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Efficacy of Phthalocyanine-Based Catalysts in Electrochemical Sensors: A Comprehensive Review

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Metal phthalocyanines (MPcs) are promising materials for electrochemical sensing due to their physicochemical properties, including redox activity, structural versatility, and chemical stability. These materials can incorporate various metals into their central core, ensuring tunable catalytic activity and enhanced sensitivity and selectivity. This makes MPcs valuable for designing advanced electrochemical sensors, which require precise and reliable performance for applications ranging from environmental monitoring to biomedical diagnostics. This review discusses the advancements in MPc-based catalysts for electrochemical sensors, focusing on their superior catalytic properties, stability under diverse operating conditions, and high functionalization potential. The unique redox behavior of the metal center in MPcs ensures improved detection capabilities of analytes like biomolecules, heavy metal ions, and environmental pollutants, positioning MPc materials as a cornerstone in future sensor technology. MPc-based sensors have diverse applications across various fields, including environmental sensing, medical diagnostics, and industrial process monitoring. Recent reports highlight the practical relevance and growing importance of MPcs in real-world applications. Challenges associated with MPc-based sensors include scalability, environmental stability, and integration into practical devices. The review concludes with a discussion on the future outlook on MPcs in the design and development of next-generation electrochemical sensors, paving the way for more efficient, cost-effective, and reliable detection technologies.

1. Introduction

The sensors are essential for detecting changes in the environment and human body by considering the physical and chemical properties of the analyte under study. The continuous monitoring of the abnormal variations in the system helps to tackle the changes with suitable remedies. Different sensors and actuators monitor various chemical components of biological and environmental interest.[1–4] Electrochemical sensors are essential in monitoring and detecting chemical compounds because of their exceptional selectivity and ability to detect, distinguish, and estimate an extensive variety of analytes.[5–7] Electrochemical techniques have been identified as essential tools for monitoring analytes, and their electrocatalytic capacities can be improved to upgrade their execution and real-time applications consistently.[8,9] In these devices, electrocatalyst material serves as a critical component, facilitating and enhancing the efficiency of various electrochemical processes. These catalysts play a pivotal role in accelerating electrode reactions, improving selectivity, and minimizing overpotentials, thereby enabling the development of advanced technologies across numerous applications.[10–13] Various materials have been investigated as electrocatalysts for these sensors, including metals, metal oxides, metal chalcogenides, carbon-based materials, and organic molecules.[14–17] Metal phthalocyanines (MPcs) are one of many catalysts being studied because of their unique electrical properties and wide range of catalytic activities. MPcs are a kind of N4 macrocyclic compound that has stimulated researchers' interest because of its intriguing structural features and redox activity.[18–20] These substances are steady and electrochemically dynamic, making them appropriate materials for synergist use in electrochemical sensors. They comprise a central metal atom with a planar arrangement of four nitrogen atoms.[21,22] MPc-based catalysts are promising in the development of electrochemical sensor systems. These catalysts may improve the electrochemical detection platform in terms of charge transfer, sensitivity, and selectivity.[23–26]

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1.1. Fundamentals of Electrochemical Sensors

Electrochemistry, a science dating back 200 years, plays a crucial role in numerous fields, such as battery technology, solar energy, diabetes management, fuel cells, supercapacitors, and pH sensing. Its strength lies in its ability to provide fast, cost-effective, and susceptible analytical results, making it ideal for miniaturization and point-of-care testing. At its core, electrochemistry focuses on the movement of charges at the interface. Imagine a molecule that can exist in two forms: reduced (gained an electron) and oxidized (lost an electron). By applying a voltage, we can push this equilibrium in either direction, causing the molecule to gain or lose an electron, resulting in a measurable electrical current. The strength of the current produced directly reflects the concentration of the molecule in the solution.[27–31]

