CHAPTER- 1

Introduction and Literature Review

1.1 Introduction

Analytical detection approaches are continuing to garner the close attention of researchers and industry experts due to their growing utility in a wide range of disciplines. These disciplines include medical diagnostics[1], healthcare [2], environmental pollution monitoring[3], drug delivery [4], food quality testing [5], warfare agent detection [6], and pharmaceutical industries [7], etc. Such analytical methods are mostly employed to identify, quantify, separate, and characterize the physicochemical properties of a given chemical or collection of chemicals. Analytical approaches provide good accuracy, high specificity, good linearity, high sensitivity, low detection limits, and better selectivity. Because of the aforementioned characteristics, analytical approaches play an essential role in the selection, stability analysis, development, and quality control of the produced product [8,9]. In medical diagnostics, these approaches are important because they identify specific diseases or pathogens by detecting related peptides [10], epitopes [11], nucleic acids [12], and other biomarkers [13–15]. The analytical techniques provide specific information about the patient's condition as well as the illness's cause and pathway. Analytical detection approaches are extremely helpful in various applications, such as fermentation industries [16], and food quality monitoring to guarantee the end products' quality and provide a thorough sensory analysis. Furthermore, analytical techniques could be applied to generate a reliable and fatigue-free tool for identifying potentially harmful substances in environmental pollution monitoring [17], evaluating the chemical and physical stability of produced drug molecules [18], and characterizing and quality-checking medicinal product materials for pharmacokinetics analysis [19]. Several methods are commercially accessible and widely utilized for diverse analytical purposes, and many of them are based on titrimetric [20], chromatographic [21], spectroscopic [22], electrophoretic [23,24], and electrochemical investigations [25,26]. Electrochemical methods have sparked widespread attention due to their ease of sample preparation, low cast, selectivity, portability, and rapid analysis [27]. Electrochemical techniques are well-known for their excellent sensitivity, specificity, selectivity, and ability to conduct quick analyses. Electrochemical sensors provide more sensitivity than other conventional approaches such as colorimetry [28]. The electrochemical sensors are also cost-effective compared to other techniques, such as high-performance liquid chromatography (HPLC) and spectroscopic techniques [29,30]. With the advancement of portable electrochemical sensors on a chip, in-situ monitoring of environmental pollutants in real samples has become significantly more sensitive [31]. In this particular circumstance, biosensors or electrochemical biosensors may be a practical substitute for the currently expensive, time-consuming, and labor-intensive analytical tools and procedures such as HPLC and gas chromatography utilized in various industries, including medical diagnosis and other fields.

1.2 Biosensor

The word "biosensor," is defined as per the IUPAC terminology; it is a device that detects chemical molecules, through electrical, thermal, or optical signals, that utilizes specific biochemical processes mediated by tissues, organelles, immune systems, isolated enzymes, or whole cells [32].

Leland C. Clark developed an enzyme electrode in 1962, which represents the beginning of the history of biosensors. Since afterward, researchers from a variety of disciplines, including chemistry, material science, physics, biotechnology, and medicine, have collaborated to create more advanced, dependable, and mature biosensing devices for use in biotechnology such as agriculture, medicine, and the military as well as in the detection and prevention of bioterrorism. The primary goal for using biosensors is to estimate the concentration of one or more required components, or perhaps other biologically significant parameters, by utilizing biological recognition elements. Owing to the specificity in the binding between an analyte and the immobilized biomolecule such as enzymes, antibodies, and nucleic acids. These devices are usually highly specific. They also include a support matrix platform (such as planar carbon, metal, nanostructured metal, metal oxide, and other inorganic, organic, and carbon-based nanoparticles) to stabilize the immobilized biomolecules, to serve as a signal transducer (which include optical, piezoelectric, magnetic, and electrochemical ones) and to convert the measured response into an electrical signal, and additional accessories such as processors, display systems, and signal amplifiers [33]. The vital components of the biosensor are the bioreceptor, transducer, and electronic device as shown in Figure 1.1.

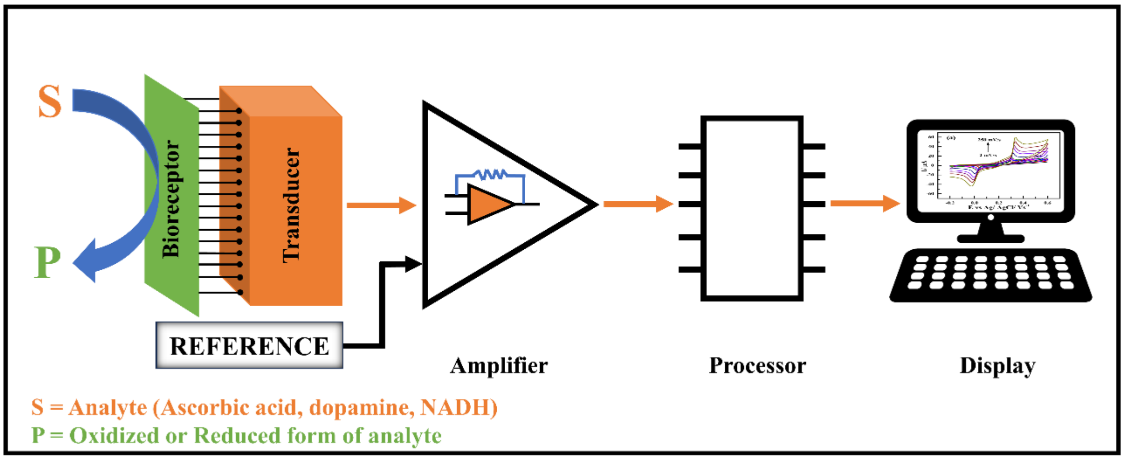

Figure 1.1 Components of biosensor.

1.2.1 Bioreceptor

Bioreceptors are biomolecules that recognize and bind to specific target molecules, playing a crucial role in various biological processes. These molecules act as sensors, detecting changes in their surroundings environment. The receptor and analyte interact differently depending on the sensor. The bioreceptor can be categorized into enzyme, antibody, nucleic acid, whole cell, and nanoparticle-based receptor [34].

1.2.2 Transducer

Transducers are essential parts of sensors that convert one form of energy into another form. The interaction between the analyte and the receptor produces a response that is detected by the transducer and converted into a measurable signal. The process of transforming energy into a signal is known as signalization [35]. Typically, transducers produce electrical or optical signals that represent the target analyte concentrations. Recently, the term "Nanotransducer" has been introduced to categorize transducers that facilitate signal transduction through structures meeting the criteria of nanostructures, with at least one dimension below 100 nm and another dimension smaller than 1 µm. Nano transducers are just those sensors that relate to nanotechnology based on geometrical dimensions [36,37]. The transducer can be classified into electrochemical, mass-based, and optical based on its mode of functioning.

1.3 Types of biosensors

Biosensors are classified based on the basis of transducer elements or the nature of bioreceptor elements [38]. Figure 1.2 shows the image of the type of biosensor which is based on a transducer and bioreceptor.

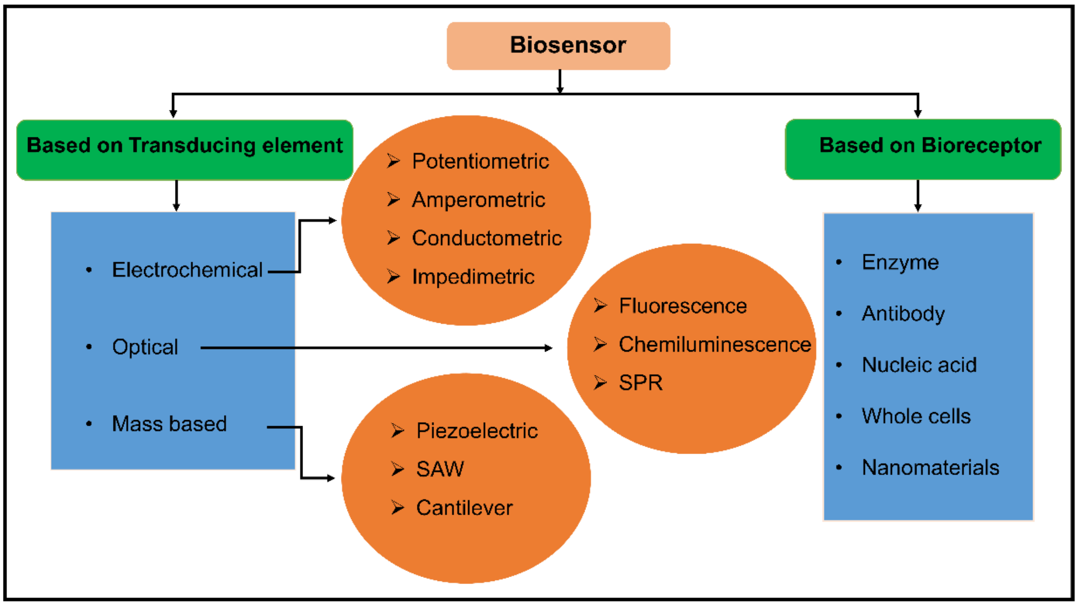

Figure 1.2 Classification of biosensors based on transducer and bioreceptor.

1.3.1 Based on the transducing element

Based on transducing elements, the biosensor is classified as follows:

1.3.1.1 Electrochemical biosensor

At present time, the most popular and accessible biosensors on the market are electrochemical ones. They are utilized to develop point-of-care (POC) devices because they are very portable, easy to use, and more affordable than other biosensors. Numerous biomolecules found in the human body, including blood ketones, hemoglobin, glucose

[39,40], cholesterol [41,42], uric acid [43], lactate [44], folic acid [45], and DNA [46] can be detected by electrochemical sensors. As a result, they hold a great deal of promise for treating illnesses caused by biomolecule imbalances. There are few studies on biosensing-drug delivery applications, and they are primarily utilized for biosensing applications. There is a lot of research being done on enzyme- and protein-based electrochemical biosensors to identify particular analytes [47–49]. These electrochemical biosensors use immobilized proteins or enzymes on the transducer to determine a particular analyte using detectable electroactive by-products. In the future, drug-release-capable protein or enzyme-based electrochemical biosensors may be used to treat numerous types of diseases.

Electrochemical methods offer the advantages of sensitivity, simplicity, low cost, and the ability to fabricate portable devices for on-site determination. These techniques have sparked widespread interest in biomolecule analysis because they are electroactive and easily subjective to redox electron transfer reactions [50]. However, electrochemical sensors necessitate the use of modified electrodes to increase electrochemical performance, such as sensitivity, stability, and antifouling ability. In the most recent findings, different types of nanomaterials, such as carbon nanomaterials, metal nanoparticles, and metal oxide nanomaterials [51], have been effectively used as electrode-modifying agents for electrochemical identification of biomolecules. Recently, metal-based nanomaterials and, their composites have been the most often utilized improved materials for electrochemical sensors due to their large specific surface area, good electrocatalytic activity, and exceptional electronic transport capabilities. A series of carbon-based hybrid materials, such as graphene-metal nanoparticles [52] and graphene-metal oxide nanocomposites [53], are particularly interesting in the field of electrochemical sensors because they exhibit the synergistic effect of catalytic properties of both graphene and other nanomaterials. Ascorbic acid, dopamine, and NADH are electroactive materials and play an essential role in cellular processes such as enzymatic reactions, oxidative stress, and neurotransmission so electrochemical sensors are well-suited for detecting these molecules in real-time within biological samples.

1.3.1.2 Potentiometric biosensor

Potentiometric sensors have received significant interest as a platform for the ex-situ and in-situ monitoring of various analytes in complicated matrices. Potentiometric sensors measure the analyte concentration by measuring the potential difference between the working and reference electrodes at various analyte concentrations. Such sensors include ion-selective electrodes. The pH meter is a common example. Potentiometric sensors are widely employed in several disciplines such as environmental and water analysis [54], food quality assurance [55], pathogen detection [56], and health monitoring [57]. Although a large number of potential potentiometric sensors have been published or brought to market, their repeatability, reproducibility, stability, and sensitivity for monitoring analytes of interest in complex media and real-world samples still need to be improved. These enhancements can be achieved with new technologies and advances in nanomaterials.

1.3.1.3 Amperometric biosensor

Amperometric biosensors monitor the current generated by the oxidation or reduction of an electroactive biological constituent, demonstrating particular quantitative analytical data. An amperometric biosensor produces a current that is directly proportional to the concentration of substrate that needs to be detected. The most readily available biosensors are amperometric biosensors, which are the oldest and dependent on electron-transfer monitoring techniques. The most common example of an amperometric sensor is the Clark Oxygen electrode [58].

The most important factors in developing amperometric biosensors are sensitivity, accuracy, selectivity, and response time. The remarkable feature of amperometric biosensors is that any fundamental component necessary for the analytical reaction is tightly attached to the transducer surface. The working electrode potential value ranges from an initial potential (E_i) to a final potential (E_f), concerning variations in current values measured. The amperometric measurement of biomolecules is based on the direct electrochemical oxidation or reduction of metabolic reaction products [59]. The current intensity is directly related to the concentration of the electroactive analyte. Amperometric detection is based on the intensity of current over time, which is determined by the applied voltage and analyte concentration. Amperometric biosensors are classified into three types: (1) based on the estimation of the concentration (2) electron carriers as mediators, and (3) utilizing direct electron transfers.

1.3.1.4 Conductometric biosensor

Conductometric biosensor is an example of an electrochemical biosensor. It contains a small electrode and exhibits excellent sensitivity. Conductometric biosensors typically detect an alteration in conductivity throughout a reaction. The majority of reactions include a compositional change. As a result, relative changes in the solution can be detected using conductometric biosensors [60]. This approach has limitations, including low specificity, signal-to-noise ratio should not exceed 2 %, and limited stability when measuring tiny conductivity modifications within high ionic strength media. One problem is the lack of specificity, which makes it difficult to distinguish between distinct reactions. One strategy involves monitoring electrode conductivity changes following immobilization on the surface. Microelectronic devices, such as field effect transistors (FET), have been used to create multi-analyte conductometric biosensors and polymer-based devices [61–63]. There are numerous instances of practical uses such as identifying narcotics in human urine and contaminants in environmental monitoring [64,65]. Whole cells can serve as biological recognition molecules for toxicity testing.

1.3.1.5 Impedimetric biosensor

These analyses provide a range of information about the physicochemical processes taking place within the electrolytic environment that is being studied, including ion migration, charge distribution at the electrode/electrolyte interface, and the kinetics of the electrochemical reaction [66]. These analyses provide a wealth of information on the physicochemical processes taking place within the electrolytic environment that is being studied, including ion migration, charge distribution at the electrode/electrolyte interface, and the kinetics of the electrochemical reaction or reactions. The specifications of the sensing device in conjunction with the electrochemical setup may be linked to all of these activities. Particularly, the system is connected to an AC voltage, and the electrode/electrolyte interface variation in electrochemical impedance is measured. To investigate the metabolic activities taking place within a biological system, impedimetric and conductometric sensors are typically utilized [67].

