characteristics are heavily influenced by the size, shape, and functional groups linked to the material's surface [155]. The ideal structure is a single-atom sp^2 monolayer graphene with minimum imperfections, which is a completely hybridized carbon structure. However, because to the ease with which graphene sheets may be stacked, a multilayer graphene structure will be created. As previously stated, installing such structures from the ground up has proven difficult for industrial purposes [156]. As a result, it is easier to generate the highly oxidized form of graphene, GO, with sp^2 and sp^3carbons containing abundant oxygen groups, which upon reduction (rGO) can remove most of the oxygen groups and sp^3carbon to generate a more "graphene-like" material with significantly improved properties. The top-down method may then be used to control GO and rGO to create quantum dots of both GOQD and rGQD [157]such as graphite, macromolecules polysaccharides, and fullerene. This contribution emphasizes the utilization of GQD-based materials in the fields of sensing, bioimaging, energy storage, and corrosion inhibitors. Inspired by these numerous applications,

Table 2.
Summary and comparison of the most important synthesis procedures for CNTs.

Synthesismethod	Principle	SWCNTs or MWCNTs	Refs.
Arc-discharge	Carbon atoms are produced via an arc discharge between two electrodes at temperatures exceeding 3000°C. Nanotubes (Fe, Co, or Ni) form when appropriate catalyst metal particles are present.	Both	[135] [136]
Laser-ablation	Carbon nanotubes are created utilizing laser ablation technique, which involves irradiating a graphite rod with stimuli heated to 1,000 °C or more with a pulsed laser.	SWCNTs	[137]
ChemicalVaporDeposition(CVD)	Metal nanoparticles (Co or Fe) increase the breakdown of the gaseous source of hydrocarbons at high temperatures (500-1000 °C) (ethylene or acetylene). Carbon has a poor solubility in some metals at high temperatures, causing it to precipitate and form nanotubes.	Both	[138] [139]

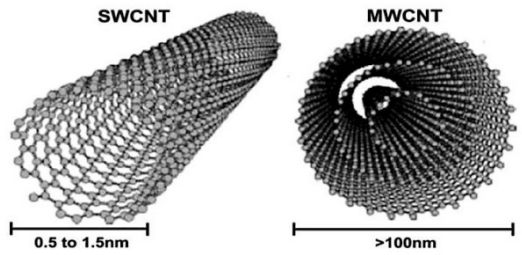


Fig. 5. Schematic of an individual (left) SWCNTs and (right) MWCNTs. Reproduced with permission from Scielo [129].

various synthetic approaches have been developed to design and fabricate GQD, particularly bottom-up and top-down processes. In this context, the prime goal of this review is to emphasize possible eco-friendly and sustainable methodologies that have been successfully employed in the fabrication of GQDs. Furthermore, the fundamental and experimental aspects associated with GQDs such as possible mechanisms, the impact of size, surface alteration, and doping with other elements, together with their technological and industrial applications have been envisaged. Till now, understanding simple photo luminance (PL.

5.1.2.1.1. Synthesis of GO

Bottom-up procedures, in which single carbon molecules are utilized to produce pure graphene, and "top-down" methods, in which layers of graphene derivatives are removed from a layer, are the two primary types of GO synthesis. Graphite is a common carbon source [158, 159]. Bottom-up synthesis (for example, chemical vapor deposition, epitaxial growth on silicon carbide wafers, and so on) is time-consuming and has scaling issues [160, 161]. As a result, top-down techniques that produce GO and/or rGO first are more common for producing graphene derivatives, particularly for usage in nanocomposites materials. Brodie [162], Staudenmaier [163], Hummers, and Offeman [164] are generally credited with the first synthesis of GO, both of which are produced from graphite oxide by oxidizing graphite using distinct methods. To make the two original techniques safer, Hummers and Offeman modified them by using $KMnO_4$ as an oxidant (rather than $KClO_3$, which generates hazardous ClO_2 gas) and adding sodium nitrate (to create nitric acid on site rather than using nitric acid as a solvent). Because the Hummers technique is more safe and scalable, it is generally used (or, in most cases, somewhat modified) to construct GO [162, 165].

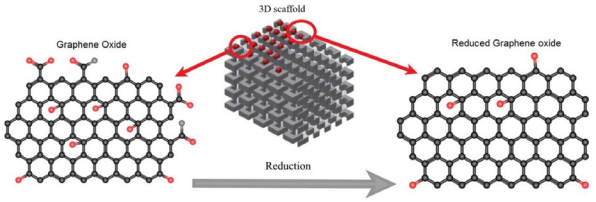


Fig. 6. The structure of Graphene, Graphene Oxide and Reduced Graphen Oxide. Reproduced from Science direct [148].

5.1.2.1.2. Reduction of GO to rGO

Extensive research has been conducted to remove functional oxygen groups from GO in order to generate materials with characteristics as near to pure graphene as feasible [166, 167]. This reduction can be accomplished by a variety of methods, ranging from thermal to chemical to electrochemical, each of which results in variations in morphology, electrical characteristics, and so on [166, 168]. The final product's C/O ratio, selectivity in eliminating one kind of oxygen group (hydroxyl vs. carboxylic acid vs. epoxy, etc.), and healing of surface defects are all important design variables for GO reduction. Oxidation, selection of green reducing agents, and preservation or enhancement of the required physical and chemical properties of GO (mechanical resistance, conductivity, optical properties, solubility/dispersion of nanosheets, and so on).

5.1.2.2. Electrochemical sensors and RGO

As previously stated, when encapsulated in carbon nanomaterials and/or metal-based arrays, rGO exhibits excellent electrical conductivity characteristics. It is not unexpected, then, that this rGO has good operability in the presence of electrical catalysts [169, 170]. Recently, the combination of nanomaterials with electrochemical sensing platforms has shown to be a strong analytical technique for detecting phenolic compounds [170, 153] (Table 4).

5.2. Layered double hydroxide (LDH)

Layered double hydroxides (LDHs) are two-dimensional nanostructured materials with unique physicochemical properties. They are the enthralling class of inorganic materials with adjustable chemical composition and structures. They are also identified as hydrotalcite or anionic clays. By composition, they consist of positively charged layers of metal hydroxides with charge-balancing anions and some water molecules situated in between the layers. They are denoted by the general formula $[M^{2+}1{-}xM^{3+}x\ (OH)_2]x+\ (An\ x/n\ {-}).mH_2O$, where M^{2+} and M^{3+} are di- and trivalent metal cations and An− is the interlayer guest ions with n- valence [179, 180]. From the structural point of view, LDHs

Table 3.
Comparison with state-of-the-art catechol sensors based on carbon nanotubes.