A typical electrochemical setup involves a cell containing the target molecule, a solvent (usually water), and a conductive salt (electrolyte) to enhance the current flow. Application of a positive voltage to the working electrode results in extraction of electrons from the target molecule resulting in oxidation with the generation of current. Conversely, a negative voltage causes the reduction of the target molecule. A vital component of this setup is the potentiostat, which acts as both a power source and a measuring tool. The application of a voltage and measurement of the resulting current (amperometry), or vice versa (potentiometry), is carried out using a potentiostat. Depending on its features and applications, a potentiostat can range in price from a few hundred to several thousand dollars or pounds. Another crucial element is the reference electrode, which maintains a stable voltage and the working electrode potential is measured against the reference electrode. This ensures consistent and accurate measurement of potential irrespective of the target solution's specific properties. While various materials can be used as reference electrodes, a model reference electrode offers superior stability across different pH and temperature conditions. A typical example is the Ag/AgCl electrode, which consists of a silver wire coated with silver chloride and immersed in a potassium chloride solution. Finally, the counter electrode completes the electrical circuit in an electrochemical cell by balancing the current generated at the working electrode. It is typically made of a high surface area conductive metals like platinum gauze, carbon, etc., **Figure 1**.[32]

The current generated from the oxidation or reduction of a target analyte is related to various experimental variables and constants. It can be expressed as follows.

$$i = nAFj \tag{1}$$

where n = electrons transferred, A = surface area of the working electrode (cm^2), F = Faraday constant (96,485 C mol^{-1}), and j = flux of the target analyte toward the electrode (expressed in $cm^{-2}s^{-1}$). The flux term is crucial to the redox reaction and a species must reach the electrode surface from the bulk solution (mass transfer).[32] **Figure 2** depicts these processes in the modification and respective electrochemical response.

In various electrochemical systems, the rate of electron transfer surpasses that of mass transport and, leads to the turnover of any species reaching the electrode, and hence mass transport becomes the constraining factor (mass transport limited). The primary modes of mass transport encompass diffusion (species movement along a concentration gradient), migration (movement of charged species influenced by an electric field), and convection (species displacement driven by mechanical forces or temperature gradients). Consequently, the Nernst–Planck equation delineates the overall flux, portraying 1D mass transport to an electrode.[32] **Figure 3** represents the schematic illustration of heterogeneous electron transfer.

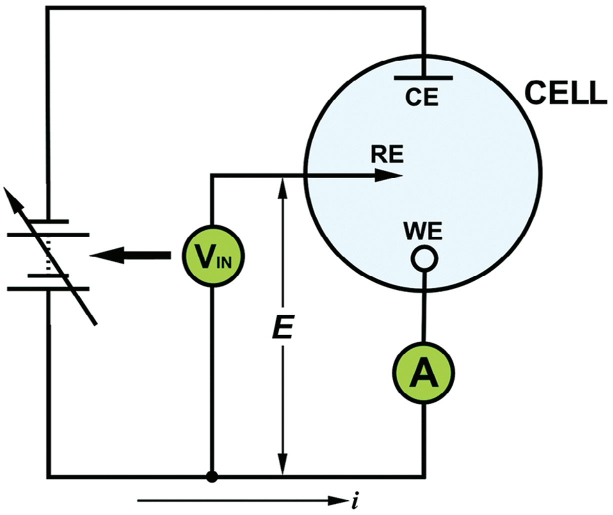

Figure 1. Standard three-electrode configuration of the voltammetric cell.

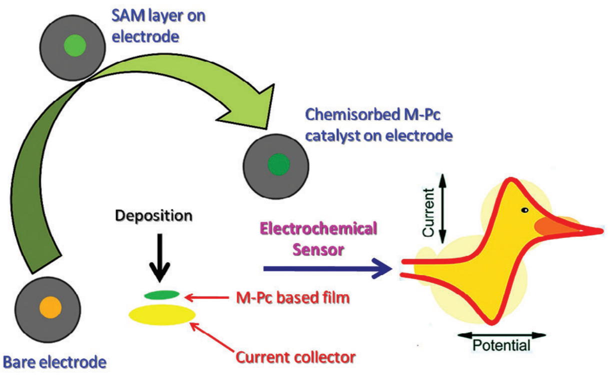

Figure 2. General schematic representation of the voltammetric sensor with MPc.