1.3.1.6 Optical biosensor

An optical biosensor is a compact analytical instrument that includes a biorecognition sensing element coupled with an optical transducer system. The primary components of an optical biosensor are an optical detecting device, optical transmission media such as fiber, immobilized bio-recognition element, and light source. This technique is based on the interaction of light, which includes infrared, ultraviolet, gamma, and X-ray light. Optical biosensors are a type of analytical device that finds use in the following areas such as environmental monitoring [68], clinical diagnostics [69,70], drug discovery, biomedical research, healthcare [71], and food process control [72]. Because of its efficacy, quick reaction time to analytes, selectivity, specificity, and sensitivity, this biosensor is regarded as being frequently employed. Any analyte that interacts with the receptor and reacts to it generates a biological signal, which the transducer then converts into an electrical signal by altering the phase, amplitude, and frequency of the light that is supplied to the system. Optical biosensors have the advantage over other sensors that utilize different changes [73] because there is no current flowing in the system detecting area. The transduction principle is that, depending upon binding its surface receptor to ligands. The sensor experiences a reoccurring change in its optical properties such as a change in thickness or refractive index. Optical biosensors are commonly employed because they are free from electromagnetic interference.

1.3.1.7 Mass-based biosensor

Mass variations are the only source of information for mass-based biosensors. Mass-based sensors evaluate the change in oscillation frequency resulting from the interaction of biomolecules or any other form of analyte with a change in mass. These biosensors include magnetoelastic biosensors, surface acoustic sensors, piezoelectric quartz sensors, and microcantilevers, based on their successful performance and cost-efficiency. Among the types listed, piezoelectric quartz sensors are the most commonly used mass sensors because of their short detection times, affordability, ease of use, and ability to produce label-free sensors [74]. Piezoelectric crystals undergo deformation and oscillation when they come into contact with an electric field. It is measured at this oscillation frequency. It is discovered that piezo sensors are employed in the identification of poisons and pathogens. An AT-cut quartz crystal wafer is positioned between two metal electrodes to form a piezo quartz biosensor [75]. The sensor's resonance frequency is sensitive to changes in mass at the crystal's surface. Because of its excellent stability and capacity to tolerate a wide variety of temperatures, an AT-cut piezo sensor is recommended. The mass on the sensor determines how much the frequency drops. Therefore, germs can be directly detected by combining the Quartz Crystal Microbalance (QCM) device with highly specific interactions like antigen-antibody. Both an increase in mass and a modification to the receptor's elastic characteristics occur when heavy metals attach to the receptor [76]. Further reduction in oscillation frequency is achieved with increased bulk. Changes in mass across the sensor surface are closely correlated with frequency variations that the piezoelectric biosensor detects [77]. Similar to the Surface Plasmon Resonance (SPR) biosensor, this biosensor has the advantage of real-time reaction detection, which permits kinetic investigation of affinity interactions. Despite being economical, each crystal must be calibrated.

Surface Plasmon Resonance (SPR): Surface Plasmon Resonance (SPR) is a real-time optical technique for measuring molecular interactions. It occurs when plane-polarized light strikes a metal film under total internal reflection conditions. The surface plasmon resonance signal directly correlates with the refractive index of the medium present on the sensor chip.

1.3.2 Based on receptor

Based on the receptor and the kind of interaction occurring, biosensors are divided into several classes.

1.3.2.1 Enzyme as receptor

Enzymes are biocatalysts that speed up reactions. Enzymes are proteins that exhibit high catalytic activity and substrate/analyte selectivity [78]. The binding and catalytic characteristics of the enzymes toward the target analyte to be measured dictate how the enzyme-based sensor works [79]. There are certain limitations, such as ionic strength, temperature, pH, and chemical inhibitors that can affect the catalytic activity. Generally, enzymes become denatured at temperatures above 60 °C and lose their activity [80]. The majority of oxidase enzymes, such as cholesterol oxidase, glucose oxidase, etc, are utilized in the construction of biosensors that use dissolved oxygen to produce hydrogen peroxide. Various immobilization techniques, such as adsorption, covalent attachment, and entrapment, are used to immobilize enzymes at the surface of transducers to construct biosensors [81,82]. Typically, enzymes are connected to optical and electrochemical transducers.

1.3.2.2 Antibody as receptor

Antibodies are protein molecules that have specific binding capabilities to specific antigens and are also used to produce biosensors. Generally, antibodies are immobilized on the transducer surface through physical and covalent interactions of carboxyl, sulfhydryl, aldehyde, or amino groups. It is often necessary to functionalize the transducer surface beforehand with hydroxyl, amino, carboxyl, or other groups. The interaction between antibody and antigen is unique and determined by the lock-and-key fit model [83]. This binding process leads to physicochemical changes that can be detected using labeled molecules such as enzymes, radioisotopes, and fluorescent compounds. The effectiveness of antibodies in sensors relies heavily on factors such as their binding capacity, the interaction between antibodies and antigens, as well as assay conditions such as temperature and pH [84,85].

1.3.2.3 Nucleic acid as a receptor

Nucleic acids are utilized in the construction of genosensors, which is based on the base pairing mutually beneficial hypothesis, i.e. adenine: thymine, and cytosine: guanine [86]. If the molecular sequence of the target nucleic acid is known, then the corresponding sequences are synthesized, labeled, and immobilized on the biosensor surface. An optical signal is produced when the target sequences and hybridization probes join together. The most effective transduction theory is applied in the optical detection process of such kinds of sensors [87].

1.3.2.4 Whole cell as a receptor

Microbes such as fungi, protozoa, algae, viruses, and bacteria have been utilized in the development of whole-cell-based sensors due to their capacity to identify biological material. These cells replicate themselves for the production of pure identification molecules like antibodies [88]. Whole-cell-based biosensors are simpler to utilize than plant or animal cells. Electrochemical signals can be measured by normal interactions between the cells and different analytes for quantification. Whole cell-based biosensors may objectively detect information about the condition of living animal or bacterial cells, by transforming signals that are part of their homeostasis into detectable electrical and optical outputs.

1.3.2.5 Nanomaterials as receptor

After the discovery of nanoscience and nanotechnology, nanomaterials have attracted a lot of attention as a receptor in the field of biosensors. The high surface-to-volume ratio of nanomaterials facilitates the immobilization of analytes more easily in a small area. Analytes can be immobilized on nanomaterial surfaces by adsorption, covalent bonding, encapsulation, cross-linking, and entrapment techniques. Various kinds of nanomaterials, such as metal nanomaterials, metal oxide nanoparticles, carbon nanomaterials, metal-organic frameworks, and quantum dots, have received the most attention in biosensing due to their large surface area and excellent electrocatalytic activity [89]. Because they are comparable in size to the analytes (such as biomolecules, antibodies, DNA, pathogens, and metal ions). Nanomaterial-modified sensors demonstrate exceptional sensitivity under certain conditions, making it possible which was previously impossible.

Furthermore, the utilization of organic compounds such as polyanaline, polyphenazine and polytriphenylmethane in conjunction with nanomaterials provides exceptional sensitivity and selectivity in the identification of specific compounds [90,91]. Furthermore, the integration of nanomaterials with natural receptors demonstrates a highly sensitive and selective detection of the target analytes. Examples of this include G-protein-coupled receptors for cadaverine, hormones, dopamine, and trimethylamine, and nanobioelectronic tongues and noses for tastants and odorants, respectively [92].

1.4 Characteristics of biosensor

A few static and dynamic prerequisites must be required to develop a biosensor system that is both extremely competent and effective. Due to these characteristics, the performance of biosensors can be broadly enhanced for commercial applications.

Selectivity: Selectivity is the ability of a bioreceptor to detect a specific analyte in a sample containing a mixture of analytes. It is one of the most significant aspects of a biosensor and is required for the development of reliable point-of-care biosensors.

Sensitivity: The least quantity of analyte that can be statistically detected or recognized in low concentrations (ng/mL or fg/mL) and in the lowest steps necessary to confirm the presence of analyte traces in the sample.

Linearity: Linearity is an indicator of the consistency of measurements over the entire range of measurements. The accuracy of the observed outcomes is influenced by linearity.

Response time: Response time is defined as the time it takes for the sensor to change its output signal from the initial state in the air (baseline) to a certain percentage of the final value. It takes time to achieve 95 % of the findings.

Reproducibility: Reproducibility is the biosensor's capability to yield consistent outcomes when the same sample is evaluated multiple times using the same procedure.

Stability: The ability of a sensor to deliver repeatable response performance over time is known as sensor stability. A good sensor has the capability of generating a steady and repeatable signal over time. Two factors that contribute significantly to the stability of biosensors are affinity and degradation of bio-receptors over time.

1.5 Nanomaterials

Materials with one exterior dimension that quantifies the nano-scaled structure (size range of 1-100 nm) are referred to as nanomaterials. These are classified into zero, one, two, and three-dimensional nanomaterials, among other categories based on their form and size (Figure 1.3). Zero-dimensional nanomaterials are those that have all three dimensions (x, y, and z) inside the nanoscale range or do not have any dimensions outside the nanometric range (>10 nm) [93]. Fullerenes and quantum dots are examples of zero-dimensional nanomaterials. The one-dimensional class of nanomaterials has two of its three dimensions (x, y) in the nanoscale range, but one of the nanostructure's dimensions is beyond the non-metric range (>10 nm). Nanotubes, nanorods, nanofibers, and thin films are some examples of one-dimensional nanomaterials. Two-dimensional nanomaterials contain plate-like structures with two dimensions outside of the nanometer range, whereas one dimension of three dimensions (x) is at the nanoscale (1-100 nm) [94]. Examples of two-dimensional nanomaterials are thin films, nanoplates, and layered structures. Materials that are not limited to the nanoscale in any dimension or range of dimensions are known as three-dimensional nanomaterials. Since the three-dimensional nanomaterial is composed of discrete blocks that fall between 1 and 100 nm in size, three-dimensional nanomaterials have three arbitrary dimensions above 100 nm. All other dimensions of a three-dimensional material are beyond the nanometer range or larger than 100 nm [95]. It consists of dispersed nanoparticles, nanowire and nanotube bundles, and multi-nano layers with closely related 0D, 1D, and 2D structural elements forming interfaces. Bulk nanomaterials and polycrystals are examples of three-dimensional nanomaterials [96].

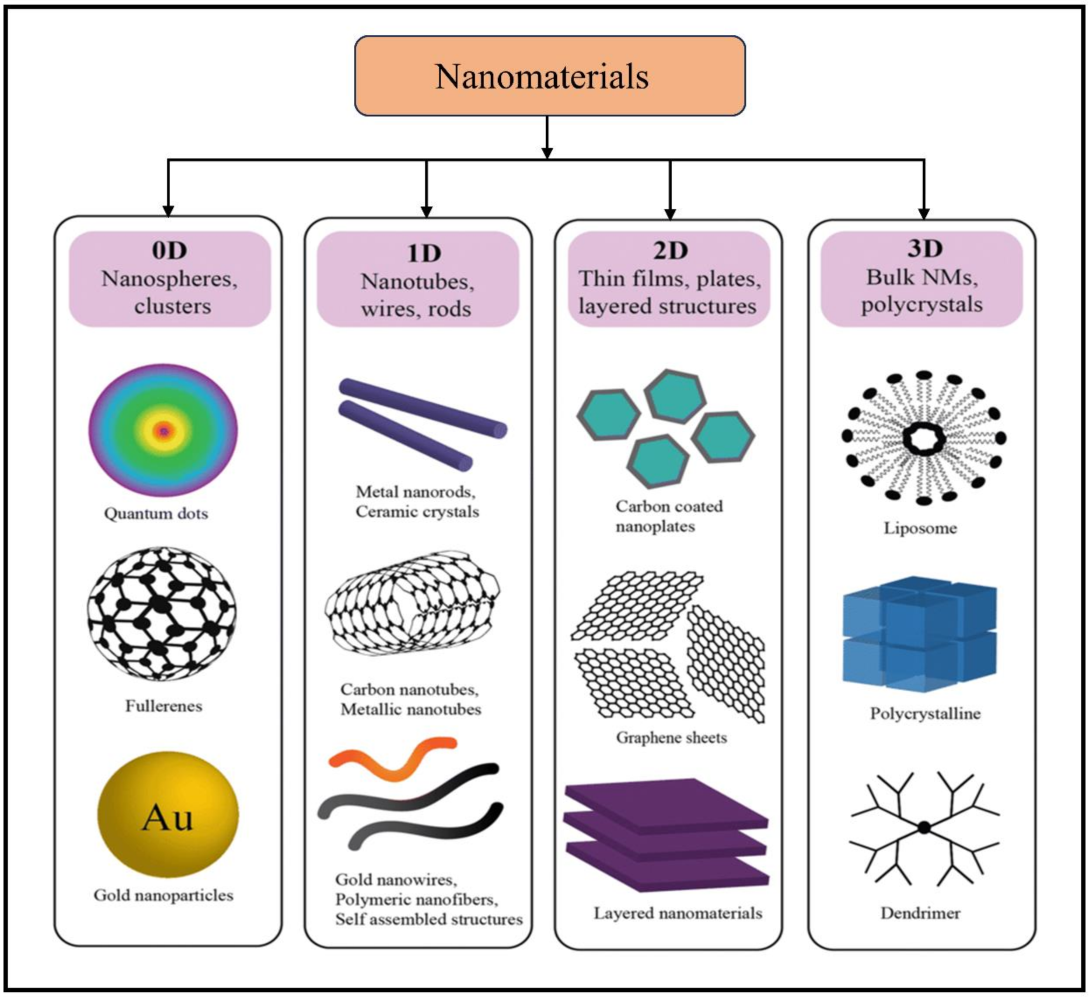

Figure 1.3 Types of nanomaterials on the basis of dimension [97]

These nanomaterials are attracting the interest of researchers in several different fields, due to their high surface-to-volume ratio, small particle size, excellent electrical conductivity, and high surface energy. Shape and size are crucial in nanomaterials because they affect optical characteristics like absorbance and refractive index, which are constant in bulk materials. In general, nanomaterials can be divided into two categories: (A) metal-based nanomaterials and (B) carbon-based nanomaterials, depending on the primary source material.

1.5.1 Metal based nanomaterials

Metal and metal oxide nanoparticles (MONPs) are currently receiving a lot of interest in scientific research because of their unique characteristics, which include a high surface energy, extended surface absorption, and a greater surface area-to-volume ratio [98]. As shown in Figure 1.4 there are numerous examples, such as iron oxide nanoparticles, molybdenum trioxide, cerium oxide, titanium dioxide, and zinc oxide nanoparticles, etc. These MONPs can be synthesized via a variety of experimental techniques, including biological techniques, chemical vapor deposition, hydrothermal reaction method, laser ablation, thermal decomposition, sol-gel process, and thermal decomposition. Metal nanoparticles (MNPs) have a metal center composed of an inorganic metal that is usually encased in an organic, inorganic, or metal oxide shell. Metal nanoparticles have recently received a lot of attention due to their unique properties when compared to bulk metal [99]. The characteristic color of metallic nanoparticles is generated by plasmon resonance absorption, which is extremely dependent on the size of the particle and interfacial interaction [100,101]. AgNPs are considered noble metal nanoparticles (AgNPs) because of their wide variety of applications in antiviral, antibacterial, and anticancer therapy [102–104]. AuNPs have significant advantages in several sectors, including biosensing, medicine, electronics, cancer treatment, and catalysis [105,106] However, due to agglomeration, metal nanoparticles are unstable and reside outside of the equilibrium state.