Sensing interface	Pollutant	Linear range (µM)	LOD (µM)	Refs.
Lac/MWCNTsCOOH/AuNPsSDBS/PEDOT/GCE	CC	11.99 – 94.11	12.26	[141]
GCE/MWCNT@CADE	CC	0 – 1000	-	[142]
Co_3O_4/MWCNTs/GCE	CC	10 – 700	8.5	[143]
MWCNTs@reduced graphene oxidenanoribbon/GCE	CC	15 –1101	1.73	[144]
PDEA-PS/C_{60}MWCNT/GCE	CC	4 –135	1.45	[145]
c-MWCNTs/PDAd(b-CDe)/c-MWCNT/GCE	CC	0.25 – 4000	0.04	[29]
Gr-CDP-MWCNTs/GCE	CC	0.1 – 27.2	0.03	[30]
Modified CPE (RGO-MWNTs)	HQ	1-120	0.3	[51]
Modified GCE [Cu(Sal-β-Ala)(3, 5- $DMPz)_2$]/SWCNTs	HQ	8-391	1.46	[145]
MWCNTs@RGONR/GCE	HQ	15-921	3.89	[144]

have resemblance with brucite, $Mg(OH)_2$, in which Mg^{2+} is surrounded by six OH^- ions and the resulting octahedral structures are connected to each other forming an infinite two-dimensional layer. Brucite layers get positively charged by replacing some divalent ions with trivalent ions. This positive charge is then balanced or neutralized by localizing anions in the interlayer spaces. Water molecules are also intercalated in the interlayer spaces stabilizing the structure of resulting LDHs. The stability of LDH structure comes from electrostatic interaction and hydrogen bonding between the layer and interlayer contents. The structures of LDHs are amenable to desired fine-tuning by changing the divalent and trivalent ions and intercalated anions. The selected di and trivalent ions should have their radii not significantly different from those of Mg^{2+} and Al^{3+}.LDHs are characterized by the unique features of being low-cost, nontoxic, high surface area, two-dimensional structure, replaceable intercalated anions, positively charged surface and tunable internal and external architecture [181]. Their unique applications emerge from their highly porous structure, large anion exchange capacities, and water-resistant structures. LDHs have been extensively used in catalysis [182], flame retardants [183]a series of functionalized layered double hydroxides (LDHs, fuel cells [184], drug delivery [185], analytical extractions [186], and in many other areas [187].

5.2.1. Synthesis and preparation

Layered double hydroxide based electrochemical sensors fabrication is facile and their miniaturization in the laboratory is easy. Numerous methods are being used for the synthesis of the LDH including sol-gel method, urea hydrolysis, hydrothermal synthesis and the co-precipitation.

5.2.1.1. Urea hydrolysis

LDH with large crystallites, homogeneous distribution of particle size and with high crystallinity could be achieved using urea hydrolysis [188]. Urea considered as attractive precipitation agent for several metal ions as their hydroxide due to controllable hydrolysis rate using temperature and high-water solubility. One of the major drawbacks of the Urea hydrolysis as only the carbonate containing LDH could be prepared. The carbonate is continuously being generated due to the decomposition of the urea. It put a severe limit to get a wide variety of the LDH for varied applicability. R. Xu et al. synthesized 3D hierarchical flower-like Mg–Al-LDHs using urea for electrochemical sensor development and applied for the sensing of Cd(II) [189]. Similarly, a biosensor was developed consist of bi-protein/layered double hydroxide (LDH) ultra-thin film for catechol. The LDH for the fabrication of the biosensor was synthesized by urea method under hydrothermal treatment [190]. In some reports, synthesized LDH was vigorously agitated in formamide under a N_2 flow at room temperature for several hours. The formamide allows to swell and exfoliate the LDH particles and it is a facile method to get LDH single nanosheets without provision of heat or refluxing treatment [191].

5.2.1.2. Hydrothermal synthesis

Hydrothermal method is generally used when co-precipitation or ion exchange method is not feasible for synthesis of the desired LDH and especially in a situation where organic guest species of low affinity are required to intercalate in the LDH layers [192]. Yang et al [193], proposed a facile hydrothermal strategy is adopted to synthesize the composite of NiCo-layered double hydroxide(NiCo-LDH) with biomass carbon while another group prepared a novel Zn-Mg-based LDHs over a copper substrate by using a hydrothermal method. The work reported Two types of Zn-Mg-based LDH coating are prepared based on hydrothermal reaction time [194].

5.2.1.3. Ion exchange method

Ion exchange is another method through which the LDH could be prepared. The ion exchange method is preferred over co-precipitation where the divalent or trivalent metal cations or the anions involved are unstable in alkaline solution. The ion exchange method is promising when there is more feasibility of the direct reaction between metal ions and the guest anions. This method could be used to replace the interlayer anions with guest anions to achieve desired characteristic LDH. J. Dong replaced the interlayer's anions of the LDH by EDTA2− anion to attained EDTA-LDHs composites for ultra-trace level determination of Pb (II) [195]. Mg–Al– thioglycolic acid (TGA) LDH nanoparticles were also synthesized by anion exchange method. The method consisted of two steps; synthesis of LDH and then incorporation of TGA through anion exchange reaction [196].

5.2.1.4. Co-precipitation method

For most of the LDH and LDH-hybrid modified electrochemical sensors, LDH was synthesized using Co-precipitation method [197, 198]. For instance, a co-precipitation method was used to synthesize Fe/Mg/Ni ternary LDHs which were later used for fabrication of modified electrode [199]. Generally, the hydrothermal assisted co-precipitation was used for the synthesis of the desired LDH [200]. M. Asif et al. synthesized core-shell Fe_3O_4@CuAl LDH NSs using a facile hydrothermal and co-precipitation method, and it was drop cast on GCE [201]. The schematic is given below in Figure 7. Similarly, CuO@MnAl NSs were prepared by facile co-precipitation and hydrothermal routes. The synthesis protocol is given in Figure 8**.**

5.2.1.5. Electrochemical synthesis of LDH on the electrode surface

In this method, LDH is electrochemically synthesized on the bare or previously modified electrode surface [202, 203]. This is accomplished through dipping the electrode into a solution containing LDH precursors of known concentration. Some other methods have been reported for electrosynthesis of LDHs on different electrode surfaces [204, 205].

Table 4.
Comparison with state-of-the-art catechol sensors based on reduced graphene oxide.