1.2. Advantages of ECS Over Other Analytic Techniques

Electrochemical sensors stand out in the domain of analytical sensing due to their remarkable attributes, which find applications in diverse fields. One of the essential advantages is their exceptional sensitivity and selectivity. These sensors excel in detecting even trace and minute concentrations of analytes. They can be engineered to specifically target particular molecules or ions, providing a crucial capability in precise analytical measurements.[33,34] The low detection limits inherent to electrochemical sensors enable the identification of trace amounts of substances, making them particularly valuable in scenarios where detecting subtle changes is essential. The miniaturization

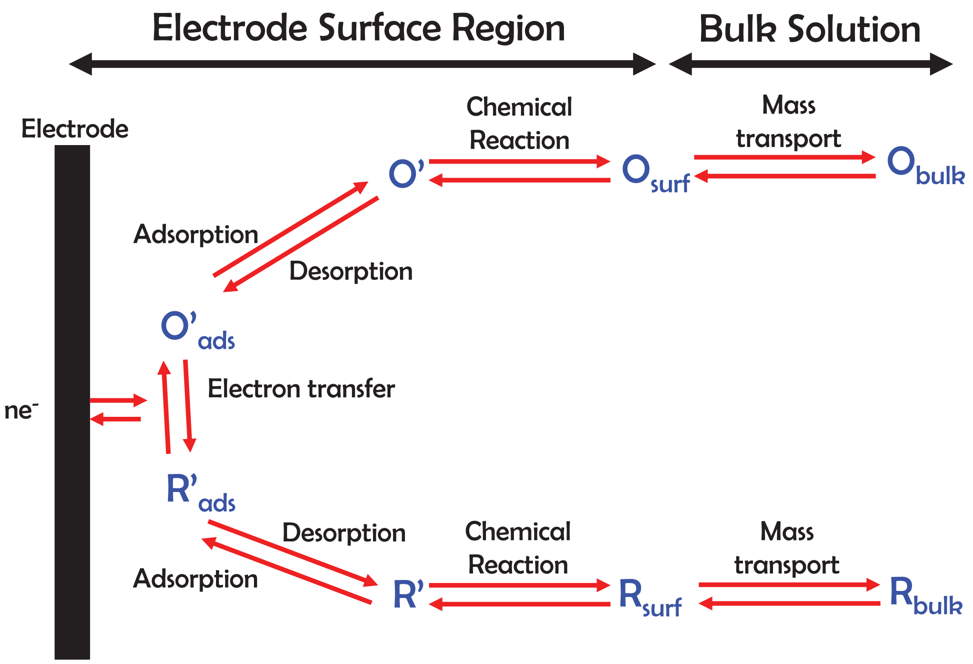

Figure 3. Schematic illustration of heterogeneous electron transfer, where all processes within the surface region are encompassed under electron transfer.

and portability of electrochemical sensors contribute significantly to their practicality. Their compact form allows for seamless integration into portable devices, enabling on-site analysis and real-time monitoring which are invaluable features for applications ranging from environmental monitoring to medical diagnostics. Moreover, the cost-effectiveness of both fabrication and operation enhances their accessibility across various industries and research domains. Beyond these practical advantages, electrochemical sensors exhibit versatility in their adaptability to different applications. Their integration into electronic systems facilitates the creation of sensor arrays and multi-sensor platforms, expanding their utility in complex analytical scenarios. Additionally, the low power consumption of sensors aligns with the demand for energy-efficient technologies. Long-term stability is a hallmark of many electrochemical sensors, ensuring sustained performance over extended periods. This attribute, coupled with the ease of functionalization, enables the customization of sensor surfaces to enhance selectivity, stability, and sensitivity for specific analytes.[36,37] The compatibility of electrochemical sensors toward complex sample matrices, including biological fluids, underscores their applicability in challenging real-world environments. The electrochemical sensors represent a sophisticated and multifaceted analytical toolset. Their sensitivity, selectivity, portability, versatility, and cost-effectiveness position them as vital components in the contemporary landscape of analytical chemistry and sensor technology.[33,38–42] As technology continues to evolve, the development and refinement of electrochemical sensors hold great promise for advancement in various scientific, industrial, and healthcare applications. **Table 1** provides a brief discussion on the comparison of analytical sensors vs. electrochemical sensors along with their advantages and disadvantages.