In addition to these metal nanoparticles, a promising substitute is provided by a novel class of two-dimensional materials called transition metal dichalcogenides

(TMDCs). TMDCs are semiconductors in the form of MX_2, where X is an atom of a chalcogen (such as S, Se, or Te) and M is an atom of a transition metal (such as Mo or W). Because of its resilience, MoS_2 is the most researched material in this family [107]. Similar to graphite, van der Waals attraction holds 2D TMD monolayers together. Due to their high surface-area-to-mass ratio and ultrathin structure (0.6–0.7 nm), 2D TMDs are ideal for loading a wide range of biomolecules [108]. The gap is indirect in bulk TMDs, but it becomes direct in a monolayer form.

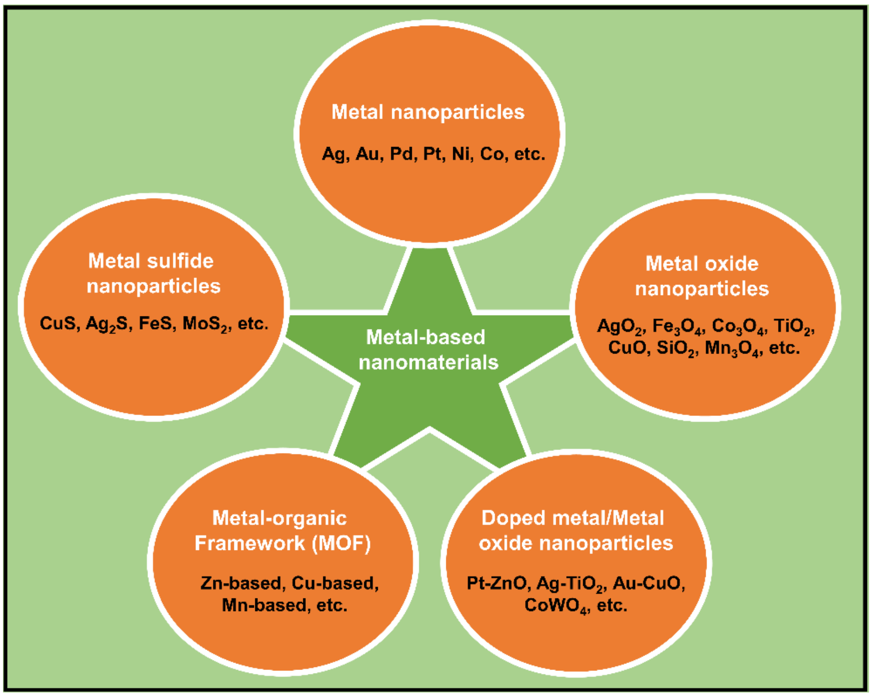

Figure 1.4 Different types of metal-based nanomaterials.

Numerous applications, such as inventive nanoelectromechanical systems, flexible electronics, energy storage, chemical sensors, optoelectronics, etc., are made possible by the special qualities of 2D materials with vast surface areas. Owing to their remarkable catalytic abilities and substantial surface area, metal-doped 2D nanomaterials, such as iron-doped MoS_2, have also discovered remarkable uses in numerous domains [109].

1.5.2 Carbon nanomaterials

Currently, a number of carbon-based nanomaterials, including fullerene, graphene, graphite, carbon nanotubes (CNTs), and graphene oxide, have been identified [110]. These are demonstrating increased potential for a wider range of applications, including biosensing, electronics, optics, and biomedicine. Since different allotropes and nanostructures can appear, carbon-based materials currently display a broad spectrum of characteristics as shown in (Figure 1.5). Carbon atoms make up fullerenes (C_{60}), a spherical carbon molecule bound together by sp^2 hybridization [111]. A fullerene has between 28 to 1500 carbon atoms in its spherical structure. There are various forms of carbon, such as graphene, fullerene, and CNT [112]. Graphene is a two-dimensional planar surface with carbon atoms

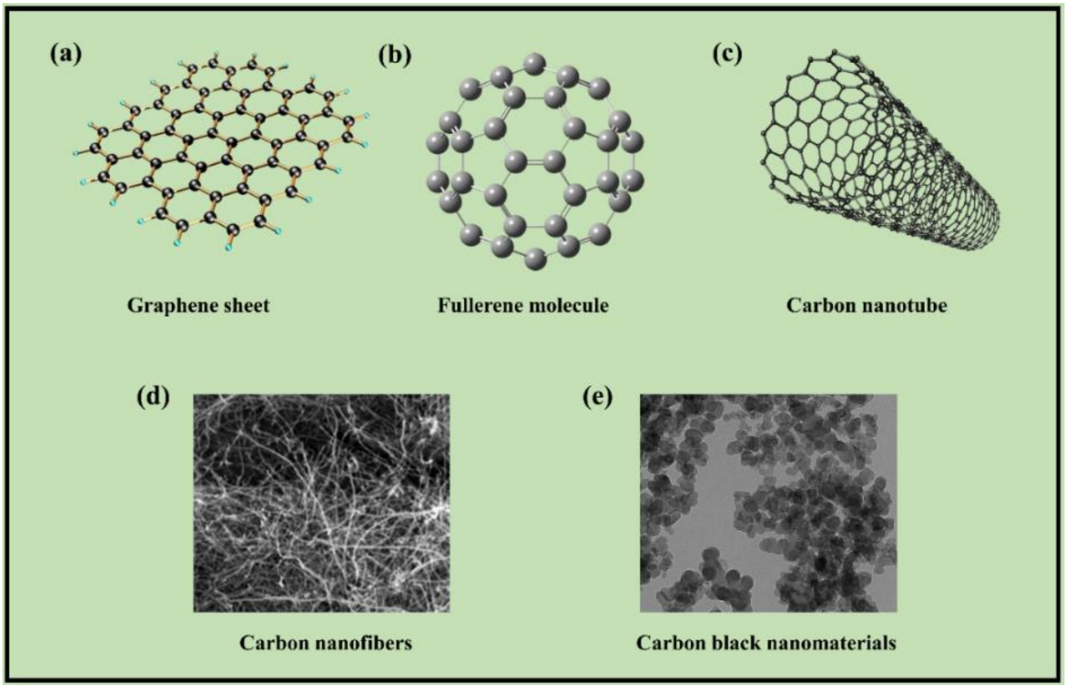

Figure 1.5 Structure of various carbon nanomaterials (a) graphene sheet (b) fullerene molecule (c) carbon nanotube (d) carbon nanofibers and (e) carbon black nanomaterials [113].

arranged into a hexagonal honeycomb lattice [114,115]. Graphene has unique physicochemical properties such as large surface area, exceptional thermal conductivity, strong tensile strength, and rapid electron transport [116]. Carbon nanotubes (CNTs) are made of carbon atoms wound into hollow cylinders on a graphene nanofoil. There is a range of nanotube lengths from several micrometers to several millimeters. Rolling up graphene sheets creates hollow tubes known as carbon nanotubes (CNTs). According to Jacobs *et al.,* 2011 there are multiple types of carbon nanotubes (CNTs), including single-walled carbon nanotubes (SWCNT), double-walled carbon nanotubes (DWCNT), and multi-walled carbon nanotubes (MWCNT). Each kind varies in thickness and has unique metallic/semiconducting properties [117]. Similar graphene nanofoils are used to form carbon nanofibers (CNFs), but instead of being twisted into a typical cylindrical tube, CNTs are shaped more like cones or cups. When used as catalysts, a variety of metals whether in supported or powdered form can quickly generate CNFs. Powdered metals are not more successful in forming CNFs than other catalyst arrangements including wires, foils, gauzes, or supported metal particles. Carbon nanofibers (CNFs) are a promising class of materials with applications in photocatalysis, sensors, energy devices, tissue engineering, nanocomposites, filtration, and drug delivery, among other fields. Biochar and biomass can be activated to produce activated carbon using physical, chemical, physiological, and microwave methods [118]. Physical activation uses heat and gas (such as steam, CO_2, N_2, or a combination), chemical activation uses chemicals (such as acids, bases, metal oxides, and alkaline metals), physiochemical activation uses heat and chemical, and microwave-assisted activation uses microwave radiation [119]. The activation is determined by the precursor's properties, retention time, impregnation ratio, method configuration, activation period, and chemical components. Biochar is produced by thermally decomposing raw materials in an inert atmosphere in a furnace with an N_2 purge to remove volatile, non-carbon species like nitrogen, hydrogen, and oxygen, and to raise the fixed carbon content. The testing of different analytes has benefited greatly from the use of nanomaterials in electrochemical, colorimetric, and chemiluminescence sensing.

1.6 Application of transition metal nanomaterials in biosensor

In the daily lives of humans, sensors are used in many fields, including industry, healthcare, fitness, and lifestyle. One of the main challenges in the development of sensing platforms is the growing need for low-cost, dependable sensors that can measure data in real time for point-of-care testing. Nanotechnology and nanoscience have played an important role in resolving a significant portion of the problem. The development of economically viable sensors with excellent sensitivity and selectivity is greatly possible with the use of nanomaterial-based sensors. Additionally, a sensor's selectivity is determined by the precise way in which target molecules interact with receptors. Nevertheless, the transducer's physical and chemical properties have a significant impact on the sensors' selectivity, stability, sensitivity, reaction time, and limit of detection. Nanoparticles can improve the transducer's characteristics by acting as an interface or redox mediator between receptors and the transducer. At present, sensors based on nanoparticles are widely used in clinical diagnosis, medical research, food safety, and environmental monitoring [120,121]. Nanosensors provide a number of advantages, but they also present some challenges, particularly when used in biological systems. These sensors have the potential to impact cell metabolism [122]. There are some challenges with separation techniques, mass production, quality assurance, validation, repeatability, and the integration of sensors with other elements. For use in sensing applications, a wide range of nanomaterials have been studied, including semiconductor nanoparticles (quantum dots), metallic nanoparticles (palladium, silver and gold), graphene and its derivatives (GO, rGO), polymeric, dendrimers, liposomal, and transition metal oxides ($CoWO_4$, Co_3O_4, Fe_2O_3). Because of their excellent electrical, optical, and thermal properties, high surface area, high degree of specificity and selectivity, ease of functionalization, strong adsorption ability, and a high degree of biocompatibility, nanomaterials are essential to the advancement of nanotechnology and nanoscience [123,124]. Therefore, they are a promising candidate for use in the fabrication of efficient sensors.

The usage of nanoparticles resulted in significantly improved performance, including increased sensitivities and lower limit of detection [125]. The choice of nanomaterials is heavily influenced by the sensing approach used and the target analyte selected. The high specific surface area of all nanoscale objects allows for the immobilization of a large number of receptor units. Nanomaterials have become an essential component of biosensors, increasing sensitivity and detection limits to single molecules. The unique properties of nanoparticles offer substitutes for traditional transduction methods. Furthermore, combining multiple nanomaterials, each with its own features, to improve sensor performance is a widely acknowledged method. These nanocomposites have a transformative function in the creation of sensing platforms [126]. Nanocomposites are composed of two or more ingredients with distinctly different physical and chemical characteristics. When two separate materials of nanoscale dimensions are combined, they form new materials with distinct properties from their respective components [127]. Numerous studies on nanocomposites and hybrid materials have been published in the literature, demonstrating their value with highly tunable qualities and lower costs [128–130].

Among various metal nanomaterials, noble metal nanoparticles such as gold, silver, platinum, and palladium have been intensively studied because of their unique catalytic, electrical, and optical capabilities, as well as their tunable size and shape [131–134] Palladium nanoparticles have the ability to transport electrons between the electroactive species and the electrode. This idea is especially useful in redox enzyme sensing, in which receptor moieties catalyze the analyte's oxidation/reduction [135]. Furthermore, palladium nanoparticles have excellent optical characteristics and have shown promise in sensing applications via surface plasmon resonance transduction [136]. Accordingly, many effective electrochemical biosensors were fabricated to detect H_2O_2 [137,138]and ascorbic acid [139,140]. Palanisamy *et al.*, 2015 developed a palladium nanoparticle decorated activated fullerene-C_{60} enhanced electrochemical sensor for electrochemical sensing of dopamine [141]. Wang *et al.*, 2013 prepared a chemically modified palladium nanoparticle/graphene/chitosan (PdNPs/GR/CS) glassy carbon electrode which exhibits tremendous electrocatalytic activities towards ascorbic acid (AA), uric acid (UA), and dopamine (DA) [142]. Although palladium nanoparticles have many benefits, they also have certain drawbacks, such as agglomeration susceptibility, problems with long-term storage, and somewhat higher production costs. The agglomeration problem can be overcome by utilizing a cross-linker or immobilized on the surface of a solid support such as metal oxide [143], polystyrene [144], carbon nanotubes [145], silica [146], and activated carbon [147].

Further, the research is going on to enhance the stability of nanoparticles by modifying their surfaces and through functionalization. Many researchers have reported noble metal nanoparticles including silver and gold play an important role in electrochemical sensing. Sookhakian *et al.,* 2019 reported an electrochemical sensor for the selective detection of dopamine by using a silver molybdenum disulfide composite. The electrocatalytic activity is significantly increased by silver which shows a 0.2 µM limit of detection [148]. Bekmezci *et al.,* 2023 have developed a Pt-Ag bimetallic-modified electrode for dopamine sensing and shows an excellent limit of detection (LOD) value, i.e. 0.03 µM [149] Govindhan *et al.,* 2015 have reported a gold nanoparticle/graphene nanocomposite-based amperometric sensor for detecting NADH in human urine. The fabricated sensor exhibits a broad linear range from 50 µM to 500 µM with a limit of detection of 0.001 µM, along with a high sensitivity of 0.916 µA/µM cm^2 [150].