Modified electrode	Linear range (µM)		Detection limit (µM)		Refs.
	CC	HQ	CCHQ		
CNCs-rGO	1–400	1-300	0.4	0.87	[171]
Au-PdNF/rGO	2.5-100	1.6-10	0.8	0.5	[172]
P-rGO	5-120	5-90	0.18	0.08	[173]
AgNP/MWCNT	20-260	2.5-260	0.2	0.16	[174]
rGO	1-200	6-200	0.1	0.2	[176]
rGO-MWCNTs	5.5-540	8-391	1.8	2.6	[177]
rGO/Fe_3O_4/AuNPs	0.05–550	0.1–500	0.02	0.17	[178]
NiO/rGO/fMWCNTs	10-300	10-300	0.019	0.040	[13]

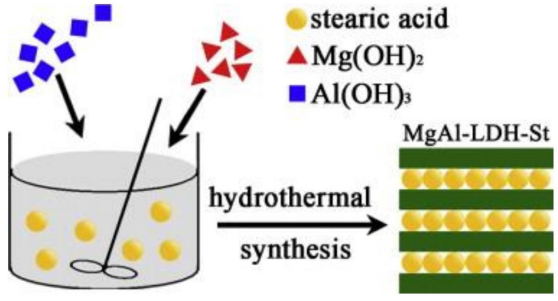


Fig. 7. Flow chart of the synthesis mechanism of MgAl-LDH-St. Reproduced from Science Direct [201].

5.2.2. LDH in electrochemical sensors

Several studies have shown that LDHs are emerging materials for chemical modification of electrode surfaces (Figure 9). Generally, in trace and ultra-trace analysis, such materials allow analytes to confine into a minimal volume near the electrode during preconcentration step leading to low limits of detection (LODs). LDHs can improve sensitivity and selectivity of detection as they allow to immobilize electrocatalytic reagents [206].

LDHs in electrochemical sensing play one or more of the following roles.

- *Electrocatalysts.*
- *Adsorbents for stripping analysis.*
- *A surface for immobilization of other modifiers or biomolecules.*

J. Dong et al. fabricated a highly sensitive carbon paste electrode for the detection of the Pb based on the EDTA/Mg/Al/LDH. EDTA [H4Y] is a well-recognized chelating agent. It forms stable complexes with the heavy metals. In LDH, the EDTA is intercalated by anion exchange method. EDTA can easily replace the anions of the interlayer of the LDH when pH is maintained from 4 to 6 due to its presence in form of anion $[H_2Y]^{-2}$. The fabricated electrode is suitable for the stripping analysis of different metal cations. Modified electrode displayed an excellent electrocatalytic activity and sensitivity for the sensing of ultra-trace level Pb in the tap water and demonstrated very low limit of detection 0.95 ng/L. Apart from this, the developed method was also validated by ICP-AES [195]. Isa et al. successfully used Zn/Al-LDH-MPP/SWCNT/PE for the determination of Hg (II) in various samples. In this method, the synergistic effect of the SWCNT and the LDH has been used to enhance the sensitivity of the electrode. The SWCNTs have excellent conductivity, fast response time and a wide working range while LDH has an excellent ion exchange capability. The developed sensor exhibited superb detection limit of 1 nM. The regeneration of the surface could be attained by mechanical polishing and does not need for various cleaning agents [207] .

The sensitivity and the selectivity of the electrochemical sensor for the determination of the Hg (II) can also be improved by introducing the chelating agent. Thiol group demonstrates an excellent chelating capability for the Hg (II). The thiol group eSH form the mercaptides by interacting with the metal ions [208]. K. Asadpour-Zeynali and Roghayeh Amini incorporated thioglycolic acid (TGA) in the interlayers of the Mg–Al LDH. TGA was intercalated into the LDH using anion exchange method. The developed electrochemical sensor was applied for the trace level quantification of Hg (II). The response of the Mg–Al–TGA LDH/GCE towards Hg (II) was infulenced by the pH change. The maximum response was attained at pH 4. At higher pH, the response was decreased due to the hydrolysis of the metal ions and at lower pH due to LDH instability. TGA in LDH is playing great role for accumulation of Hg (II) due to the strong chelating capability thiol group for the Hg (II). The chelating behavior is one of the factors that improve the sensitivity

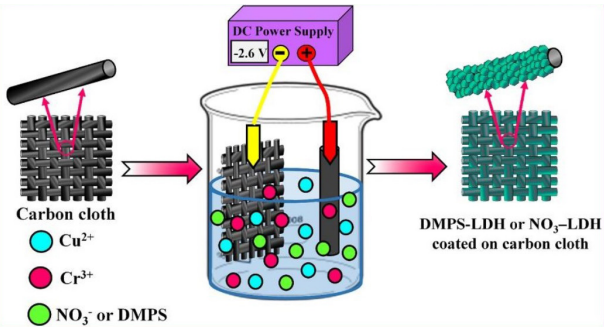


Fig. 8. Schematic illustration of the fabrication mechanism of Cu Cr-layered double hydroxide nanosheet intercalated with 2,3-dimercaptopropane sulfonate (DMPS-LDH). Reproduced from Elsevier [202].

of the Mg–Al–TGA LDH/GCE and helps to achieve very low limit of detection 0.8 nM [196].

Due to its increasing use in different applications and concerns about toxicity, it is imperative to monitor H_2O_2 levels in various environmental compartments. CoAl LDH/MWCNTs nanocomposite modified CPE was used for determination of H_2O_2. Cobalt species in the composite catalyzed the electrooxidation reaction, and CoAl-LDH enhanced the electro-reduction process while MWCNTs have shown the significant electrocatalytic effect on both the electro-reduction and electrooxidation of hydrogen peroxide. The applicability of the proposed sensor was tested in river and wastewater, and very good recoveries were obtained [209]. Silver was electrodeposited on LDH-modified GCE to fabricate a sensor for H_2O_2 detection. LDH provided a stable matrix for electrodeposition of Ag structures. The porous structure of the Ag nanodendrites provided a large surface area for the electrochemical reactions and enhanced the sensitivity of the sensor. The LOD was 2.2 µM. The sensor was used to determine H_2O_2 in spiked milk samples, and outstanding recoveries were obtained [200]. LDH modified electrodes have been fabricated for the sensitive, selective and low-cost detection of various pesticides. S. Khan et al. used zinc and vanadium for the formation of LDH on the silver electrode. The i-v curve was attained at different concentrations of thiourea. The current was increased as the concentration of the thiourea increased. The change in current due to the addition of thiourea could be explained by the adsorption of atmospheric oxygen on the LDH prior to analysis. The LDH attained positive charge due to the transfer of electrons to oxygen and formed Oads−. The potential barrier increased at grain boundaries and the transducer conductance decreased. Oads− could decrease the potential barrier at grain boundaries by releasing the trapped electrons to LDH conduction band. The conductance of the sensor increased as the energy released by the decomposition of the adsorbed molecule is sufficient for transfer of an electron to the conduction band. Thiourea reacts with negative charged adsorbed oxygen and facilitates the transfer of electrons to the conduction band. The linear range was observed from 10 to 500 µM for thiourea [210]. Similarly, pentachlorophenol is also included in priority pollutants list by USEPA. At a large scale, the pentachlorophenol is being used as bactericide, disinfectant and the wood preservative. The territorial and the aquatic ecosystem is badly contaminated due to large scale use of pentachlorophenol. S. Yuan developed a bi-functional sensor which could simultaneously analyze the copper ions and the pentachlorophenol. For this purpose, the multilayers films of the humic acid and the Mg–Al-LDH were developed on the ITO electrode using a layer-by-layer methodology. The layer-by-layer assembly is facilitated by electrostatic attraction of the negatively charged humic acid and positively charged LDH. The combined properties of humic acid and Mg–AlLDH facilitate the fast charge transfer, enrichment of the target analytes and simultaneous sensing. Very low limit of detection 0.4 nM and 2 nM was attained using (LDH/HA)8/ITO for pentachlorophenol and copper ions, respectively

Fig. 9. Key characteristics of LDH modified electrodes.