1.3. The Tale of Phthalocyanine Materials

In 1907, Braun and Tchernic on investigating the properties of o-cyanobenzamide derived from the reaction of phthalimide and acetic anhydride, stumbled upon a fortuitous discovery at the South Metropolitan Gas Company in London. After cooling the heated o-cyanobenzamide, it was dissolved in alcohol and filtered to notice the presence of a faint blue substance. This unexpected finding led to the accidental discovery of phthalocyanines. The "phthalocyanine" originates from Greek, combining "naphtha" (referring to oil) and "cyanine" (indicating dark blue). Ancient texts described naphtha as a clear, combustible rock oil obtained from Babylonian asphalt, while "cyanine" was a term found in the written works of various ancient Greek authors, including Homer. Phthalocyanines (Pcs) represent a novel class of organic compounds structurally akin to porphyrins and are categorized as chromogens or coloring agents. The discovery of Pc and its derivatives marked a significant breakthrough in the textiles and dyes industries.[43,44]

Pc is a large, aromatic, macrocyclic organic compound possessing four isoindole units linked by four nitrogen atoms. Analogous to porphyrins, Pcs feature four nitrogen atoms at the meso position of aromatic rings attached to the pyrrole rings in a coplanar configuration. Instead of methane corner links, substitution with aza groups endows the molecule with a 2-D geometry and an 18 π-electron ring system, facilitating extensive electron delocalization. Consequently, Pcs exhibit enhanced properties, making them versatile across interdisciplinary fields such as textiles, medicine, dyes, pigments, electronics, and electrochemistry. Derivatives of Pcs are synthesized by replacing carbon atoms of the macrocycles with nitrogen atoms or by substituting peripheral or axial hydrogen atoms with various functional

Table 1. Analytical sensors versus electrochemical sensors: comparison of advantages and disadvantages. Both analytical and electrochemical sensors are valuable tools for measuring and analyzing various substances based on their particular property. However, they have distinct characteristics, advantages, and disadvantages, making them suitable for different applications.

Analytical Sensors	
Advantages	Disadvantages
1) Wide range of measurement capabilities: Can measure diverse parameters like temperature, pressure, flow, pH, chemical composition, and biological markers	1) Complexity: It can be intricate and requires specialized knowledge for operation and maintenance.
1) High sensitivity and accuracy: Can detect minute changes in measured values	1) Cost: Initially high and in addition ongoing equipment, calibration, and maintenance costs.
1) Variety of technologies: Options include optical, mass spectrometric, chromatographic, and biosensors, each with specific strengths.	1) Size and portability: May be bulky and not suitable for field applications
1) Data analysis and interpretation:Often integrated with software for real-time analysis and interpretation of data.	
Electrochemical Sensors	
Advantages	Disadvantages
1) Simple and compact: Smaller and easier to use than many analytical sensors.	1) Limited measurement range: Primarily measure specific parameters like current, pH, conductivity, and ionic concentration
1) Low cost: Generally affordable compared to complex analytical sensors	1) Sensitivity: May be less sensitive than some analytical sensors, especially for low concentrations.
1) Portability: Well-suited for field measurements and remote monitoring	1) Interferences: Susceptible to interference from other substances in the sample
1) Direct conversion: Convert measured values directly into electrical signals	

groups like halogens, hydroxyl, amino, alkyl, thiol, alkoxy, and nitro groups, among others.

The intensely blue-green aromatic Pc molecule possesses an 18 π electron inner core and, the delocalization is further expanded by the four peripheral benzo units. Aza-nitrogens impart excellent stability to Pcs compared to porphyrins, particularly against heat and oxidation. Prof. Linstead and colleagues discovered the metal-free phthalocyanines, abbreviated as H_2Pc, in 1929. Metal derivatives of Pc, known as metal phthalocyanines (MPcs), serve as excellent organic semiconductors and exhibit high thermal stability. Various methods are employed for the synthesis of MPcs with high purity and structural integrity. Common methods of synthesis include the reaction of phthalonitrile, or ligand-substituted phthalonitrile with metal salts or metal oxides in the presence of 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU) catalyst and 1-pentanol solvent under high temperature and pressure conditions, known as the classical method.[19–22,35,45] The strategies can also be modified to tailor the MPcs' properties, such as controlling the metal center, substituent groups, and crystal structure, which affects their optical, electronic, and catalytic properties.

The MPcs have fascinating electron transfer abilities and hence, contribute to their noteworthy properties. The central cavity of Pc can accommodate various metal ions, including hydrogen (metal-free Pc/H_2Pc). In recent years, MPcs have found applications in molecular electronics and photonics due to their electron transfer capabilities, predominantly based on the 18-π electron conjugated ring system.