Although noble metals have been found extremely valuable in the advancement of sensing technologies, their high cost and potential for aggregation limit their storage and usage in practical applications. Inorganic transition metal-based nanomaterials have recently received a lot of interest due to their potential to build advanced reliable and affordable sensors [151]. The inorganic transition metal nanomaterials such as manganese oxide nanoparticles (MnO and Mn_3O_4), cobalt oxide nanoparticles (Co_3O_4), cobalt tungstate ($CoWO_4$), iron oxide (Fe_3O_4), vanadium pentaoxide (V_2O_5), cobalt nitrogen doped carbon (Co@NC), molybdenum disulfide nanosheet (MoS_2), nickel diselenide ($NiSe_2$), tungsten disulfide (WS_2), molybdenum diselenide ($MoSe_2$), cobalt diselenide ($CoSe_2$) etc. are extensively used in various fields owing to their tremendous electrocatalytic activity. Aneesh *et al.*, 2017 developed $CuWO_4$ modified glassy carbon electrode for NADH sensing. The NADH sensor demonstrated a significant linear relationship within the concentration range of 0.2 μM to 380 μM, with an acceptable 0.2 μM detection limit [152]. Habibi *et al.*, 2022 developed a nonenzymatic electrochemical sensor based on g-C_3N_4/$CuWO_4$ composite for determining H_2O_2. The g-C_3N_4/$CuWO_4$/GC electrode displayed outstanding electrochemical behavior under neutral circumstances with a broad linear range (0.001-5.2 mM), low detection limit (0.4 μM), higher sensitivity (35.91 and 11.02 μA mM^{-1} cm^{-2}), significant stability, and excellent selectivity [153]. Liu *et al.*, 2023 fabricated Co–N–C/rGA modified glassy carbon electrodes for simultaneous electrochemical detection of dopamine and uric acid, and the limits of detection are 0.32 μM and 3.59 μM, respectively. The result shows that the Co-N-C/rGA nanocomposite has good electrocatalytic activity [154]. Ganesha *et al.*, 2022 presented a nanocomposite-based electrochemical sensor composed of polypyrrole nanotube-cobalt oxide (PPYNTs/Co_3O_4) to detect ascorbic acid. The electrochemical sensor, which was modified with PPYNTs/Co_3O_4 on a glassy carbon electrode (GCE), demonstrated a broad linear range spanning from 5 μM to 80 μM. In addition, the sensor exhibited a low limit of detection of 0.23 μM and a high sensitivity of 14.48 μA μM^{-1} cm^{-2} [155].

Palladium (Pd) and cobalt (Co) are the most active metal which have interesting properties such as high electrocatalytic activity, high surface area, good chemical stability, versatility, non-toxicity, and relatively low cost in comparison to Au and Pt metals [156–159]. Therefore, they are widely used in the development of electrochemical sensors. *Wang et al.*, 2013 developed a palladium nanoparticle/graphene/chitosan-modified electrode for simultaneous electrochemical determination of dopamine in the presence of ascorbic acid and uric acid, which shows the limit of detection 0.1 µM [160]. *Hongyan et al.*, 2024 developed Co_2P hybrid screen printed electrode for simultaneous electrochemical detection of dopamine in the presence of ascorbic acid, and uric acid, which shows the limit of detection 0.018 µM [161]. *Tian-Qi et al.*, 2014 developed Pt nanoparticles supported on reduced graphene oxide modified glassy carbon electrode for simultaneous determination of dopamine in the presence of uric acid and ascorbic acid, which shows the limit of detection 0.25 µM [162]. *Wang et al.*, 2014 developed a facile electrochemical sensor based on reduced graphene oxide and Au nanoplates modified glassy carbon electrode for simultaneous detection of dopamine in the presence of ascorbic acid and uric acid which shows the limit of detection 1.4 µM. The Palladium and cobalt nanoparticle-modified electrodes show low detection limits in comparison to gold and platinum nanoparticle-modified electrodes [163,164]. That's why we have chosen palladium and cobalt nanoparticles for electrochemical sensing.

1.7 Redox Mediator

Redox mediators, commonly known as electron shuttles, are organic compounds capable of undergoing reversible reduction and oxidation processes by acting as electron shuttles repeatedly [165]. The redox mediator bridges this gap by transporting electrons between the analyte and the electrode. The redox mediator undergoes an oxidation and reduction process which facilitates the overall electron transfer process. To function as a proficient electron carrier, a redox mediator must possess a standard redox potential that falls within the range of the two half-reactions, namely the electron-donating and electron-accepting reactions [166]. Redox mediators play a crucial role in various electrochemical processes because of their electrochemical stability ($I_{pa}/I_{pc} = 1$) and high diffusion coefficient. It is widely used in applications such as batteries, fuel cells, and sensors. Examples of some well-known redox mediators include Ferrocene (Fc), $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$, quinone, anthraquinone, benzophenones, viologens, fluorenones, phenazines, phenothiazines, tetrathiafulvalene (TTF), and tetracyanoquinodimethane (TCNQ), etc. The majority of redox mediators reported to date are organic compounds, predominantly characterized by their aromatic or heterocyclic nature. Aromatic molecules are highly favored as redox-active mediators due to their delocalized π systems, which provide stability to the radical cation/anion formed through their one-electron oxidation/reduction processes, respectively [167]. Tetrathiafulvalene (TTF) was the first organic redox molecule that was successfully used as a redox mediator [168,169].

1.7.1 Tetracyanoquinodimethane (TCNQ)

Tetracyanoquinodimethane (TCNQ) is an organic redox mediator that functions as a highly effective electron acceptor. TCNQ accepts one electron and converts into TCNQ radical anion this radical anion further accepts one electron and converts into TCNQ dianions as shown in Figure 1.6.

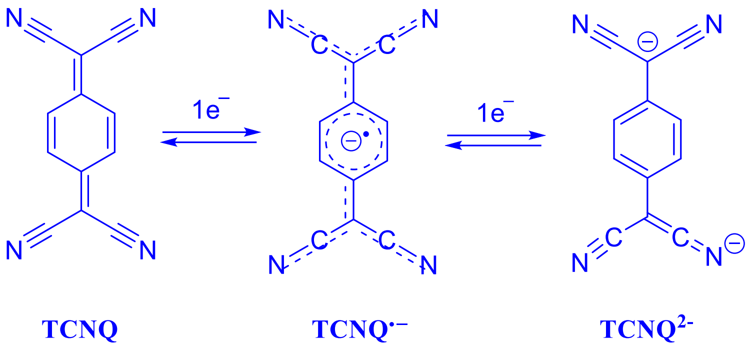

Figure 1.6 Reduction process of TCNQ.

This organic compound is characterized by its remarkable electron affinity, which is determined to be 2.8 ± 0.1 eV, and this property can be attributed to its flat structure and possession of four cyano groups [170]. The distinctive feature of TCNQ lies in its ability to form charge-transfer complexes with an extensive array of electron donor species, whether they are in the form of molecules or metals. Consequently, these charge-transfer complexes exhibit robust electrical conductivity, thus reinforcing the significance of TCNQ as an electron acceptor. TTF-TCNQ salt was discovered in 1973 and marked a groundbreaking milestone in the field of organic conductivity, it represented the first instance of an organic conductor displaying conductivity comparable as to metal.[171,172]. This important discovery showed the way for further advancements in the realm of organic conductivity and solidified the prominent role of TCNQ as an electron acceptor. The TCNQ-TTF is an organic charge transfer complex that is highly conductive. Due to excellent electrochemical stability, and ability to form charge transfer complexes TCNQ is used in various fields as shown in (Figure 1.7) [173].

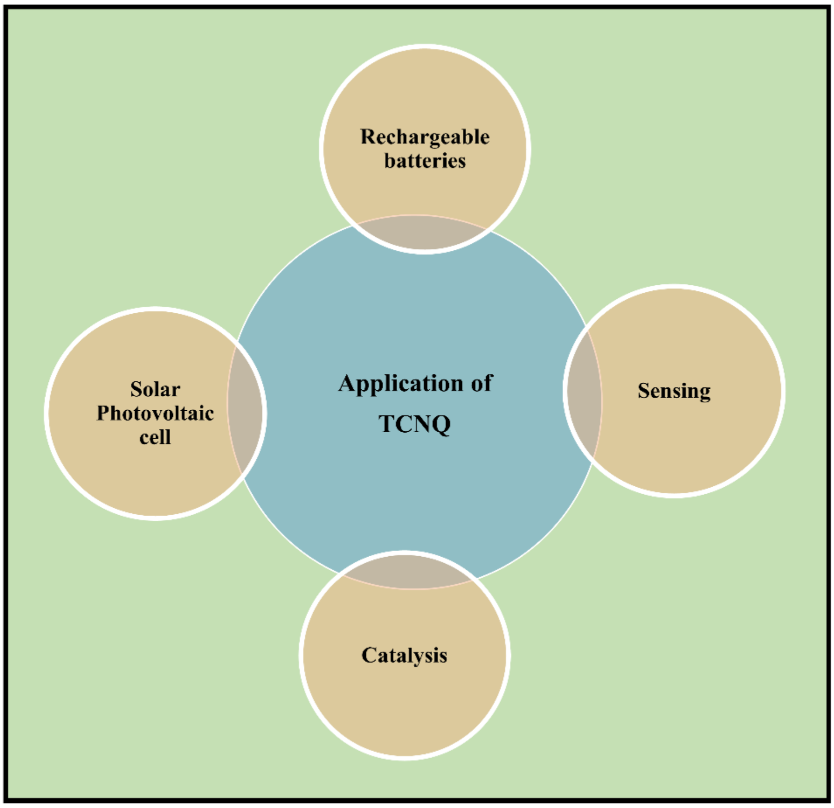

Figure 1.7 Applications of TCNQ.

Yu *et al.*, 2019 have reported that TCNQ is utilized in the non-fullerene-based active layer in order to comprehensively examine its impact on the morphology of the film as well as its photovoltaic efficiency [174]. The findings of this research will contribute significantly to the current understanding of the role of TCNQ in enhancing the performance of organic solar cells. Jouve *et al.*, 1995 have provided a significant report on the observation of irreversibility in the detection of nitrogen dioxide (NO_2) and partial reversibility in the detection of oxygen (O_2) and water (H_2O), by utilization of a TTF–TCNQ complex containing polymer film [175].

1.8 Challenges faced during current sensing technology and their solutions

The effectiveness and broad applicability of electrochemical sensing methods are hampered by several issues, especially when it comes to the detection of biomolecules such as ascorbic acid, dopamine, and NADH. The difficulties faced are:

1. ***Stability and durability:*** One of the major challenges with electrochemical sensors is long-term stability. Many sensors experience degradation over time due to fouling, oxidation of the electrode surface, or instability of the material in the sensing. This reduces their reliability in continuous or repeated measurements.
2. ***Poor selectivity:*** Many sensors have poor selectivity due to interference from other chemicals found in complex biological environments. For example, uric acid, glucose, and dopamine frequently coexist in biological samples and have similar oxidation potentials, making it difficult to discriminate between them.
3. ***Low sensitivity:*** High sensitivity is essential for identifying low concentrations of target analytes, particularly in medical diagnostics, where trace levels of biomolecules such as NADH are essential. Conventional electrodes may lack sufficient surface area or catalytic activity to provide the required sensitivity at low detection limits.
4. ***Slow electron transfer:*** Slow electron transfer reaction between the electrode surface and the analyte interface can lead to slower response times and lower current densities.

5. ***Cost and complexity of fabrication of electrodes:*** High-performance sensors may need expensive or difficult production procedures, restricting their accessibility and potential for scaling to commercial use.

Our research aim was to address these challenges and overcome these problems by using nanomaterials with TCNQ-modified carbon paste electrodes for the detection of ascorbic acid, dopamine, and NADH.

1. The stability of the fabricated electrodes is enhanced by the stability of the electrode material used. For example, palladium, $CoWO_4$, and Co@NC nanoparticles offer excellent stability, and the incorporation of TCNQ improves durability and prevents degradation over time. This leads to more reliable and consistent sensor performance for prolonged periods, tackling the common issue of electrode fouling and instability.
2. In different nanomaterials and their composites such as palladium, $CoWO_4$, and Pd-Co@NC incorporation of TCNQ helps in distinguishing between biomolecules like uric acid, dopamine, and glucose by providing more specific catalytic sites and better differentiation of their redox potentials. This reduces interference from other species, addressing the selectivity issue.
3. Nanomaterials like palladium and cobalt-based composites significantly increase the surface area of the electrodes, providing more active sites for the redox reaction of target analytes. The incorporation of TCNQ further enhances electron transfer, which in turn increases the sensitivity of the sensors. This enables the

detection of lower concentrations of ascorbic acid, dopamine, and NADH, filling the gap in sensitivity.

4. TCNQ is a well-known electron acceptor. The main advantage of using TCNQ as a modifier is its ability to facilitate electron transfer by acting as an electron mediator. TCNQ coupled with the high catalytic activity of palladium nanoparticles and cobalt-based materials through synergistic interaction, thus sensors demonstrate faster response times compared to traditional electrodes, overcoming the issue of slow electron transfer kinetics.
5. The nanomaterials and TCNQ are relatively low cost and synthesis procedures are cost-effective. The TCNQ nanomaterial-modified fabrication process is very easy and cheaper materials are used. These are superior in performance and remain cost-effective to produce in comparison to other high-end sensor technologies, which increases their suitability for real-time applications.

In conclusion, the current research fills crucial gaps in electrochemical sensing by introducing highly selective, sensitive, stable, cost-effective, and scalable electrodes that offer faster response times and lower detection limits for ascorbic acid, dopamine, and NADH. This advances the current state-of-the-art sensing technologies and provides potential applications in healthcare diagnostics and biochemical analysis where accurate, rapid, and reliable detection is essential.

1.9 Motivation and Objective of the Thesis

Nanotechnology has played a crucial role in the development of advanced sensors with a low detection limit for analytes due to their huge surface area, which allows for greater functionalization, better biocompatibility, sensitivity, and selectivity. Nanotechnology has enabled the sensor to be miniaturized and turned into transportable sensors. Numerous diseases, such as Alzheimer's, tuberculosis, Parkinson's, neurological disorders, and cancer, can become serious and fatal if not detected early on. As a result, there is a critical need for portable, low-cost, and dependable sensors capable of identifying them. Inspired by these, we have developed an electrochemical sensor to measure the concentration of biomolecules, including ascorbic acid, dopamine, and nicotinamide adenine dinucleotide (NADH). An increased concentration of these biomolecules in the body can produce various types of side effects. Thus, keeping an eye out for disease is crucial to preserving both our health and the effectiveness of our immune system.

Recently, studies have shown that transition metal nanomaterials, including PdNPs, $CoWO_4$, and Pd-Co@NC have great potential for the fabrication of efficient sensors. Because they are innovative, easy to use, and need simple, inexpensive equipment, these materials are used as biomimetic materials. More stability and catalytic activity are produced via surface modification in these nanomaterials. The signal stability is improved for a longer period of time when these modified nanomaterials are added to our electrochemical sensing probe. It has been claimed that a variety of sensors on essential biomolecules, such as dopamine [176], ascorbic acid [177], and NADH [178], can forecast many diseases and their constituents in critical conditions. However, there are deficiencies in the stability, reliability of sensors, detection limits, and device usability. Therefore, we produced budget-friendly, stable nanomaterials to fabricate biosensors.

This research aims to synthesize nanomaterials and apply them to sensing applications by electrochemical techniques, which are grounded in a comprehensive literature review and the background details mentioned above. Thus, considering these aspects as well as the possible uses of nanomaterials for sensors in the future, the thesis's main objective is:

- To synthesize metal nanomaterials, and nanocomposites for simple and low-cost catalysts and biosensors, and their characterization by using various techniques.
- To explore the outstanding physical, chemical, and catalytic properties of nanomaterials for catalysis and sensing of biomolecules such as ascorbic acid, dopamine, and NADH.