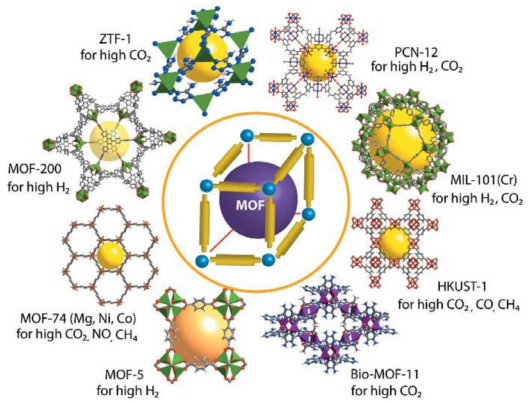


Fig. 10. Schematic representation of important reported MOFs which are known for high gas storage properties. Reproduced from Iucr [223].

[211]. Similarly, the simultaneous determination of catechol and hydroquinone in the presence of resorcinol was done by fabricating a dihydroxybenzene sensor. The Zn/Al layered double hydroxide film sensor was developed by direct electrochemical deposition of the divalent Zn and trivalent Al on the surface of the glassy carbon electrode. The developed sensor exhibited good capability to cope with potential interferences in the presence of targeted analytes [212]. M. Shen et al. synthesized hierarchical NiAl/LDHs using room temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate as a soft template. The hierarchical NiAl/LDHs could provide more exposure to the electroactive site, huge surface area, fast charge transfers and better stability. The fabricated sensor with H-NiAl/LDHs exhibited a great electroactivity for the electrooxidation of hydroquinone and catechol by shortening the diffusion path and facilitating with mass transport channels and easing the electron transfer. The limit of detection 3 nM was observed for the hydroquinone and catechol [213]. Table 5 represents recent electrochemical sensors based on LDH as sensing platform.

5.3. Metal organic framework (MOF)

Metal organic framework(MOF) are a developing class of porous nanostructures formed by ions/metal groups and membership connections, with promising applications in gas absorption, rejection, stimulation, energy storage, chemical sensors, cancer therapy, and medicines [217-219].

Delivery Particularly considering its wide selective surface space, multi-chemical activities, changeable pore size, and close relationships with essential molecules.; plus, apparent interactions, including π-π stacking, hydrogen bonding, and electrostatic force, can be formed between the functional groups (-NH2 or -COOH) in MOFs linkers and probe biomolecules, making MOFs an excellent platforms for biomolecules and drug delivery systems in the environment or medicine applications [220,221].

More precisely, as shown in Figure 10, metal organic frameworks (MOFs) are a kind of crystal porosity composed of inorganic metal centers and organic bridge connections [222]. Because of its high surface area, numerous and customizable pores, and chemical resistance, it has been widely used in heterogeneous stimulation, absorption, medication administration, power storage, and sensors [218, 219].

Metal organic reinforcements have piqued the interest of numerous researchers during the last two decades as novel functional materials. These novel hybrid porous materials are created by combining organic and aggregate connections that include metals or contractual metals. Almost any metal, as well as a wide range of organic species, may be utilized to construct adhesion frames, resulting in a wide range of organic metal tires with varying topologies and properties [224]. Hence, metal organic frameworks have the capacity to adapt during their chemically changed state due to the presence of functional groups in organic dependency. The capacity to create pores and their functions by selecting organic connectivity, functional group, metals, and activation technique distinguishes mineral organic frameworks from other solids

5.3.1. Synthesis and preparation

Because of the potential of customizing its structure dependent on its uses, it has been clearly focused on table spoliation of metal organic frameworks during the last decade. There are several ways for producing metal organic frameworks, including conventional, aided microwave, sonochemical, and chemical [225,226]. The primary difference between these methods is the type of the power input, which will be discussed in the following sections.

5.3.1.1. Conventional Synthesis routes (Ca)

It should be mentioned that the conventional method of assembling metal organic frameworks is the most popular. The needed energy is delivered into the system via typical heating sources. Because temperature is crucial in chemical processes, this path differs from the tract of heat solvent interactions (hydrothermal) and maximal thermal. While heat reactions take place in the CSS reactor (which is generally closed by baggage) under self-contained pressure, the temperature of the reaction must be higher than the solvent boiling point [227]. Typically, the temperature range for enlarging metal organic frameworks extends from ambient temperature to around 250 °C. Because of the simplicity of installation, most metal organic frameworks are produced using heat solvents. As previously stated, this interaction often happens via the format link between organic and mineral salt in the solvent under the aforementioned circumstances, with the end result taking the shape of crystal or powder. Although temperature is an important component in most combinations, only few of the known metal organic frameworks, notably HKUST-1, MOF-5, MOF-177, MOF-74, and ZIF-8, were produced at ambient temperature [228].

The aspect associated with such interactions is that the sediment happens in a short period of time, which is sometimes referred to as direct sedimentation reaction; as a result, there will be a considerable decrease in interaction time [229]. In instance, ZIF-8 has superior chemical stability when compared to other compounds [230]. In general, the organic frameworks are significantly affected by the temperature of interaction, so that metal organic frameworks with different properties, such as different surface spaces and crystallization, can be obtained at different temperatures, whereas intensive metal organic frameworks are generally obtained at high interaction temperatures [231]. Furthermore, not only

does high synthesis affect crystallization, but it also increases interaction rates, particularly when more intractive ions are employed [232]. As a result of the long reaction time and significant energy consumption, other techniques of synthesis were developed.

Furthermore, different approaches can only diminish interaction. Save time and energy while simultaneously having a significant impact on particle formation, dispersion, and size. Pores, which have a significant impact on the properties of metal organic frameworks. In terms of gas separation and storage, the size of holes influences the distribution of guest molecules as well as the adsorption properties of porous materials such as metal organic frames. Because of these objectives, other artificial means such as microwave-assisted tracks, sonocular chemical corridors, mechanical and electrical systems have been used.