The core structure of Pcs consists of porphyrins which comprise a cyclic structure with four condensed pyrrols and play a crucial role in biological processes such as photosynthesis and oxygen transport. Porphyrin metal complexes, including chlorophyll and heme, are not only pivotal in biological processes but also utilized in materials science for applications like solar cells and artificial photosynthesis. Pcs and porphyrins possess planar tetradentate dianionic ligands and metal ions which bind through inwardly projecting nitrogen centers. The versatile and unique properties of these complexes hold promise in advancing various technological applications.[46–49]

1.4. Why Phthalocyanines in Electrochemical Applications?

MPcs are extensively utilized in electrochemical applications owing to their exceptional properties, which make them well-suited for a wide range of processes and devices. These compounds exhibit remarkable abilities that are crucial for efficient electron transport in electrochemical systems such as sensors, fuel cells, and batteries. Additionally, MPcs are known for their outstanding stability, particularly against heat and oxidation. Their longevity can be envisaged through structural modification that tailors their electrochemical properties, making them adaptable for diverse applications. Furthermore, Pcs readily form stable metal complexes, resulting in unique electrochemical behavior in catalysis, sensors, and other electroactive materials. Their high chemical stability in various environments ensures robust performance over extended periods, while some specific MPc complexes exhibit good electrical conductivity which makes them potential candidates in developing conductive materials. Moreover, the extraordinary sensitivity of MPcs to change their properties according to the surroundings is being harnessed in sensing applications, enabling the detection of specific analytes with high precision and selectivity. Due to their photoelectrochemical properties, these compounds are also used in photoelectrochemical devices like solar cells. Overall, MPcs have excellent electron transfer properties, stability, versatility, and specific characteristics like conductivity and catalytic activity, which make them indispensable in advancing various electrochemical technologies and applications.[50–54]

1.5. Modification Techniques

To enhance the electrochemical performance of MPcs and other electroactive materials in electrochemical sensors, various modification techniques such as functionalization, fabrication of nanocomposites, and surface modification are employed. These methodologies help to further enhance sensitivity, selectivity, stability, and other key boundary fundamentals for effective sensor performance. The functionalization refers to the tuning of MPcs by attaching different functional groups or substituents to the phthalocyanine ring. This method modifies MPcs' electronic and structural properties resulting in improved electrochemical performance. Functionalization with electron-donating groups such as alkyl or amine groups, augments the electron density on the MPc ring leading to increased conductivity and electron movement, which is crucial for sensors focused on the detection of electron-rich species like gases or biomolecules.

Substituents like fluorine, nitro, or cyano groups influence the sensitivity toward analytes by modifying the redox potential of MPcs and, empowering specific interactions with analytes. Integrating MPcs into nanomaterials such as carbon nanotubes (CNTs), graphene, metal nanoparticles, or metal oxides forms nanocomposites that exponentially upgrade their electrochemical properties. MPc composites with graphene or CNTs make a synergistic impact on the properties by combining the superior conductivity and surface area of carbon materials with the versatile properties of MPcs. This improves the electrochemical response, and sensitivity, with better LOD. Nanocomposites of MPcs with metal oxides such as TiO_2, ZnO, or MnO_2 further improve redox strength and provide extra active sites, enhancing the material's ability to detect small amounts of gases or pollutants. The presence of metal oxides also affects the sensor's durability and cycling stability.

Surface modification techniques such as electrode deposition, self-assembled monolayers (SAMs), doping with conductive polymers, and immobilization techniques involve altering the surface of MPcs and composites which improve their surface activity and interaction with target analytes and in turn, enhance the electrochemical performance.

2. Metal Phthalocyanine: A Prospective Catalyst Material for Electrochemical Sensors

MPcs have significant potential as electrochemical sensors because of their excellent stability, tunable electronic structure, and electrocatalytic properties. They serve in numerous applications, such as organic transformation, biological analysis, and chemical industries. Metalloporphyrin/ MPc complexes are suitable for electrochemical applications due to their tendency to promote redox processes. The electrical properties of MPcs may be altered by choosing suitable metal centers which results in enhanced selectivity and sensor properties. The characteristics to control the catalytic activity and properties are accomplished with numerous electrode materials and the differentiation of multiple phases is achieved, including screen-printed electrodes, carbon-based electrodes, and modified nanomaterial-based electrodes. Additionally, MPcs are highly active, flexible, and stable for electrochemical applications, particularly electrochemical sensors.[55–57] Their flexibility corresponds to their ability to incorporate into numerous sensor configurations. MPcs are highly useful in applications that require molecular organization accuracy, as they help in the selective recognition of specific analytes or their combinations. These metal–organic frameworks, consisting of a central metal atom and four embedding aromatic rings of nitrogen, are characterized by stable electronic structure, conductivity, and high electroactivity, making them a promising candidate for designing and development of electrochemical sensors. Because of their outstanding strength, flexibility, strong electrical properties, and electrocatalytic activity, MPcs are excellent materials for electrochemical sensors yielding remarkable activity and play a crucial role in building new electrochemically significant innovations.[58–61]