Furthermore, the thesis is focused on the following sub-objectives, as listed below:

- Synthesis of Palladium nanoparticles and mixed with TCNQ to form (TCNQ-PdNPs) nanocomposite and detection of ascorbic acid in a real sample of ascorbic acid tablets.
- Synthesis of $CoWO_4$ nanoparticles and mixed with TCNQ to form TCNQ-$CoWO_4$ nanocomposite and used for the fabrication of TCNQ-CoWO4/CPE for electrochemical sensing of dopamine.
- Synthesis of Co@NC and Pd-Co@NC and mixed with TCNQ to form (TCNQ-Co@NC, and TCNQ-Pd-Co@NC) nanocomposite and used for the fabrication TCNQ-Pd-Co@NC/CPE for electrochemical sensing of NADH.

1.10 Benefits of the proposed materials for sensing application

In the last ten years, nanomaterials played an important role in the sensing area. The remarkable physicochemical characteristics of nanomaterials including their large surface area, good electrochemical conductivity, biocompatibility, and catalytic activity make them a promising option for the fabrication of effective sensors. In the present thesis, we have synthesized some nanoparticles such as PdNPs, $CoWO_4$, Co@NC, Pd-Co@NC, and their composites. These nanomaterials itself not show very good catalytic activity and other properties like stability and surface area. To enhance the catalytic activity, surface area, and stability of these nanomaterials we incorporated tetracynoquinodimethane (TCNQ) into these nanomaterials. The synthesized materials (TCNQ-PdNPs, TCNQ-$CoWO_4$, TCNQ-Co@NC, TCNQ-Pd-Co@NC) exhibited outstanding catalytic activity, making them appropriate for use in electrochemical methods for the sensing of various biomolecules such as ascorbic acid, dopamine, and NADH. Because these nanoparticles can tolerate greater pH and temperature, we may use them to fabricate a portable test kit that can be used for real sample analysis of the concentration of specific biomolecules in body fluids including human serum, and urine. Many researchers also reported dopamine in non-invasive samples (human serum) using the same methodology. Using an electrochemical technique, nanomaterials ($CoWO_4$/CE-BN) are employed to detect compounds like ornidazole [179], and ($CoWO_4$) is used to detect hydroquinone and chloramphenicol [180]. CoNC/CNT/MB is used to detect tert-butylhydroquinone because of its good electrocatalytic activity and high conductivity [181]. Palladium nanoparticles were used for the sensing of terazosin drug which is also known as alpha-adrenergic blocker [182]. Table 1.1 demonstrates the various features exhibited by different nanomaterials. It is evident that after modification to the surface, nanomaterials show increased stability, conductivity, and sensitivity, resulting in superior catalytic capabilities.

Table 1.1 Typical characteristics of TCNQ-modified nanomaterials utilized in sensing in the present thesis work.

	TCNQ-PdNPs	**TCNQ-$CoWO_4$**	**TCNQ-Pd-Co@NC**
High surface area	✓	✓	✓
Nano size	✓	✓	✓
Highly catalytic	✓	✓	✓
Conducting	✓	✓	✓
Stability	✓	✓	✓
Biocompatible	✓	✓	✓
Sensitive	✓	✓	✓

In this thesis work, we have performed the electrochemical sensing of biomolecules including ascorbic acid, dopamine, and NADH by using different types of nanomaterial-modified electrodes. This thesis aims to fabricate stable electrodes that can perform with precise efficiency, provide better sensitivity, and have a low detection limit. To enhance the stability of the electrodes we have incorporated TCNQ into nanomaterial. The synergistic interaction of TCNQ and the nanostructures (PdNPs, $CoWO_4$, and Pd-Co@NC) improved electron transfer, electrocatalytic activity, lower detection limits, selectivity, and sensitivity for each target molecule.

1.11 References

[1] I.H. Alsohaimi, Analytical detection methods for diagnosis of COVID-19: developed methods and their performance, Biotechnology and Biotechnological Equipment 35 (2021) 196–207. https://doi.org/10.1080/13102818.2020.1865838.

[2] A. Sharma, M. Badea, S. Tiwari, J.L. Marty, Wearable biosensors: An alternative and practical approach in healthcare and disease monitoring, Molecules 26 (2021) 748. https://doi.org/10.3390/molecules26030748.

[3] N. Colozza, V. Caratelli, D. Moscone, F. Arduini, Paper-based devices as new smart analytical tools for sustainable detection of environmental pollutants, Case Studies in Chemical and Environmental Engineering 4 (2021). https://doi.org/10.1016/j.cscee.2021.100167.

[4] C. Domingo, J. Saurina, An overview of the analytical characterization of nanostructured drug delivery systems: Towards green and sustainable pharmaceuticals: A review, Anal Chim Acta 744 (2012) 8–22. https://doi.org/10.1016/j.aca.2012.07.010.

[5] D. Rodríguez-Lázaro, B. Lombard, H. Smith, A. Rzezutka, M. D'Agostino, R. Helmuth, A. Schroeter, B. Malorny, A. Miko, B. Guerra, J. Davison, A. Kobilinsky, M. Hernández, Y. Bertheau, N. Cook, Trends in analytical methodology in food safety and quality: monitoring microorganisms and genetically modified organisms, Trends Food Sci Technol 18 (2007) 306–319. https://doi.org/10.1016/j.tifs.2007.01.009.

[6] A.A. Tomchenko, G.P. Harmer, B.T. Marquis, Detection of chemical warfare agents using nanostructured metal oxide sensors, in: Sens Actuators B Chem, 108 (2005) 41–55. https://doi.org/10.1016/j.snb.2004.11.059.

[7] M.R. Siddiqui, Z.A. AlOthman, N. Rahman, Analytical techniques in pharmaceutical analysis: A review, Arabian Journal of Chemistry 10 (2017) S1409–S1421. https://doi.org/10.1016/j.arabjc.2013.04.016.

[8] A. Roldão, T. Vicente, C. Peixoto, M.J.T. Carrondo, P.M. Alves, Quality control and analytical methods for baculovirus-based products, J Invertebr Pathol 107 (2011) S94-S105. https://doi.org/10.1016/j.jip.2011.05.009.

[9] H.E. Anderson, I.C. Santos, Z.L. Hildenbrand, K.A. Schug, A review of the analytical methods used for beer ingredient and finished product analysis and

quality control, Anal Chim Acta 1085 (2019) 1–20. https://doi.org/10.1016/j.aca.2019.07.061.

[10] H. John, M. Walden, S. Schäfer, S. Genz, W.G. Forssmann, Analytical procedures for quantification of peptides in pharmaceutical research by liquid chromatography-mass spectrometry, Anal Bioanal Chem 378 (2004) 883–897. https://doi.org/10.1007/s00216-003-2298-y.

[11] S. M, G. N, R. R, Epitope Imprinting Approach to Monitor Diseases, Journal of Molecular and Genetic Medicine 11 (2017) 1000270. https://doi.org/10.4172/1747-0862.

[12] M. Zhang, J. Ye, J. song He, F. Zhang, J. Ping, C. Qian, J. Wu, Visual detection for nucleic acid-based techniques as potential on-site detection methods. A review, Anal Chim Acta 1099 (2020) 1–15. https://doi.org/10.1016/j.aca.2019.11.056.

[13] I.T. Gug, M. Tertis, O. Hosu, C. Cristea, Salivary biomarkers detection: Analytical and immunological methods overview, TrAC - Trends in Analytical Chemistry 113 (2019) 301–316. https://doi.org/10.1016/j.trac.2019.02.020.

[14] A. Van Gool, F. Corrales, M. Čolović, D. Krstić, B. Oliver-Martos, E. Martínez-Cáceres, I. Jakasa, G. Gajski, V. Brun, K. Kyriacou, I. Burzynska-Pedziwiatr, L.A. Wozniak, S. Nierkens, C. Pascual García, J. Katrlik, Z. Bojic-Trbojevic, J. Vacek, A. Llorente, F. Antohe, V. Suica, G. Suarez, R. t'Kindt, P. Martin, D. Penque, I.L. Martins, E. Bodoki, B.C. Iacob, E. Aydindogan, S. Timur, J. Allinson, C. Sutton, T. Luider, S. Wittfooth, M. Sammar, Analytical techniques for multiplex analysis of protein biomarkers, Expert Rev Proteomics 17 (2020) 257–273. https://doi.org/10.1080/14789450.2020.1763174.

[15] K. Vorkamp, A. Castaño, J.P. Antignac, L.D. Boada, E. Cequier, A. Covaci, M. Esteban López, L.S. Haug, M. Kasper-Sonnenberg, H.M. Koch, O. Pérez Luzardo, A. Osīte, L. Rambaud, M.T. Pinorini, G. Sabbioni, C. Thomsen, Biomarkers, matrices and analytical methods targeting human exposure to chemicals selected for a European human biomonitoring initiative, Environ Int 146 (2021) 106082. https://doi.org/10.1016/j.envint.2020.

[16] D. Schorn-García, J. Cavaglia, B. Giussani, O. Busto, L. Aceña, M. Mestres, R. Boqué, ATR-MIR spectroscopy as a process analytical technology in wine alcoholic fermentation – A tutorial, Microchemical Journal 166 (2021) 106215. https://doi.org/10.1016/j.microc.2021.

[17] B.S. Rathi, P.S. Kumar, D.V.N. Vo, Critical review on hazardous pollutants in water environment: Occurrence, monitoring, fate, removal technologies and risk assessment, Science of the Total Environment 797 (2021) 149134. https://doi.org/10.1016/j.scitotenv.2021.

[18] A. De Simone, M. Naldi, D. Tedesco, M. Bartolini, L. Davani, V. Andrisano, Advanced analytical methodologies in Alzheimer's disease drug discovery, J Pharm Biomed Anal 178 (2020) 112899. https://doi.org/10.1016/j.jpba.2019.

[19] A. Marzo, E. Heftmann, Enantioselective analytical methods in pharmacokinetics with specific reference to genetic polymorphic metabolism Journal of Biochemical and Biophysical Methods 54.1-3 (2002) 57-70. https://doi.org/10.1016/S0165-022X(02)00128-8.

[20] K. Junka, I. Filpponen, T. Lindström, J. Laine, Titrimetric methods for the determination of surface and total charge of functionalized nanofibrillated/microfibrillated cellulose (NFC/MFC), Cellulose 20 (2013) 2887–2895. https://doi.org/10.1007/s10570-013-0043-z.

[21] J. Peris-Vicente, J. Esteve-Romero, S. Carda-Broch, Validation of Analytical Methods Based on Chromatographic Techniques: An Overview, in: Analytical Separation Science, Wiley, 5 (2015) 1757–1808. https://doi.org/10.1002/9783527678129.assep064.

[22] A. El Orche, O. Elhamdaoui, A. Cheikh, B. Zoukeni, M. El Karbane, M. Mbarki, M. Bouatia, Comparative study of three fingerprint analytical approaches based on spectroscopic sensors and chemometrics for the detection and quantification of argan oil adulteration, J Sci Food Agric 102 (2022) 95–104. https://doi.org/10.1002/jsfa.11335.

[23] B. Buszewski, E. Maślak, M. Złoch, V. Railean-Plugaru, E. Kłodzińska, P. Pomastowski, A new approach to identifying pathogens, with particular regard to viruses, based on capillary electrophoresis and other analytical techniques, TrAC - Trends in Analytical Chemistry 139 (2021) 116250. https://doi.org/10.1016/j.trac.2021.

[24] M.C. Breadmore, P.R. Haddad, Approaches to enhancing the sensitivity of capillary electrophoresis methods for the determination of inorganic and small organic anions, Electrophoresis 22 (2001) 2464–2489. https://doi.org/10.1002/1522-2683(200107)22:12<2464::AID-ELPS2464>3.0.CO;2-U.

[25] R. Rajakumaran, A. Krishnapandi, S.M. Chen, K. Balamurugan, F.M. Chang, S. Sakthinathan, Electrochemical investigation of zinc tungstate nanoparticles; a robust sensor platform for the selective detection of furazolidone in biological samples, Microchemical Journal 160 (2021) 105750. https://doi.org/10.1016/j.microc.2020.

[26] M.H. Hassan, R. Khan, S. Andreescu, Advances in electrochemical detection methods for measuring contaminants of emerging concerns, Electrochemical Science Advances 2 (2022) 202100184. https://doi.org/10.1002/elsa.

[27] C. Gibi, C.H. Liu, S.C. Barton, S. Anandan, J.J. Wu, Carbon Materials for Electrochemical Sensing Application – A Mini Review, J Taiwan Inst Chem Eng 154 (2024) 105071. https://doi.org/10.1016/j.jtice.2023.

[28] T. Mahmudiono, D. Olegovich Bokov, S. Abdalkareem Jasim, W.K. Abdelbasset, M.K. Dinora, State-of-the-art of convenient and low-cost electrochemical sensor for food contamination detection: Technical and analytical overview, Microchemical Journal 179 (2022) 107460. https://doi.org/10.1016/j.microc.2022.

[29] Q. He, B. Wang, J. Liang, J. Liu, B. Liang, G. Li, Y. Long, G. Zhang, H. Liu, Research on the construction of portable electrochemical sensors for environmental compounds quality monitoring, Mater Today Adv 17 (2023) 100340. https://doi.org/10.1016/j.mtadv.2022.

[30] T. Rajarathinam, M. Kang, S. Hong, S.C. Chang, Nanocomposite-Based Electrochemical Sensors for Neurotransmitters Detection in Neurodegenerative Diseases, Chemosensors 11 (2023) 103. https://doi.org/10.3390/chemosensors11020103.

[31] R. Manikandan, T. Rajarathinam, S. Jayaraman, H.G. Jang, J.H. Yoon, J. Lee, H. jong Paik, S.C. Chang, Recent advances in miniaturized electrochemical analyzers for hazardous heavy metal sensing in environmental samples, Coord Chem Rev 499 (2024) 215487. https://doi.org/10.1016/j.ccr.2023.

[32] F. Baldini, M. Minunni, New developments in biosensors, Anal Bioanal Chem 411 (2019) 7605–7606. https://doi.org/10.1007/s00216-019-02232-z.

[33] U. Chadha, P. Bhardwaj, R. Agarwal, P. Rawat, R. Agarwal, I. Gupta, M. Panjwani, S. Singh, C. Ahuja, S.K. Selvaraj, M. Banavoth, P. Sonar, B. Badoni, A. Chakravorty, Recent progress and growth in biosensors technology: A critical review, Journal of Industrial and Engineering Chemistry 109 (2022) 21–51. https://doi.org/10.1016/j.jiec.2022.02.010.

[34] M.A. Khaleque, S.I. Hossain, M.R. Ali, M. Aly Saad Aly, H.S. Abuelmakarem, M.S. Al Mamun, M.Z. Hossain Khan, Bioreceptor modified electrochemical biosensors for the detection of life threating pathogenic bacteria: a review, RSC Adv 14 (2024) 28487–28515. https://doi.org/10.1039/d4ra04038d.

[35] E.O. Polat, M.M. Cetin, A.F. Tabak, E.B. Güven, B.Ö. Uysal, T. Arsan, A. Kabbani, H. Hamed, S.B. Gül, Transducer Technologies for Biosensors and Their Wearable Applications, Biosensors (Basel) 12 (2022) 385. https://doi.org/10.3390/bios12060385.