5.3.1.2. Microwave Synthesis (MW)

Microwave irritation is a well-known method for creating materials [233]. This technique is based on the interaction of mobile electric charge with electromagnetic radiation. Electrons or ions in solids, as well as the presence of polar solvent and molecules / ions in solution, can offer electric shipment. As a result, the power supply and heating are generated in a solid form and a solution on the basis of the aforementioned discriminating mechanism. In the case of a solid article, the power is generated as a machine to compensate for the electrical resistance of the solid object Materials. The power supply is created in the solution by aligning the particles / ions when exposed to an electromagnetic field, the direction of which is constantly changing. where, For the best final product, a suitable frequency is required to create a suitable collision between The reagents contribute to increasing kinetic energy and temperature reaction Furthermore, due to the possibility of interaction between raw materials and megawatic radiation [234], the selection of selective power inputs and appropriate solvents is required and must be taken into account.

The synthesis reaction takes place in a microwave oven, and the interaction conditions must be met. It is specifically regulated in terms of temperature and pressure. Be reactionary for organic frameworks. It was finished at temperatures exceeding 100 ° C in less than an hour, which is faster than traditional procedures. The MW advised on how to raise the syrup rate while keeping the crystalline size low (mainly in the nanoscale). This artificial road is an excellent heating energy Effective technique due to its high reaction speed, short reaction time, and the interaction between the detector and radiation. As a result, the synthesis reaction can also take place at a rapid rate of heating. Many studies reported the advantages of using microwave synthesis of MOF [235, 236]. These studies confirmed that microwave irradiation reduces the time of reaction considerably, suggesting the effectiveness of this methodology in the synthesis of metal-organic frameworks. It is noteworthy that microwave assisted synthesis produces monocrystals suitable for X-ray diffraction studies, reducing reaction time and with higher yield than the classical hydrothermal procedures. To construct metal organic frameworks, other routes are available, including electrochemical, mechanochemical, and Ultrasound-mediated chemical interactions.

5.3.2. MOF in electrochemical sensors

Because of the structure of the macro / total porosity, high connector, and wide surface area, the composite of the organic metal works (MOFs) are becoming more attractive in the field of electrochemical senses [237]. However, the rational design of metal-metallic metal frameworks is still in its early stages for electrochemical vital sensors, and more significantly, there were a few metallic metal organic frameworks to detect phenolic compounds [27, 28]. When employed in electrochemical vital sensors, nickel and copper-based organic frameworks, in particular, have good stability, stimulation, and low fascination activity, as well as a low vital conflict [238].

A series of nanoscale MOFs, such as Ni-MOFs and Cu-MOFs, have been reported to be efficient electrocatalysts for detecting analytes [239"title-short":"Size controlled synthesis of Ni-MOF using polyvinylpyrrolidone","volume":"829","author":[{"family":"Arul","given":"P."},{"family":"John","given":"S. Abraham"}],"issued":{"date-parts":[["2018",11]]}}],"schema":"https://github.com/citation-style-language/schema/raw/master/csl-citation.json"} -241]. Compared with their bulk analogues, the nano-MOFs based electrochemical sensors showed significantly improved sensitivities and greatly decreased detection limits, even down to Nm or pM concentrations. Liu group [231] also investigated the influence of the nanostructure and particle size of Cu-BTC MOFs on the electrochemical response of sensors for detecting glucose. However, the decrease in the particle size may to a large extent result in serious aggregation during the electrode preparation process, which may in turn reduce the number of exposed active sites. To solve this problem, Liu et al. prepared monolayer-oriented Cu-BTC nanotube arrays via a facile interfacial emulsion synthesis method and further integrated these arrays in a flexible amino-functionalized graphene paper (NH_2-GP) electrode for both the static and dynamic measurement of lactate and glucose in human sweat [232].

MOF-based materials with core–shell heterostructures have been reported to have a good selectivity for detecting analytes. For instance, Yanng et al. [233] prepared a core–shell heterostructure of Cu_xO NPs@ ZIF-8 via the direct calcination of $Cu_3(BTC)_2$@ZIF-8 composites by considering the different thermostability of the two MOFs. The small Cu_xO NPs cores derived from $Cu_3(BTC)_2$ were uniformly dispersed inside the ZIF-8 shell, which allows only small sized H_2O_2 molecules to pass through, while larger molecules are blocked. As a result, the fabricated electrochemical H_2O_2 sensor displayed a high selectivity towards interferents including uric acid, dopamine, amino acid, ascorbic acid, etc. Meanwhile, Cu_xO NPs without protecting MOFs suffered from serious interference effect. Although noble MNPs@MOFs were also widely reported for use in electrochemical sensor applications, noble MNP-based electrochemical sensors usually work best at high potentials, leading the electrochemical sensors to exhibit a poor selectivity.

Various methods have been employed to prepare MOF/MNP composites, most of which involve loading the MNPs on the as prepared

Table 5.
Comparison with state-of-the-art electrochemical sensors based on LDH.

Sensing interface	Pollutant	Linear range (μM)	LOD	Refs.
Co-Al-SDBS HT/GCE	2-chlorophenol	0.005–0.5 μM	0.002 μM	[197]
(LDH/HA)8/ITO	Cu(II), pentachlorophenol	3–320 nM,	2.0 nM,	[211]
Mg-Al-SDS/GCE	Bisphenol A	0.008–2.808 μM	2.0 nM,	[214]
CHT/[Zn3-Al-Cl]/PPO/GCE	CC	3.6 nM–40 μM	0.36 nM	[215]
HeNiAl/LDHs	CC/HQ	0.6 μM–6 mM	0.1 μM	[213]
$LDH/HB/LDH/HRP)_2$UTF	CC	6–170 μM	5 μM	[190]
LDH-PCNT/GCE	CC	10–200 μM	0.27 μM	[216]

MOF surfaces, forming surface attached structures, or encapsulating the as-prepared MNPs into MOF cages/channels, forming a totally surrounded structure [242]. For instance, Ma et al. [243] reported the attachment of AuNPs on metal metalloporphyrin frameworks (Au NPs/MMPF-6(Fe)) via electrostatic adsorption. Due to the strong synergistic catalysis effects, enlarged active surface area, and high conductivity, the AuNPs/MMPF-6(Fe) composite could ultra-sensitively detect hydroxylamine at concentrations as low as nanomolar levels in real pharmaceutical and water samples. Likewise, Li et al. prepared composite by decorating Ag NP surfaced with MIL-101 MOFs to detect tryptophan [244]. In similar work, Ce-MOF/CNTs nanocomposites were prepared by a simple method and post-treated with $NaOH/H_2O_2$ mixed solution was prepared by Huang et al., [69]. The electrochemical behaviors of nanocomposite were also investigated on electrochemical work station. By utilization of the good electrical conductivity of CNT, the two-valence of Ce and the high surface area of MOF, the nanocomposites were used to fabricate the electrochemical sensor for the simultaneous electrochemical detection of hydroquinone (HQ) and catechol (CC). Compared to the Ce-MOF/CNTs/GCE, the post-treated Ce-MOF (TV)/CNTs/GCE exhibited two well-defined peaks for the electrochemical oxidation of HQ and CC. The linear ranges responding to HQ and CC are 10 ~ 100 μM and 5 ~ 50 μM respectively. Another work published by Dand et al, AuNPs-NH_2/Cu-MOF/GCE exhibits itself as a highly sensitive and selective electrochemical enzyme-free sensor for H_2O_2 detection. A quantitative detection to H_2O_2 can be found with a wide linear response toward H_2O_2 concentrations ranging 5–850 μM, its limit of detection (LOD) is as low as 1.2 μM with a high sensitivity of 1.71 $\mu A/cm^2 \cdot \mu M$. AuNPs-NH_2/Cu-MOF/GCE sensor has been applied to determine H_2O_2 effectively in human cervical cancer cells by adding the ascorbic acid as the stimulant. Our work presented a AuNPs-NH_2/Cu-MOF/GCE composite electrode which is a promising enzyme-free electrochemical sensor for quantitively H_2O_2 detection in human cervical cancer cells [245].