2.1. Structure

MPcs are fascinating molecules because of their macrocyclic structure with four nitrogens in the ring, and a core metal atom at the center of the Pc ring. This core metal ion coordinated to the ligand maintains a uniform and standardized structure and influences the electrical and synergist barriers and electroactive capacity of the MPc. Altering of the central metal atom in MPc generates variations in redox potential, electromagnetic arrangement, and coordination geometry. The extraordinary electrochemical properties of MPcs are imparted by the unique macrocyclic structure. **Figure 4** presents a general structure of the MPc, which contains all the elements like nitrogen, carbon, and metal atoms in a planar core. The ensuing planar structure influences the electrical properties via delocalization of π electrons throughout the ring. The nitrogen atoms in the middle of the ring coordinate with the metal atom. The feasibility of modifying the MPc structure for specified electrochemical investigation depends on the metal center, which affects the overall capability and reactivity of the MPc. The exceptional interaction and relationship between the core metal atom and the Pc structure facilitates the desired redox capabilities of MPcs, making them versatile materials suited for constructing sensors with broad electrochemical activity and modes. The variation in the electroactivity of MPcs is a direct consequence of the choice of a metal atom, as each metal exhibits different electrochemical properties. The coordinated metal atom in the MPc contributes to the overall performance and facilitates their potentiality in electrochemical sensors. MPcs exist in mainly two unique structural phases, such as α- and β-structures.[62,63] The β-structure possesses monoclinic cell parameters and a more stable phase which is thermally acquired from the α-structure. Metal-free phthalocyanine contains two hydrogen atoms at the central core of the molecule, as shown in **Figure 5**. To extend the flexibility of π-electrons, the two hydrogen atoms are replaced by either a lone metal atom or two

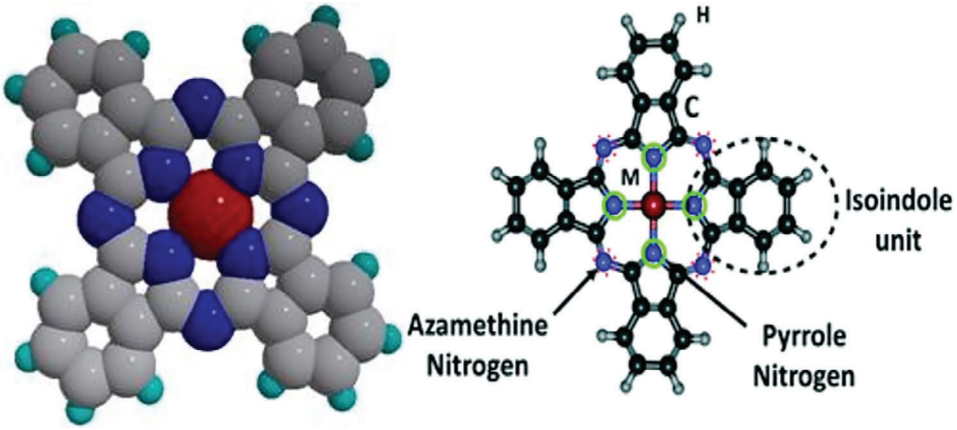

Figure 4. The general structure of metal phthalocyanines.

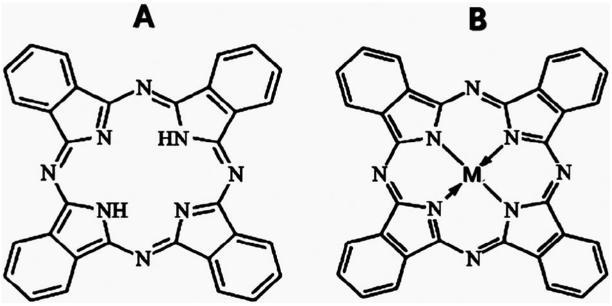

Figure 5. A) Metal-free phthalocyanine molecule and B) Metal phthalocyanine molecule.