[36] X. Huang, Y. Zhu, E. Kianfar, Nano Biosensors: Properties, applications and electrochemical techniques, Journal of Materials Research and Technology 12 (2021) 1649–1672. https://doi.org/10.1016/j.jmrt.2021.03.048.

[37] I.S. Kucherenko, O.O. Soldatkin, D.Y. Kucherenko, O. V. Soldatkina, S. V. Dzyadevych, Advances in nanomaterial application in enzyme-based electrochemical biosensors: a review, Nanoscale Adv 1 (2019) 4560–4577. https://doi.org/10.1039/c9na00491b.

[38] M.A. Najeeb, Z. Ahmad, R.A. Shakoor, A.M.A. Mohamed, R. Kahraman, A novel classification of prostate specific antigen (PSA) biosensors based on transducing elements, Talanta 168 (2017) 52–61. https://doi.org/10.1016/j.talanta.2017.03.022.

[39] Q. Dong, H. Ryu, Y. Lei, Metal oxide based non-enzymatic electrochemical sensors for glucose detection, Electrochim Acta 370 (2021) 137744. https://doi.org/10.1016/j.electacta.2021.

[40] F. Gao, Y. Yang, W. Qiu, Z. Song, Q. Wang, L. Niu, Ni3C/Ni Nanochains for Electrochemical Sensing of Glucose, ACS Appl Nano Mater 4 (2021) 8520–8529. https://doi.org/10.1021/acsanm.1c01845.

[41] M.A.H. Nawaz, M. Majdinasab, U. Latif, M. Nasir, G. Gokce, M.W. Anwar, A. Hayat, Development of a disposable electrochemical sensor for detection of cholesterol using differential pulse voltammetry, J Pharm Biomed Anal 159 (2018) 398–405. https://doi.org/10.1016/j.jpba.2018.07.005.

[42] H.M. Yadav, J.D. Park, H.C. Kang, J.J. Lee, Recent development in nanomaterial-based electrochemical sensors for cholesterol detection, Chemosensors 9 (2021) 98. https://doi.org/10.3390/chemosensors9050098.

[43] J. Lv, C. Li, S. Feng, S.M. Chen, Y. Ding, C. Chen, Q. Hao, T.H. Yang, W. Lei, A novel electrochemical sensor for uric acid detection based on PCN/MWCNT, Ionics (Kiel) 25 (2019) 4437–4445. https://doi.org/10.1007/s11581-019-03010-8.

[44] J. Madden, E. Vaughan, M. Thompson, A. O' Riordan, P. Galvin, D. Iacopino, S. Rodrigues Teixeira, Electrochemical sensor for enzymatic lactate detection based on laser-scribed graphitic carbon modified with platinum, chitosan and lactate oxidase, Talanta 246 (2022) 123492. https://doi.org/10.1016/j.talanta.2022.

[45] P.S. Ganesh, S.Y. Kim, D.S. Choi, S. Kaya, G. Serdaroğlu, G. Shimoga, E.J. Shin, S.H. Lee, Electrochemical investigations and theoretical studies of biocompatible niacin-modified carbon paste electrode interface for electrochemical sensing of folic acid, J Anal Sci Technol 12 (2021) 1-14. https://doi.org/10.1186/s40543-021-00301-6.

[46] L. Krejcova, L. Richtera, D. Hynek, J. Labuda, V. Adam, Current trends in electrochemical sensing and biosensing of DNA methylation, Biosens Bioelectron 97 (2017) 384–399. https://doi.org/10.1016/j.bios.2017.06.004.

[47] D. Kang, S. Sun, M. Kurnik, D. Morales, F.W. Dahlquist, K.W. Plaxco, New Architecture for Reagentless, Protein-Based Electrochemical Biosensors, J Am Chem Soc 139 (2017) 12113–12116. https://doi.org/10.1021/jacs.7b05953.

[48] A.K. Yagati, J.W. Choi, Protein Based Electrochemical Biosensors for H2O2 Detection Towards Clinical Diagnostics, Electroanalysis 26 (2014) 1259–1276. https://doi.org/10.1002/elan.201400037.

[49] A. Navaee, A. Salimi, Enzyme-based electrochemical biosensors, in: Electrochemical Biosensors, Elsevier, 12 (2019) 167–211. https://doi.org/10.1016/B978-0-12-816491-4.00007-3.

[50] A.D. Mülazimoğlu, I.E. Mülazimoğlu, Electrochemical Behaviors of 2-Amino-3-Hydroxypyridine onto the Glassy Carbon Sensor Electrode: Simultaneous and Independent Determinations of Quercetin, Galangin, 3-Hydroxyflavone, and Chrysin, Food Anal Methods 6 (2013) 845–853. https://doi.org/10.1007/s12161-012-9492-5.

[51] S. Thulasiprevinnah, S. Bashir, K. Ramesh, S. Ramesh, Recent advances in electrochemical biosensors for the determination of biomolecules on modified and unmodified electrodes, Journal of the Iranian Chemical Society 21 (2024) 1739–1768. https://doi.org/10.1007/s13738-024-03050-6.

[52] I. Khalil, S. Rahmati, N. Muhd Julkapli, W.A. Yehye, Graphene metal nanocomposites — Recent progress in electrochemical biosensing applications, Journal of Industrial and Engineering Chemistry 59 (2018) 425–439. https://doi.org/10.1016/j.jiec.2017.11.001.

[53] Y. Wu, C. Hu, M. Huang, N. Song, W. Hu, Highly enhanced electrochemical responses of rutin by nanostructured Fe2O3/RGO composites, Ionics (Kiel) 21 (2015) 1427–1434. https://doi.org/10.1007/s11581-014-1310-1.

[54] G. Lisak, Reliable environmental trace heavy metal analysis with potentiometric ion sensors - reality or a distant dream, Environmental Pollution 289 (2021) 117882. https://doi.org/10.1016/j.envpol.2021.

[55] C.G. Amorim, R.C. Souza, A.N. Araújo, M.C.B.S.M. Montenegro, V.L. Silva, SI lab-on-valve analysis of histamine using potentiometric detection for food quality control, Food Chem 122 (2010) 871–876. https://doi.org/10.1016/j.foodchem.2010.02.055.

[56] N.F.D. Silva, C.M.R. Almeida, J.M.C.S. Magalhães, M.P. Gonçalves, C. Freire, C. Delerue-Matos, Development of a disposable paper-based potentiometric immunosensor for real-time detection of a foodborne pathogen, Biosens Bioelectron 141 (2019) 111317. https://doi.org/10.1016/j.bios.2019.

[57] G. Ibáñez-Redín, G. Rosso Cagnani, N. O. Gomes, P.A. Raymundo-Pereira, S.A. Sergio, M.A. Gutierrez, J.E. Krieger, O.N. Oliveira, Wearable potentiometric biosensor for analysis of urea in sweat, Biosens Bioelectron 223 (2023) 114994. https://doi.org/10.1016/j.bios.2022.

[58] L.C. Clark, R. Wolf, D. Granger, Z. Taylor, Contimozls Recording of Blood Oxygen Tensions by Pohzroognz Journal of applied physiology 6.3 (1953) 189-193. https://doi.org/10.1152/jappl.1953.6.3.189

[59] M. Ahmad, C. Pan, L. Gan, Z. Nawaz, J. Zhu, Highly sensitive amperometric cholesterol biosensor based on Pt-incorporated fullerene-like ZnO nanospheres, Journal of Physical Chemistry C 114 (2010) 243–250. https://doi.org/10.1021/jp9089497.

[60] D. Grieshaber, R. Mackenzie, J. Vörös, E. Reimhult, Electrochemical Biosensors-Sensor Principles and Architectures, Sensors 8 (2008) 1400–1458. www.mdpi.org/sensors.

[61] E. Song, J.W. Choi, Multi-analyte detection of chemical species using a conducting polymer nanowire-based sensor array platform, Sens Actuators B Chem 215 (2015) 99–106. https://doi.org/10.1016/j.snb.2015.03.039.

[62] H. Kumar, N. Kumari, R. Sharma, Nanocomposites (conducting polymer and nanoparticles) based electrochemical biosensor for the detection of environment pollutant: Its issues and challenges, Environ Impact Assess Rev 85 (2020) 106438. https://doi.org/10.1016/j.eiar.2020.

[63] D.G. Prajapati, B. Kandasubramanian, Progress in the Development of Intrinsically Conducting Polymer Composites as Biosensors, Macromol Chem Phys 220 (2019) 201800561. https://doi.org/10.1002/macp.

[64] T. Acar, K. Nur Çimen, E. Özalp, Ö. Ilıca, E. Ahlatcıoğlu Özerol, Recent Advances in Biosensors Based on Conducting Polymers for Biomedical Applications, ChemistrySelect 8 (2023) 202300819. https://doi.org/10.1002/slct.

[65] S. Raza, X. Li, F. Soyekwo, D. Liao, Y. Xiang, C. Liu, A comprehensive overview of common conducting polymer-based nanocomposites; Recent advances in design and applications, Eur Polym J 160 (2021) 110773. https://doi.org/10.1016/j.eurpolymj.2021.

[66] E.B. Bahadir, M.K. Sezgintürk, A review on impedimetric biosensors, Artif Cells Nanomed Biotechnol 44 (2016) 248–262. https://doi.org/10.3109/21691401.2014.942456.

[67] C. Canali, L.B. Larsen, O.G. Martinsen, A. Heiskanen, Conductometric analysis in bio-applications: A universal impedance spectroscopy-based approach using modified electrodes, Sens Actuators B Chem 212 (2015) 544–550. https://doi.org/10.1016/j.snb.2015.02.029.

[68] K. Sharma, M. Sharma, Optical biosensors for environmental monitoring: Recent advances and future perspectives in bacterial detection, Environ Res 236 (2023) 116826. https://doi.org/10.1016/j.envres.2023.

[69] A.K. Singh, S. Mittal, M. Das, A. Saharia, M. Tiwari, Optical biosensors: a decade in review, Alexandria Engineering Journal 67 (2023) 673–691. https://doi.org/10.1016/j.aej.2022.12.040.

[70] B. Kaur, S. Kumar, B.K. Kaushik, Recent advancements in optical biosensors for cancer detection, Biosens Bioelectron 197 (2022) 113805. https://doi.org/10.1016/j.bios.2021.

[71] K. Sadani, P. Nag, X.Y. Thian, S. Mukherji, Enzymatic optical biosensors for healthcare applications, Biosens Bioelectron X 12 (2022) 100278. https://doi.org/10.1016/j.biosx.2022.

[72] K. Narsaiah, S.N. Jha, R. Bhardwaj, R. Sharma, R. Kumar, Optical biosensors for food quality and safety assurance-A review, J Food Sci Technol 49 (2012) 383–406. https://doi.org/10.1007/s13197-011-0437-6.

[73] A. Tereshchenko, M. Bechelany, R. Viter, V. Khranovskyy, V. Smyntyna, N. Starodub, R. Yakimova, Optical biosensors based on ZnO nanostructures: Advantages and perspectives. A review, Sens Actuators B Chem 229 (2016) 664–677. https://doi.org/10.1016/j.snb.2016.01.099.

[74] U. Chadha, P. Bhardwaj, R. Agarwal, P. Rawat, R. Agarwal, I. Gupta, M. Panjwani, S. Singh, C. Ahuja, S.K. Selvaraj, M. Banavoth, P. Sonar, B. Badoni, A. Chakravorty, Recent progress and growth in biosensors technology: A critical review, Journal of Industrial and Engineering Chemistry 109 (2022) 21–51. https://doi.org/10.1016/j.jiec.2022.02.010.

[75] Y.C. Lin, T. Ono, M. Esashi, Fabrication and characterization of micromachined quartz-crystal cantilever for force sensing, Journal of Micromechanics and Microengineering 15 (2005) 2426–2432. https://doi.org/10.1088/0960-1317/15/12/026.

[76] J. P J, K. Prabakaran, J. Luo, D.H. M G, Effective utilization of quartz crystal microbalance as a tool for biosensing applications, Sens Actuators A Phys 331 (2021) 113020. https://doi.org/10.1016/j.sna.2021.

[77] M. Pohanka, Overview of piezoelectric biosensors, immunosensors and DNA sensors and their applications, Materials 11 (2018) 448. https://doi.org/10.3390/ma11030448.

[78] J. Song, W. He, H. Shen, Z. Zhou, M. Li, P. Su, Y. Yang, Exquisitely designed magnetic DNA nanocompartment for enzyme immobilization with adjustable catalytic activity and improved enzymatic assay performance, Chemical Engineering Journal 390 (2020) 124488. https://doi.org/10.1016/j.cej.2020.

[79] G. Díaz-Díaz, D. Antuña-Jiménez, M. Carmen Blanco-López, M. Jesús Lobo-Castañón, A.J. Miranda-Ordieres, P. Tuñón-Blanco, New materials for analytical biomimetic assays based on affinity and catalytic receptors prepared by molecular imprinting, TrAC - Trends in Analytical Chemistry 33 (2012) 68–80. https://doi.org/10.1016/j.trac.2011.09.011.

[80] M. Pohanka, Cholinesterases in Biorecognition and Biosensors Construction: A Review, Anal Lett 46 (2013) 1849–1868. https://doi.org/10.1080/00032719.2013.780240.

[81] M. Dong, Z. Wu, M. Lu, Z. Wang, Z. Li, Combining the physical adsorption approach and the covalent attachment method to prepare a bifunctional bioreactor, Int J Mol Sci 13 (2012) 11443–11454. https://doi.org/10.3390/ijms130911443.

[82] P.N. Bartlett, J.M. Cooper, A review of the immobilization of enzymes in electropolymerized films Journal of Electroanalytical Chemistry 362 (1993) 1-12. https://doi.org/1-s2.0-002207289380001X

[83] X. Xu, M. Xie, S. Luo, X. Jia, Revisiting Protein-Copolymer Binding Mechanisms: Insights beyond the "Lock-and-Key" Model, Journal of Physical Chemistry Letters 15 (2024) 773–781. https://doi.org/10.1021/acs.jpclett.3c03200.

[84] B. Corry, J. Uilk, C. Crawley, Probing direct binding affinity in electrochemical antibody-based sensors, Anal Chim Acta 496 (2003) 103–116. https://doi.org/10.1016/j.aca.2003.01.001.

[85] S. Gao, J.M. Guisán, J. Rocha-Martin, Oriented immobilization of antibodies onto sensing platforms - A critical review, Anal Chim Acta 1189 (2022) 338907. https://doi.org/10.1016/j.aca.2021.

[86] Y. Du, S. Dong, Nucleic acid biosensors: Recent advances and perspectives, Anal Chem 89 (2017) 189–215. https://doi.org/10.1021/acs.analchem.6b04190.

[87] A. Leung, P.M. Shankar, R. Mutharasan, A review of fiber-optic biosensors, Sens Actuators B Chem 125 (2007) 688–703. https://doi.org/10.1016/j.snb.2007.03.010.