5.4. Metals and metal oxides

In the realm of electrochemical detection, nanoparticles, particularly metallic nanoparticles, provide several benefits. Nanoparticles, because to their tiny size, can enhance the surface area of the electrode utilized (Figure 11). Furthermore, metallic nanoparticles can speed up electron transport and enhance the sensitivity of the electrodes employed [252, 253]. In this section, we will discuss how different forms of metal nanoparticles may be used in electrochemical sensors.

Metal oxide nanoparticles have been the focus of extensive research in electrochemical detection in recent years. Varied techniques were used to produce different sizes, stability, and morphology. Because of these variations, they exhibit distinct electrical and photochemical characteristics, resulting in diverse applications [251]. Porous metals and porous metal oxides are examples of porous and nanostructured materials. They offer numerous exceptional properties (for example, their unique pore structure, huge apparent surface area, and high electrical conductivity) that make them an amazingly attractive candidate for a wide range of essential applications (such as energy storage, detection and catalysis). Different metal oxides, particularly transition metal oxides, have been utilized to modify electrodes for the detection of various analytes, including heavy metals. Although virtually all transition metals have been utilized to manufacture these oxides, only a handful have been employed to detect organic pollutants [254].

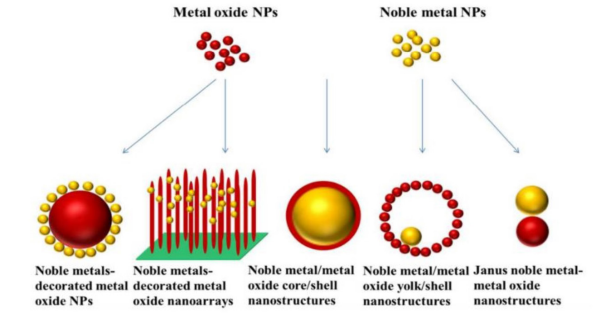


Fig. 11. Schematic representation of different structures of noble metal-metal oxide nanocomposite. Reproduced from Royal Society of Chemistry [260].

Many inorganic and organic components are found in porous materials, including carbon, metals, metal oxides, inorganic and organic hybrid materials, and polymers. Porous materials are classified as microporous (pore size 2 nm), porous (2 nm pore size 50 nm), and microporous (pore size [50 nm]) by the International Union of Pure and Applied Chemistry (IUPAC) [255]. Porous materials have pores with a diameter of less than 100 nanometers. Porous nanometals/metal oxide-based materials produced by dispersing them have garnered extensive interest in various domains such as energy storage, sensing, and catalysis due to their high-order networks and excellent pore size distributions. Excellent electrical stimulation, for example, can, on the one hand, extend the active region accessible to reactive molecules; on the other hand, it can boost electron mobility in solid ligands due to their metallic porosity frameworks [256].

Furthermore, additional significant uses of large porous materials have been investigated, ranging from sensing to energy storage systems [257]. Various strategies for adapting porous architectures and rational design of porous metal/metal oxide materials have been developed during the last decade. The physicochemical performance and fundamental information of these effectively manufactured metal/metal oxide nanomaterials allowed for a systematic experimental investigation, which led to the creation of numerous functional devices, such as microsensors and ultra-thin supercapacitors [258, 259]. The field of application of nano-metals/metal oxide-based materials is now undergoing an exciting development with growing success. It is necessary to provide timely updates of such type of advanced materials, including in the essential properties and new applications. This study summarizes major applications such as supercapacitors, lithium-ion batteries, energy stor-

Table 6.
Comparison with state-of-the-art electrochemical sensors based on MOFs.

Modified electrode	Linear range (μM)		Detection limit (μM)		Reference
	CC	HQ	CC	HQ	
Ce-MOF(TV)/CNTs/GCE	10-100	10-50	2.05	2.05	[69]
TiO_2/C900/GCE	5-10	5-10	1.24	2.05	[246]
MOF-ERGO-5 / G	0.1-566	0.1-476	0.1	0.1	[247]
ZIF-8@rGO-0.02/GCE	10-70	10-70	0.47	0.37	[248]
Cu-MOF	0.2–184.5 (H_2O_2)		0.067 mM		[249]
Ni-MOF	Nitrobenzene 0.25–1.5 mM;		NA		[250]
Cu-MOF	Histidine 0.1-200 μM		25nm		[251]
Cu-MOF	ASCORBIC ACID 0-4MM		14.97		

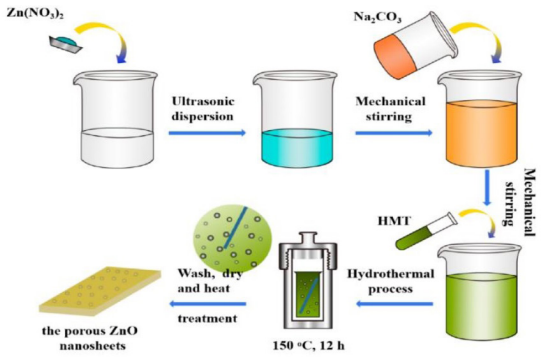


Fig. 12. Schematic Illustration of the Hydrothermal Synthesis of ZnO nanosheets. Reproduced from ACS [278].

age, detection, electrocatalysis, and photocatalysis [253, 252]. This will be useful for research on nanoscale metals and metal oxides, and it may lead to more sophisticated functional materials in associated sectors.

5.4.1. Synthesis and preparation of Metals

Metal manufacturing from mineral compounds has been a major human activity since time immemorial, and minerals have played an important part in building the modern world as it is now [261]. The chemical reduction of many minerals results in the formation of many minerals [262]. Their specific oxides and reduction technique are determined by the relative stability of the metal oxides and the oxides of the reducing agent employed. Transition metal and actinide stable oxides require reduction with strong reducing agents such as lithium, sodium, calcium, or magnesium and even plants extracts [263, 264].