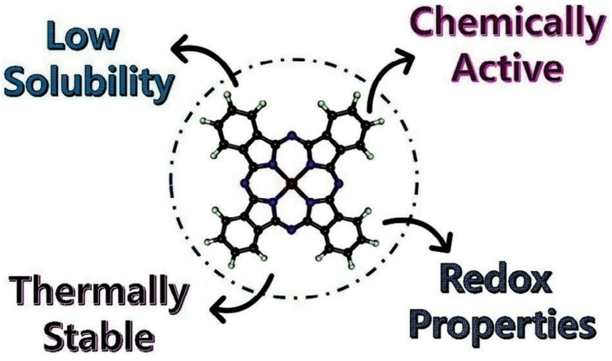

Figure 6. Schematic representation of general properties of metal phthalocyanines.

metal atoms based on the size. Metal-substituted and metal-free phthalocyanines are promising as dynamic layers for different applications.

2.2. Properties

Generally, MPc molecules exhibit high thermal and chemical stability. They are stable under a wide range of extreme environmental conditions, making them suitable for many applications in electrochemical and biological domains. **Figure 6** illustrates the general properties of MPcs, highlighting key characteristics like solubility, chemical stability, thermal stability, and redox properties. Due to their rigid and planar structure, MPcs exhibit low solubility in common organic solvents. They are highly soluble in sulfuric acid and polar aprotic solvents like dimethyl sulfoxide (DMSO), dimethylformamide (DMF), or chlorinated solvents like dichloromethane (DCM) due to their ability to integrate with the polar groups on the MPc molecule. Some Pcs with hydrophobic substituents are soluble in non-polar solvents such as toluene or hexane.[64–66] The limited solubility in aqueous solvents limits their solvent-based processes for major applications. MPcs show extensive redox behavior and operate as a catalysts in electrochemical sensors. Their redox behavior alters the electrocatalytic cycle by allowing electrons to exchange reversibly between distinct oxidation states. The energy required for the facilitation of electron movement plays a pivotal role in increasing sensor response and influencing the frequency of electron transport throughout the redox cycle. This energy is affected by various factors, including surface modification and electrode material. MPcs undergo redox reactions, either accepting or donating electrons during catalysis in the electrochemical reaction. Reactivity, selectivity, and response time of MPcs are fully controlled by conductivity and redox energy, which are necessary for the development of efficient and sensitive electrochemical sensors. Moreover, MPcs exhibit vital synergistic mechanisms in electrochemical cycles, such as hydrogen evolution reaction (HER) and the oxygen utilization reaction or oxygen reduction reaction (ORR). Their flexible structure allows them to catalyze numerous redox reactions, including ORR and HER, which makes them appropriate catalysts for an expanded range of electrochemical reactions and applications. Synergist processes in MPcs significantly influence their performance in electrochemical sensors with respect to redox nature and, electron movement energy, and in turn, the synergistic behavior is crucial for developing sensors with higher responsiveness, selectivity, and performance for various electrochemical recognition applications.[19–22]

MPc compounds possess a square planar coordination system with a central metal atom or ion surrounded by four nitrogen atoms in an aromatic ring, like porphyrins. The central metal atom can be transition metal ions like iron, cobalt, nickel, copper, and zinc, among others. The selection of the central metal atom influences the optical properties, structure, and reactivity