[88] L. Bousse, B Whole cell biosensors, Sensors and Actuators B: Chemical 34.1-3 (1996) 270-275. https://doi.org/10.1016/S0925-4005(96)01906-5

[89] Y. Alhamoud, D. Yang, S.S. Fiati Kenston, G. Liu, L. Liu, H. Zhou, F. Ahmed, J. Zhao, Advances in biosensors for the detection of ochratoxin A: Bio-receptors, nanomaterials, and their applications, Biosens Bioelectron 141 (2019) 111418. https://doi.org/10.1016/j.bios.2019.

[90] G. Sasikanth, B.V.R.S. Subramanyam, D. Maity, T.N. Narayanan, T.P. Radhakrishnan, Low Conductivity Polyaniline-Gold Nanocomposite via Interfacial Polymerization: Efficient Humidity Sensing by Thin Films and

Mechanistic Insights through In Situ Experiments, Journal of Physical Chemistry C 127 (2023) 18107–18116. https://doi.org/10.1021/acs.jpcc.3c03866.

[91] B. Dalkiran, C.M.A. Brett, Polyphenazine and polytriphenylmethane redox polymer/nanomaterial-based electrochemical sensors and biosensors: a review 188 (2021) 1-20. https://doi.org/10.1007/s00604-021-04821-1/Published.

[92] O.S. Kwon, H.S. Song, T.H. Park, J. Jang, Conducting Nanomaterial Sensor Using Natural Receptors, Chem Rev 119 (2019) 36–93. https://doi.org/10.1021/acs.chemrev.8b00159.

[93] B. Mekuye, B. Abera, Nanomaterials: An overview of synthesis, classification, characterization, and applications, Nano Select 4 (2023) 486–501. https://doi.org/10.1002/nano.202300038.

[94] L. Scarabelli, M. Sun, X. Zhuo, S. Yoo, J.E. Millstone, M.R. Jones, L.M. Liz-Marzán, Plate-Like Colloidal Metal Nanoparticles, Chem Rev 123 (2023) 3493–3542. https://doi.org/10.1021/acs.chemrev.3c00033.

[95] K. Shehzad, Y. Xu, C. Gao, X. Duan, Three-dimensional macro-structures of two-dimensional nanomaterials, Chem Soc Rev 45 (2016) 5541–5588. https://doi.org/10.1039/c6cs00218h.

[96] S.A. Ahire, A.A. Bachhav, T.B. Pawar, B.S. Jagdale, A.V. Patil, P.B. Koli, The Augmentation of nanotechnology era: A concise review on fundamental concepts of nanotechnology and applications in material science and technology, Results Chem 4 (2022) 100633. https://doi.org/10.1016/j.rechem.2022.

[97] T.Y. Poh, N.A.T.B.M. Ali, M. Mac Aogáin, M.H. Kathawala, M.I. Setyawati, K.W. Ng, S.H. Chotirmall, Inhaled nanomaterials and the respiratory microbiome: Clinical, immunological and toxicological perspectives, Part Fibre Toxicol 15 (2018) 1-16. https://doi.org/10.1186/s12989-018-0282-0.

[98] H.J. Kwon, K. Shin, M. Soh, H. Chang, J. Kim, J. Lee, G. Ko, B.H. Kim, D. Kim, T. Hyeon, Large-Scale Synthesis and Medical Applications of Uniform-Sized Metal Oxide Nanoparticles, Advanced Materials 30 (2018) 201704290. https://doi.org/10.1002/adma.

[99] K.K. Harish, V. Nagasamy, B. Himangshu, K. Anuttam, Metallic Nanoparticle: A Review, Biomed J Sci &Tech Res 4 (2018) 3765-3775. https://doi.org/10.26717/BJSTR.2018.04.001011.

[100] L. Wang, M. Hasanzadeh Kafshgari, M. Meunier, Optical Properties and Applications of Plasmonic-Metal Nanoparticles, Adv Funct Mater 30 (2020) 202005400. https://doi.org/10.1002/adfm.

[101] N. Joudeh, D. Linke, Nanoparticle classification, physicochemical properties, characterization, and applications: a comprehensive review for biologists, J Nanobiotechnology 20 (2022) 266. https://doi.org/10.1186/s12951-022-01477-8.

[102] T. Bruna, F. Maldonado-Bravo, P. Jara, N. Caro, Silver nanoparticles and their antibacterial applications, Int J Mol Sci 22.13 (2021) 7202. https://doi.org/10.3390/ijms22137202.

[103] Z.A. Ratan, F.R. Mashrur, A.P. Chhoan, S.M. Shahriar, M.F. Haidere, N.J. Runa, S. Kim, D.H. Kweon, H. Hosseinzadeh, J.Y. Cho, Silver nanoparticles as potential antiviral agents, Pharmaceutics 13.12 (2021) 2034. https://doi.org/10.3390/pharmaceutics13122034.

[104] N. Satsangi, Synthesis and Characterization of Biocompatible Silver Nanoparticles for Anticancer Application, J Inorg Organomet Polym Mater 30 (2020) 1907–1914. https://doi.org/10.1007/s10904-019-01372-0.

[105] A.A. Vodyashkin, M.G.H. Rizk, P. Kezimana, A.A. Kirichuk, Y.M. Stanishevskiy, Application of gold nanoparticle-based materials in cancer therapy and diagnostics, ChemEngineering 5.4 (2021) 69. https://doi.org/10.3390/chemengineering5040069.

[106] X. Cao, Y. Ye, S. Liu, Gold nanoparticle-based signal amplification for biosensing, Anal Biochem 417 (2011) 1–16. https://doi.org/10.1016/j.ab.2011.05.027.

[107] Y. Hu, Y. Huang, C. Tan, X. Zhang, Q. Lu, M. Sindoro, X. Huang, W. Huang, L. Wang, H. Zhang, Two-dimensional transition metal dichalcogenide nanomaterials for biosensing applications, Mater Chem Front 1 (2017) 24–36. https://doi.org/10.1039/c6qm00195e.

[108] N. Rohaizad, C.C. Mayorga-Martinez, M. Fojtů, N.M. Latiff, M. Pumera, Two-dimensional materials in biomedical, biosensing and sensing applications, Chem Soc Rev 50 (2021) 619–657. https://doi.org/10.1039/d0cs00150c.

[109] H. Shu, P. Luo, P. Liang, D. Cao, X. Chen, Layer-dependent dopant stability and magnetic exchange coupling of iron-doped MoS2 nanosheets, ACS Appl Mater Interfaces 7 (2015) 7534–7541. https://doi.org/10.1021/am508843z.

[110] E. Asadian, M. Ghalkhani, S. Shahrokhian, Electrochemical sensing based on carbon nanoparticles: A review, Sens Actuators B Chem 293 (2019) 183–209. https://doi.org/10.1016/j.snb.2019.04.075.

[111] S. Zhang, Y. Zhang, S. Huang, C. Wang, Theoretical investigations of sp-sp 2 hybridized zero-dimensional fullerenynes, Nanoscale 4 (2012) 2839–2842. https://doi.org/10.1039/c2nr30299c.

[112] T.C. Dinadayalane, J. Leszczynski, Remarkable diversity of carbon-carbon bonds: Structures and properties of fullerenes, carbon nanotubes, and graphene, Struct Chem 21 (2010) 1155–1169. https://doi.org/10.1007/s11224-010-9670-2.

[113] A.M. Ealias, M.P. Saravanakumar, A review on the classification, characterisation, synthesis of nanoparticles and their application, in: IOP Conf Ser Mater Sci Eng, Institute of Physics Publishing, 263.3 (2017) 032019. https://doi.org/10.1088/1757-899X/263/3/032019.

[114] M.J. Allen, V.C. Tung, R.B. Kaner, Honeycomb carbon: A review of graphene, Chem Rev 110 (2010) 132–145. https://doi.org/10.1021/cr900070d.

[115] A. Martín, J. Hernández-Ferrer, L. Vázquez, M.T. Martínez, A. Escarpa, Controlled chemistry of tailored graphene nanoribbons for electrochemistry: A rational approach to optimizing molecule detection, RSC Adv 4 (2014) 132–139. https://doi.org/10.1039/c3ra44235g.

[116] S. Borandeh, V. Alimardani, S.S. Abolmaali, J. Seppälä, Graphene Family Nanomaterials in Ocular Applications: Physicochemical Properties and Toxicity, Chem Res Toxicol 34 (2021) 1386–1402. https://doi.org/10.1021/acs.chemrestox.0c00340.

[117] C.B. Jacobs, T.L. Vickrey, B.J. Venton, Functional groups modulate the sensitivity and electron transfer kinetics of neurochemicals at carbon nanotube modified microelectrodes, Analyst 136 (2011) 3557–3565. https://doi.org/10.1039/c0an00854k.

[118] W. Ao, J. Fu, X. Mao, Q. Kang, C. Ran, Y. Liu, H. Zhang, Z. Gao, J. Li, G. Liu, J. Dai, Microwave assisted preparation of activated carbon from biomass: A review, Renewable and Sustainable Energy Reviews 92 (2018) 958–979. https://doi.org/10.1016/j.rser.2018.04.051.

[119] Z. Heidarinejad, M.H. Dehghani, M. Heidari, G. Javedan, I. Ali, M. Sillanpää, Methods for preparation and activation of activated carbon: a review, Environ Chem Lett 18 (2020) 393–415. https://doi.org/10.1007/s10311-019-00955-0.

[120] Y. Zeng, Z. Zhu, D. Du, Y. Lin, Nanomaterial-based electrochemical biosensors for food safety, Journal of Electroanalytical Chemistry 781 (2016) 147–154. https://doi.org/10.1016/j.jelechem.2016.10.030.

[121] P.L. Truong, Y. Yin, D. Lee, S.H. Ko, Advancement in COVID-19 detection using nanomaterial-based biosensors, Exploration 3 (2023) 20210232. https://doi.org/10.1002/EXP.20210232.

[122] L. Farzin, M. Shamsipur, L. Samandari, S. Sheibani, Advances in the design of nanomaterial-based electrochemical affinity and enzymatic biosensors for metabolic biomarkers: A review, Microchimica Acta 185 (2018) 1-25. https://doi.org/10.1007/s00604-018-2820-8.

[123] S. Radhakrishnan, K. Krishnamoorthy, C. Sekar, J. Wilson, S.J. Kim, A highly sensitive electrochemical sensor for nitrite detection based on Fe2O3 nanoparticles decorated reduced graphene oxide nanosheets, Appl Catal B 148–149 (2014) 22–28. https://doi.org/10.1016/j.apcatb.2013.10.044.

[124] C. Bhuvaneswari, A. Elangovan, C. Sharmila, K. Sudha, G. Arivazhagan, Fabrication ofcobalt tungstate/N-rGO nanocomposite: Application towards the detection of antibiotic drug-Furazolidone, Colloids Surf A Physicochem Eng Asp 656 (2023) 130299. https://doi.org/10.1016/j.colsurfa.2022.

[125] P. Feng, J. Li, H. Wang, Z. Xu, Biomass-based activated carbon and activators: Preparation of activated carbon from corncob by chemical activation with biomass pyrolysis liquids, ACS Omega 5 (2020) 24064–24072. https://doi.org/10.1021/acsomega.0c03494.

[126] Y. Sun, G.I.N. Waterhouse, X. Qiao, J. Xiao, Z. Xu, Determination of chloramphenicol in food using nanomaterial-based electrochemical and optical sensors-A review, Food Chem 410 (2023) 135434. https://doi.org/10.1016/j.foodchem.2023.

[127] S. Shrivastava, N. Jadon, R. Jain, Next-generation polymer nanocomposite-based electrochemical sensors and biosensors: A review, TrAC - Trends in Analytical Chemistry 82 (2016) 55–67. https://doi.org/10.1016/j.trac.2016.04.005.

[128] K. Chen, L. Chen, Y. Chen, H. Bai, L. Li, Three-dimensional porous graphene-based composite materials: Electrochemical synthesis and application, J Mater Chem 22 (2012) 20968–20976. https://doi.org/10.1039/c2jm34816k.

[129] S. Behrens, Preparation of functional magnetic nanocomposites and hybrid materials: Recent progress and future directions, Nanoscale 3 (2011) 877–892. https://doi.org/10.1039/c0nr00634c.

[130] F. Ahmed, A. Umar, S. Kumar, N.M. Shaalan, N. Arshi, M.G. Alam, P.M.Z. Hasan, S.M. Ramay, R. Khan, A. Aljaafari, A. Alshoaibi, Manganese dioxide nanoparticles/reduced graphene oxide nanocomposites for hybrid capacitive desalination, Adv Compos Hybrid Mater 6.1 (2023) 19. https://doi.org/10.1007/s42114-022-00601-4.

[131] J. Helmlinger, C. Sengstock, C. Groß-Heitfeld, C. Mayer, T.A. Schildhauer, M. Köller, M. Epple, Silver nanoparticles with different size and shape: Equal cytotoxicity, but different antibacterial effects, RSC Adv 6 (2016) 18490–18501. https://doi.org/10.1039/c5ra27836h.

[132] R. Ding, I.M. Padilla Espinosa, D. Loevlie, S. Azadehranjbar, A.J. Baker, G. Mpourmpakis, A. Martini, T.D.B. Jacobs, Size-dependent shape distributions of platinum nanoparticles, Nanoscale Adv 4 (2022) 3978–3986. https://doi.org/10.1039/d2na00326k.

[133] R.B. Goularte, J.P. Winiarski, E. Latocheski, C.L. Jost, Novel analytical sensing strategy using a palladium nanomaterial-based electrode for nimesulide electrochemical reduction, Journal of Electroanalytical Chemistry 920 (2022) 116622. https://doi.org/10.1016/j.jelechem.2022.

[134] S. Hong, X. Li, Optimal size of gold nanoparticles for surface-enhanced Raman spectroscopy under different conditions, J Nanomater 2013.1 (2013): 790323. https://doi.org/10.1155/2013/790323.

[135] L. Zheng, M. Cao, Y. Du, Q. Liu, M.Y. Emran, A. Kotb, M. Sun, C.B. Ma, M. Zhou, Artificial enzyme innovations in electrochemical devices: advancing wearable and portable sensing technologies, Nanoscale 16 (2023) 44–60. https://doi.org/10.1039/d3nr05728c.

[136] S. De Marchi, S. Núñez-Sánchez, G. Bodelón, J. Pérez-Juste, I. Pastoriza-Santos, Pd nanoparticles as a plasmonic material: Synthesis, optical properties and applications, Nanoscale 12 (2020) 23424–23443. https://doi.org/10.1039/d0nr06270g.

[137] J. Huang, D. Wang, H. Hou, T. You, Electrospun palladium nanoparticle-loaded carbon nanofibers and their electrocatalytic activities towards hydrogen peroxide

and NADH, Adv Funct Mater 18 (2008) 441–448. https://doi.org/10.1002/adfm.200700729.

[138] X. Chen, X.M. Chen, Z.X. Cai, Z.Y. Huang, M. Oyama, Y.Q. Jiang, Ultrafine palladium nanoparticles grown on graphene nanosheets for enhanced electrochemical sensing of hydrogen peroxide, Electrochim Acta 97 (2013) 398–403. https://doi.org/10.1016/j.electacta.2013.02.047.