Metallic thermal reduction does not pose such issues; however direct one-step reduction is frequently problematic due to oxygen contamination of the metal result. often enjoy Metal oxides must be converted to specific halides before being chemically reduced with alkaline earth metals to produce metals with low oxygen pollution [265]. Metal oxides are also difficult to electrolyze conventionally due to their limited solubility in electrolyte melting, high working temperature, strong metal affinity for oxygen, and other factors [266]. These metal manufacturing methods create huge volumes of toxic gases, such as fluorine or chlorine, salts, and used trash, all of which require extra treatment to avoid pollution of the environment [267]. In the recent past, there has been much discussion regarding the electrochemical process of molten salt in which a solid metal is produced. At very low oxygen levels, oxides can be directly reduced to related metals or alloys [268]. The patented process's simplicity and the predicted claims Capable of generating metals or alloys more effectively and inexpensively than existing traditional techniques, the novel technology has sparked global research efforts to extract various metals/alloys from their respective oxides.

Up to now, the control of the size, shape and structure of MONCs have been achieved by various synthetic methods. Vapor phase growth is always carried out in a thermal furnace. It is necessary to regulate the reaction between oxygen gas and metal vapor source. In order to achieve it, various methods have been developed to control the aspect ratio, diameter and specific surface area of the product. It mainly involves thermal chemical vapor deposition (CVD) and metal–organic chemical vapor deposition (MOCVD), etc. [269, 270] (Figure 12) . Meanwhile, the mechanism could be classified as vapor–solid (VS) and vapor–liquid–solid (VLS) [271, 272] (Figure 13). Generally, metal nanoparticles are used as the nucleation seeds, which have essential influences on the growth direction and diameter of products in VLS process. In the beginning, catalysts are molten into liquid alloy droplets which also contain source metal. When the alloy droplets achieve supersaturated, source metal start to precipitate and form metal oxide under the oxygen flow.

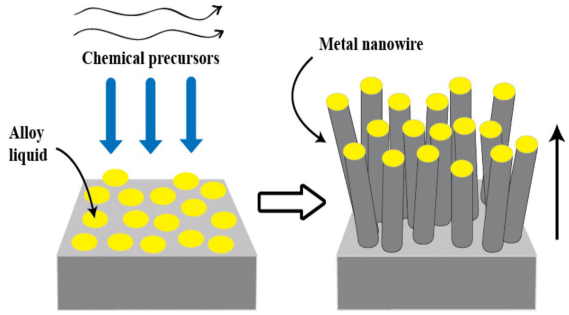


Fig. 13. Vapor-Liquid-Solid (VLS) method for vapor-phase synthesis of metal nanowires. Reproduced from Research gate [279].

In general, the as−synthesized metal oxides preferentially grow along particular orientation, which lead to the formation of 1D nanostructures. So far, the preparation of metal oxide nanowires, such as ZnO [273] and TiO_2 [274], have been achieved by means of VLS mechanism. From what have been discussed above, VLS process belongs to catalyst−assisted growth, while VS process belongs to catalyst−free growth. In the course of VS process, the reactants are first heated to form vapor under high temperature and directly condensed on the substrate, on which seed crystals will take shape and be served as the nucleation sites located. Facilitate directional growth followed will minimize the surface energy of product. Electrochemical deposition has been successfully applied to fabricate metal oxide nanostructures. It exhibits many advantages during synthesis process. Take the preparation of ZnO [275] for example, making use of appropriate electrolyte, ZnO have been successfully prepared. Meanwhile, researchers also try to introduce the template into electrochemical deposition method. A gel comprising of sol particles is essential for sol–gel process [276, 277].

Back in the 1970s, hydrothermal process was firstly employed to synthesize crystalline structures. The reactants are placed in a closed vessel with water as a reaction medium. The reaction is conducted under high temperature and pressure conditions. Hydrothermal process can accelerate the reactions between ions and promote the hydrolysis reaction. Ultimately, the growth and self−assembly of crystals will be achieved in solution. The advantages of the method involve low cost, mild reaction conditions and controlling the device easily. By changing the experimental parameters (temperature, pressure, time, the reaction medium, etc.), the morphology, structure and properties of the product can be well regulated. In order to improve the hydrothermal process, surfactants are introduced to the system. Surfactant−promoted process has been demonstrated to be an effective method to fabricate metal oxide with a variety of morphologies. The system is always composed of three phases: oil phase, surfactant phase and aqueous phase. In the course of process, surfactants can confine the growth of product.

5.4.2. Electrochemical sensors based on metals and metal oxides

Metal and metal oxide based electrochemical sensors are attracting more studies for sophisticated applications in the biomedical, environmental, and security industries because to their high sensitivity, compact size, and low cost [246, 280]. In recent years then, novel nanostructures based on metal oxides have been proposed as detecting materials to increase their detection characteristics (Table 7). Detection of hazardous compounds, toxic molecules, viruses and even cancer in real samples such as water, food, human body, industrial sites, or industrial wastewater are just a few examples of situations where using metal and metal oxide based sensors and biosensors for a sensitive, rapid and selective detection of the target analyte is critical [280, 246, 281]. Indeed, quick and precise detection is critical in light of practical applications in domains such as medical diagnosis, environmental monitoring and hazard-

ous compounds detection.

Pan et al. have prepared hierarchical hybrid films of MnO_2 nanoparticles/multi-walled fullerene nanotubes–graphene (MNPs/ MWFNTs–GS) via a simple wet chemical method for the detection of H_2O_2. Studies revealed that MWFNTs can further enhance the conductivity and catalytic performance of MNPs/GS by providing extra electron/ ion transfer paths and inhibiting the aggregation of GS and MNPs [282]. f-MWCNT/MnO_2/GCE modified film provides a good platform for the determination of ferulic acid and the synergistic effects of CNTs and the metal oxide nanocomposites could improve the electrode conductivity [283]. For the detection of catechin, a Pt/MnO_2/f-MWCNT/GCE modified electrode was developed by the electrochemical treatment of the f-MWCNT coated GCE. This electrode was able to determine catechin from real samples like red wine, black tea, and green tea and have a good linear range and low limit of detection [284]. Molecularly imprinted polymer modified electrochemical sensor based on manganese oxide nanoparticles were also studied. The synthesized MnO_2/GO/CuO nanocomposites were reinforced by poly vinyl acetate molecularly imprinted polymer of glucose which coated on copper wire surface was used as the working electrode. This sensor exhibited linear range from 0.55 to 4.4 mM and the detection limit was 53 μM [285].

Copper oxide nanoparticles integrated with carbonaceous materials like graphene [286], carbon nanotubes [287], mesoporous carbons [288] and carbon nanofibers [289] can improve the performance of the sensor by enhancing the charge transfer between support matrices and analytes. In the case of imprinted polymer-based sensors, CuO nanoparticles were used to enhance the number of imprinted sites of the electrode and thereby improving the selectivity and sensitivity of the electrochemical sensor [290]. Cu_xO NPs@ZIF-8 composite derived from core-shell metal-organic frameworks were synthesized by Yang et al. and found that well dispersed Cu_xO NPs possessed good crystalline structure and the encapsulated Cu_xO NPs presented good electrocatalysis for H_2O_2 oxidation [291].

Molecularly imprinted polymer-based sensor for 4-nitrophenol was described using ZnO nanoparticles/multiwall carbon nanotubes-chitosan nanocomposite. This was coated onto an ITO electrode and then imprinted sol-gel solution was electrodeposited onto the modified electrode to construct the sensor. The developed nanocomposites have porous electrodeposition imprinted film with abundant selective binding sites and functional monolayer with electrochemical catalytic activities [292]. Roy et al, presented a novel imprinted polymer-based sensor for the detection, removal, and destruction of Escherichia coli bacteria on the surface of Ag-ZnO bimetallic nanoparticle and graphene oxide nanocomposite. This nanocomposite provided a platform for imprinting of bacteria as well as participated in their laser-light induced photo killing. The MIP-modified glass plate is able to remove 98% of bacteria in a single analysis [293]. Nickel nanoparticles incorporated ZnO sensors possessed strong electrocatalytic ability towards the sensing of glucose, dopamine and uric acid [294]. A sensor for electrochemical monitoring of nucleic acid hybridization related to the Hepatitis B Virus (HBV) contains, ZnO NPs enriched with poly (vinylferrocenium) (PVF+) modified single-use graphite electrodes [295].

Electrodeposited cobalt oxide has been a promising material for FAD immobilization with excellent catalytic activity for nitrite reduction over a linear range of 1–30 μM and limit of detection of 0.20 μM [296]. Single crystal and vertically aligned cobalt oxide (Co_3O_4) nanowalls coated on GCE via conductive silver paint were used for the electrocatalytic oxidation and reduction of hydrogen peroxide in 0.01 M pH 7.4 phosphate buffer medium up to 10 mM concentration of H_2O_2 [297].

6. Conclusions and future insights

Design and fabrication of electrochemical sensors for organic pollutant (CC, HQ and 5-CP) is an active area of research that has drawn the interest of scientific communities due to the high toxicity of these pollutants. In the present work, several types of electrochemical sensors for CC, HQ and 5-CPdetection were developed based on advanced materials namely CNTs, MOFs, LDHs, graphene, metals and metal oxides NPs. These systems are offering new opportunities with advantages such as high sensitivity and selectivity, rapid response, and cost efficiency.

Electrochemical techniques coupled with the use of nanomaterials are useful for the development of electrochemical sensors capable of sensitive monitoring of CC, HQ and 5-CP with fast-responses. A combination of nanomaterials offers a high degree of specificity and makes the sensing formats attractive for the design and fabrication of integrated detection systems. In the present thesis, the use of nanostructured materials in the development of sensors has led to an increase in sensitivity, sensibility, and reproducibility, which confirms the benefits of nanomaterials combinations.

Nanomaterial based sensors provide a new and powerful paradigm in terms of novel and augmented functionality that encompasses a wide variety of applications in clinical diagnostics and biological research. The rapid and precise real-time detection of analytes requires that electrochemical sensors be endowed with low energy consumption, rapid response time, enhanced selectivity, sensitivity and swift recoverability (refresh ability). Each of these parameters will undoubtedly undergo further improvements and refinements in the future due to advances in nanomaterials synthesis, processing, integration and testing techniques. It is anticipated that nanomaterials will play an unprecedented role in the future development of advanced diagnostics.

Based on the results obtained in the present thesis, we highly emphasize the following points to readers:

- Because of their multiple unique properties, CNTs, MOFs, LDHs, graphene, metals and metal oxides NPs provide significant advantages. Outstanding mechanical strength, huge surface area, excellent electrical conductance, electrochemical stability in aqueous and non-aqueous samples, and high thermal conductivity. Because of their extraordinary charac-

Table 7.
Comparison with state-of-the-art electrochemical sensors based on metals and metal oxides nanoparticles.

Modified electrode	Linear range (μM)		Detection limit (μM)		Refs.
	CC	HQ	CC	HQ	
MgO/GO/MCPE	-	-	0.45	0.37	[7]
AuNPs/Fe_3O_4-APTES-GO/GCE	-	-	0.8	1.1	[298]
AuNPs@MoS_2-rGO-AuNPs/GCE	1-145	3-137	0.95	0.04	[299]
Ag/MWCNT/GCE	3-160	0.1-40	0.2	0.16	[174]
NiO/MWCNT/GCE	20-260	2.5-260	0.015	0.039	[300]
Au-PdNF/rGO/GCE	7.4-56	7.4-56	0.8	0.5	[172]

teristics, they are ideal materials for ultrasensitive nanoscale sensors and biosensors.

- The development of appropriate methods for tackling the challenges connected with the quick and sensitive detection of organic pollutant in aqueous environments is now underway in scientific research including materials science platforms. However, the path "from laboratory to reality" is difficult and must be improved by inventing new gadgets based on nanomaterials such as CNTs, MOFs, LDHs, graphene metals and metal oxides NPs, which are inexpensive to manufacture and have the fewest negative environmental consequences. However, the cost of preparation, as well as the stability and biocompatibility of these nanomaterial, must be considered, and better control over their properties is necessary.
- Researchers must explore the potential for synergistic effects of CNTs, MOFs, LDHs, graphene with other nanomaterials, in particular metals and metal oxides and its biocompatibility with biological components. Such combinations can promote performance and speed up the biosensor response to organic pollutant and even viral diagnosis including SARS-CoV-2.

In conclusion, the field of carbon nanomaterial-based sensors is growing quickly with the invention of many new carbon nanomaterials taking into consideration their synergetic effect with metals and metal oxides NPs. Carbon nanomaterials have many advantages for electrochemistry including fast electron transfer rates, high aspect ratios, and resistance to fouling. While many new materials are still being developed, future studies will likely help narrow down which are the most effective for mediating electron transfer. Newer methods that allow growth of carbon nanomaterials directly on the electrode substrate or fabrication of electrodes solely from CNTs for example might be helpful for making sensors of pure carbon nanomaterials.

However, combinations of carbon nanomaterials, polymers, and metal particles will also continue to be popular because of the synergistic effects of combining materials. In the future, advances in fundamental knowledge of new nanomaterials along with a focus on practical applications in real-world systems will drive the field and lead to breakthroughs in sensing and biosensing technology.

Acknowledgments

The authors received no financial support for the research, author-ship and/or publication of this article.

Conflict of interest

The authors declare that there is no conflict of interest.

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