[139] Y. Wei, Y. Liu, Z. Xu, S. Wang, B. Chen, D. Zhang, Y. Fang, Simultaneous Detection of Ascorbic Acid, Dopamine, and Uric Acid Using a Novel Electrochemical Sensor Based on Palladium Nanoparticles/Reduced Graphene Oxide Nanocomposite, Int J Anal Chem 2020.1 (2020): 8812443. https://doi.org/10.1155/2020/8812443.

[140] G. huang Wu, Y. fang Wu, X. wei Liu, M. cong Rong, X. mei Chen, X. Chen, An electrochemical ascorbic acid sensor based on palladium nanoparticles supported on graphene oxide, Anal Chim Acta 745 (2012) 33–37. https://doi.org/10.1016/j.aca.2012.07.034.

[141] S. Palanisamy, B. Thirumalraj, S.M. Chen, M.A. Ali, F.M.A. Al-Hemaid, Palladium nanoparticles decorated on activated fullerene modified screen printed carbon electrode for enhanced electrochemical sensing of dopamine, J Colloid Interface Sci 448 (2015) 251–256. https://doi.org/10.1016/j.jcis.2015.02.013.

[142] X. Wang, M. Wu, W. Tang, Y. Zhu, L. Wang, Q. Wang, P. He, Y. Fang, Simultaneous electrochemical determination of ascorbic acid, dopamine and uric acid using a palladium nanoparticle/graphene/chitosan modified electrode, Journal of Electroanalytical Chemistry 695 (2013) 10–16. https://doi.org/10.1016/j.jelechem.2013.02.021.

[143] M. Kaur, C. Sharma, N. Sharma, B. Jamwal, S. Paul, Pd nanoparticles decorated on ZnO/Fe3O4cores and doped with Mn2+and Mn3+for catalytic C-C coupling, nitroaromatics reduction, and the oxidation of alcohols and hydrocarbons, ACS Appl Nano Mater 3 (2020) 10310–10325. https://doi.org/10.1021/acsanm.0c02221.

[144] N. Uegaki, S. Seino, Y. Ohkubo, T. Nakagawa, Effect of Polymer Substrate on Adhesion of Electroless Plating in Irradiation-Based Direct Immobilization of Pd Nanoparticles Catalyst, Nanomaterials 12 (2022) 99-105. https://doi.org/10.3390/nano12224106.

[145] X. Zhang, P. Yang, S.P. Jiang, Pd nanoparticles assembled on Ni- and N-doped carbon nanotubes towards superior electrochemical activity, Int J Hydrogen Energy 46 (2021) 2065–2074. https://doi.org/10.1016/j.ijhydene.2020.10.096.

[146] S. Patnaik, D.P. Sahoo, K.M. Parida, Bimetallic co-effect of Au-Pd alloyed nanoparticles on mesoporous silica modified g-C3N4 for single and simultaneous photocatalytic oxidation of phenol and reduction of hexavalent chromium, J Colloid Interface Sci 560 (2020) 519–535. https://doi.org/10.1016/j.jcis.2019.09.041.

[147] Z. Wei, Z. Xie, L. Gao, Y. Wang, H. Sun, Y. Jian, G. Zhang, L. Xu, J. Yang, W. Zhang, Z. Gao, Highly crystallized Pd/Cu nanoparticles on activated carbon: An efficient heterogeneous catalyst for sonogashira cross-coupling reaction, Catalysts 10 (2020) 192. https://doi.org/10.3390/catal10020192.

[148] M. Sookhakian, W.J. Basirun, B.T. Goh, P.M. Woi, Y. Alias, Molybdenum disulfide nanosheet decorated with silver nanoparticles for selective detection of dopamine, Colloids Surf B Biointerfaces 176 (2019) 80–86. https://doi.org/10.1016/j.colsurfb.2018.12.058.

[149] M. Bekmezci, H. Ozturk, M. Akin, R. Bayat, F. Sen, R. Darabi, H. Karimi-Maleh, Bimetallic Biogenic Pt-Ag Nanoparticle and Their Application for Electrochemical Dopamine Sensor, Biosensors (Basel) 13.5 (2023) 531. https://doi.org/10.3390/bios13050531.

[150] M. Govindhan, M. Amiri, A. Chen, Au nanoparticle/graphene nanocomposite as a platform for the sensitive detection of NADH in human urine, Biosens Bioelectron 66 (2015) 474–480. https://doi.org/10.1016/j.bios.2014.12.012.

[151] F. Yuan, Y. Xia, Q. Lu, Q. Xu, Y. Shu, X. Hu, Recent advances in inorganic functional nanomaterials based flexible electrochemical sensors, Talanta 244 (2022) 123419. https://doi.org/10.1016/j.talanta.2022.

[152] K. Aneesh, C.S.R. vusa, S. Berchmans, Enhanced peroxidase-like activity of CuWO4 nanoparticles for the detection of NADH and hydrogen peroxide, Sens Actuators B Chem 253 (2017) 723–730. https://doi.org/10.1016/j.snb.2017.06.175.

[153] M.M. Habibi, M. Mousavi, Z. Shadman, J.B. Ghasemi, Preparation of a nonenzymatic electrochemical sensor based on a g-C3N4/MWO4 (M: Cu, Mn, Co, Ni) composite for the determination of H2O2, New Journal of Chemistry 46 (2022) 3766–3776. https://doi.org/10.1039/d1nj05711a.

[154] Y. Liu, P. Zhao, Y. Liang, Y. Chen, J. Pu, J. Wu, Y. Yang, Y. Ma, Z. Huang, H. Luo, D. Huo, C. Hou, Single-atom nanozymes Co–N–C as an electrochemical sensor for detection of bioactive molecules, Talanta 254 (2023) 124171. https://doi.org/10.1016/j.talanta.2022.

[155] H. Ganesha, S. Veeresh, Y.S. Nagaraju, D.S. Suresh, H. Devendrappa, Micelles self-degraded polypyrrole nanotube-cobalt oxide nanocomposite based electrochemical sensor for detection of Ascorbic acid, Inorg Chem Commun 145 (2022) 109975. https://doi.org/10.1016/j.inoche.2022.

[156] R. V. Santos, G.A. Cabrera-Pasca, C.S. Costa, B. Bosch-Santos, L. Otubo, L.F.D. Pereira, B.S. Correa, F.B. Effenberger, A. Burimova, R.S. Freitas, A.W. Carbonari, Crystalline and magnetic properties of CoO nanoparticles locally investigated by using radioactive indium tracer, Sci Rep 11.1 (2021) 21028. https://doi.org/10.1038/s41598-021-99810-y.

[157] Y. Sefid-sefidehkhan, K. Nekoueian, M. Amiri, M. Sillanpaa, H. Eskandari, Palladium nanoparticles in electrochemical sensing of trace terazosin in human serum and pharmaceutical preparations, Materials Science and Engineering C 75 (2017) 368–374. https://doi.org/10.1016/j.msec.2017.02.061.

[158] H. Ajab, A.T. Jafry, H. Sajid, M.A. Addicoat, K. Ayub, M.Z.U. Haq, An electrochemical sensing potential of cobalt oxide nanoparticles towards citric acid integrated with computational approach in food and biological media, Food Chem 455 (2024) 139869. https://doi.org/10.1016/j.foodchem.2024.

[159] Q. ZHAO, H. YU, D. HU, L.L. LI, J. JIN, M.J. AI, J. WEI, K. SONG, Recent advances in electrochemical sensors based on palladium nanoparticles, Chinese Journal of Analytical Chemistry 50.11 (2022) 100144. https://doi.org/10.1016/j.cjac.2022.100144.

[160] X. Wang, M. Wu, W. Tang, Y. Zhu, L. Wang, Q. Wang, P. He, Y. Fang, Simultaneous electrochemical determination of ascorbic acid, dopamine and uric acid using a palladium nanoparticle/graphene/chitosan modified electrode, Journal of Electroanalytical Chemistry 695 (2013) 10–16. https://doi.org/10.1016/j.jelechem.2013.02.021.

[161] H. Xu, Y. Hang, X. Lei, J. Deng, J. Yang, Synthesis of cobalt phosphide hybrid for simultaneous electrochemical detection of ascorbic acid, dopamine, and uric acid, RSC Adv 14 (2024) 14665–14671. https://doi.org/10.1039/d4ra01702a.

[162] C. Wang, J. Du, H. Wang, C. Zou, F. Jiang, P. Yang, Y. Du, A facile electrochemical sensor based on reduced graphene oxide and Au nanoplates modified glassy carbon electrode for simultaneous detection of ascorbic acid, dopamine and uric acid, Sens Actuators B Chem 204 (2014) 302–309. https://doi.org/10.1016/j.snb.2014.07.077.

[163] B. Dinesh, V. Veeramani, S.M. Chen, R. Saraswathi, In situ electrochemical synthesis of reduced graphene oxide-cobalt oxide nanocomposite modified electrode for selective sensing of depression biomarker in the presence of ascorbic acid and dopamine, Journal of Electroanalytical Chemistry 786 (2017) 169–176. https://doi.org/10.1016/j.jelechem.2017.01.022.

[164] F. Yang, J. Wang, Y. Cao, L. Zhang, X. Zhang, A highly sensitive ascorbic acid sensor based on carbon-supported CoPd nanoparticles, Sens Actuators B Chem 205 (2014) 20–25. https://doi.org/10.1016/j.snb.2014.08.050.

[165] F.P. Van der Zee, F.J. Cervantes, Impact and application of electron shuttles on the redox (bio)transformation of contaminants: A review, Biotechnol Adv 27 (2009) 256–277. https://doi.org/10.1016/j.biotechadv.2009.01.004.

[166] K.Y. Cheng, R. Karthikeyan, J.W.C. Wong, Microbial electrochemical remediation of organic contaminants: Possibilities and perspective, in: Biomass, Biofuels, Biochemicals: Microbial Electrochemical Technology: Sustainable Platform for Fuels, Chemicals and Remediation, Elsevier, 21 (2018) 613–640. https://doi.org/10.1016/B978-0-444-64052-9.00025-X.

[167] L. V. da Silva, A.K.A. de Almeida, J.A. Xavier, C.B. Lopes, F. de A. dos S. Silva, P.R. Lima, N.D. dos Santos, L.T. Kubota, M.O.F. Goulart, Phenol based redox mediators in electroanalysis, Journal of Electroanalytical Chemistry 827 (2018) 230–252. https://doi.org/10.1016/j.jelechem.2018.05.027.

[168] Y. Chen, S.A. Freunberger, Z. Peng, O. Fontaine, P.G. Bruce, Charging a Li-O2 battery using a redox mediator, Nat Chem 5 (2013) 489–494. https://doi.org/10.1038/nchem.1646.

[169] J.M. Cameron, C. Holc, A.J. Kibler, C.L. Peake, D.A. Walsh, G.N. Newton, L.R. Johnson, Molecular redox species for next-generation batteries, Chem Soc Rev 50 (2021) 5863–5883. https://doi.org/10.1039/d0cs01507e.

[170] A. Nafady, A.P. O'Mullane, A.M. Bond, Electrochemical and photochemical routes to semiconducting transition metal-tetracyanoquinodimethane coordination

polymers, Coord Chem Rev 268 (2014) 101–142. https://doi.org/10.1016/j.ccr.2014.01.017.

[171] H. Tamaya, H. Nakano, T. Iimori, 7,7,8,8-Tetracyanoquinodimethane (TCNQ) emits visible photoluminescence in solution, J Lumin 192 (2017) 203–207. https://doi.org/10.1016/j.jlumin.2017.06.051.

[172] H.L. Van De Wouw, J. Chamorro, M. Quintero, R.S. Klausen, Opposites Attract: Organic Charge Transfer Salts, J Chem Educ 92 (2015) 2134–2139. https://doi.org/10.1021/acs.jchemed.5b00340.

[173] S. Lee, J. Hong, S.K. Jung, K. Ku, G. Kwon, W.M. Seong, H. Kim, G. Yoon, I. Kang, K. Hong, H.W. Jang, K. Kang, Charge-transfer complexes for high-power organic rechargeable batteries, Energy Storage Mater 20 (2019) 462–469. https://doi.org/10.1016/j.ensm.2019.05.001.

[174] R. Yu, H. Yao, L. Hong, M. Gao, L. Ye, J. Hou, TCNQ as a volatilizable morphology modulator enables enhanced performance in non-fullerene organic solar cells, J Mater Chem C Mater 8 (2019) 44–49. https://doi.org/10.1039/c9tc04892h.

[175] C. Jouve, D. Jullien, B. Remaki, CHEMBI cAL Conductive polyethylene as sensitive layer for gas detection 28.1 (1995): 75-80. https://doi.org/10.1016/0925-4005(94)01541-O.

[176] N.S. Anuar, W.J. Basirun, M. Shalauddin, S. Akhter, A dopamine electrochemical sensor based on a platinum-silver graphene nanocomposite modified electrode, RSC Adv 10 (2020) 17336–17344. https://doi.org/10.1039/c9ra11056a.

[177] S. Yang, Y. Cheng, D. Cheng, Y. Wang, H. Xu, M. Li, T. Jiang, H. Wang, N-Doped Graphene-Supported Gold Nanorods for Electrochemical Sensing of Ascorbic Acid with Superior Sensitivity, J Electron Mater 52 (2023) 2336–2346. https://doi.org/10.1007/s11664-022-10162-3.

[178] R.D. Nagarajan, P. Murugan, A.K. Sundramoorthy, Selective Electrochemical Sensing of NADH and NAD+ Using Graphene/Tungstate Nanocomposite Modified Electrode, ChemistrySelect 5 (2020) 14643–14651. https://doi.org/10.1002/slct.202003554.

[179] C. Bhuvaneswari, S. Ganesh Babu, Scheming the best metal tungstate laden on boron nitride: Budding en route for electrochemical sensing of ornidazole, Microchemical Journal 193 (2023) 109120. https://doi.org/10.1016/j.microc.2023.

[180] V.P. Singh, G. Singh, R. Patel, U.K. Gaur, M. Sharma, Highly sensitive detection of hazardous hydroquinone and chloramphenicol in the presence of paracetamol using cobalt tungstate (CoWO4) nanoplates modified electrode, J Environ Chem Eng 11 (2023) 111208. https://doi.org/10.1016/j.jece.2023.

[181] Y. Zhang, X. Liu, Y. Tian, Y. Geng, J. Wang, M. Ma, A ratiometric electrochemical sensing strategy based on the self-assembly of Co NC/CNT and methylene blue for effective detection of the food additive tert-butylhydroquinone, Talanta 266 (2024) 125024. https://doi.org/10.1016/j.talanta.2023.

[182] Y. Sefid-sefidehkhan, K. Nekoueian, M. Amiri, M. Sillanpaa, H. Eskandari, Palladium nanoparticles in electrochemical sensing of trace terazosin in human serum and pharmaceutical preparations, Materials Science and Engineering C 75 (2017) 368–374. https://doi.org/10.1016/j.msec.2017.02.061.