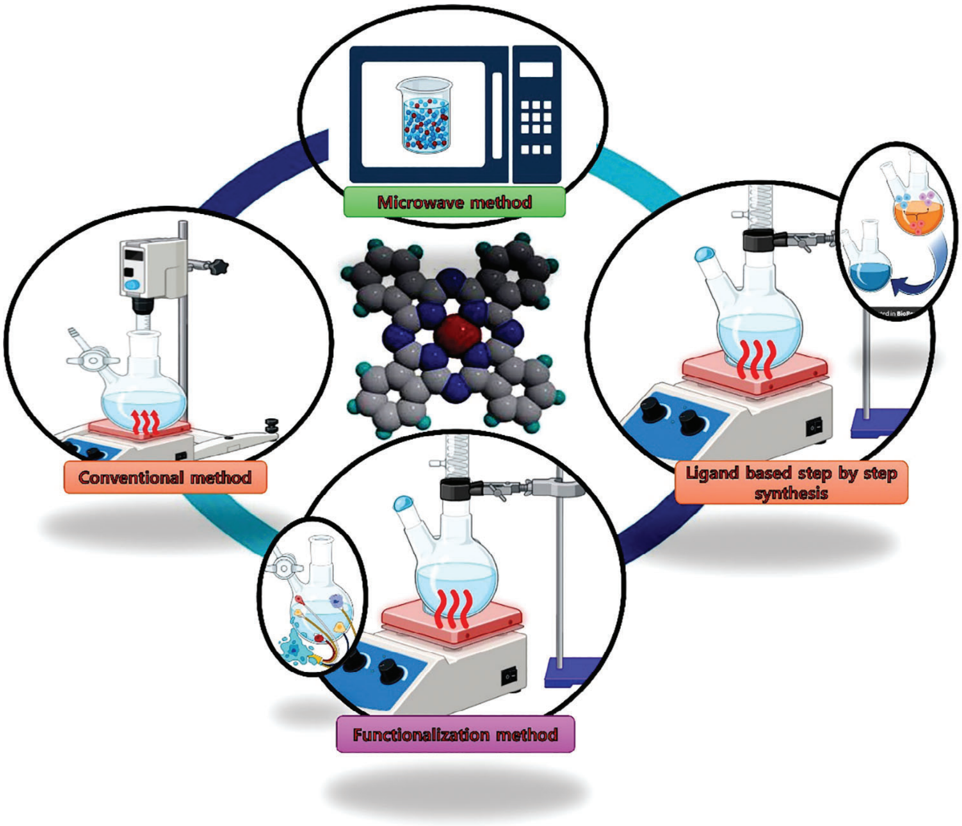

Figure 7. Schematic representation of different methods of synthesis of metal phthalocyanines.

of MPcs. In general, the ligands and the core metal alter the electronic characteristics of MPcs. The delocalized π electrons of the Pc ring expand the electronic conductivity, which significantly influences the electrochemical applications of MPcs. Their redox behavior is essential for their electrical qualities, and their synergist activity is attributed to redox activities generated by the association between the metal local area and the electronic π structure in the Pc ring. The excellent electrical characteristics of MPcs are due to the combination of the core metal atom and delocalized π electrons. The electrochemical properties of different metals, such as copper, iron, and cobalt, exhibit varying redox capabilities.[67]

The stable macrocyclic structure assures MPcs' long-term durability in electrochemical applications. Additionally, MPcs demonstrate adaptability in many standard circumstances and are impervious to gases, pH, and temperature variations, and remain stable during synergist operations.

2.3. Synthesis

MPcs are synthesized using various methodologies depending on the precursor and conditions employed during the reaction. Some of the common methods are the microwave method, the solvent-free synthesis method, the functionalization process, the chemical vapor deposition (CVD) method, and the step-by-step ligand-based synthesis or template synthesis. The synthesis process involves the selection of appropriate precursors (phthalonitrile, phthalimide, phthalic acid, etc.) and metal salts, based on the requirement of flexibility, functionalization, reactivity, electrical characteristics, and sensitivity. **Figure 7** depicts schematics for the MPc synthesis. The conventional process for the synthesis of MPcs includes heating the mixture of metal source, precursor molecule, and phthalonitrile supplements.[35,45] After reflux, the resultant MPc is typically isolated by filtration and purification. Another method via the conventional approach is the metalation of porphyrins. In this method, porphyrins can be metalated to prepare phthalocyanines by reacting the porphyrin with a suitable metal salt or metal atom in appropriate conditions. The microwave method is an efficient and quick technique for preparing MPcs. The application of microwave accelerates reaction kinetics, reducing the overall reaction time and providing rapid and uniform heat transfer for the reaction mixture. The product is isolated and purified, often with a higher yield than conventional synthetic methods.[68–71]

The ligand-based step-by-step synthesis, or template synthesis, involves a series of steps to yield the final Pc product. This approach necessarily utilizes a template molecule to direct the formation of MPc complex. The template molecule guides the assembly of the Pc units around the metal atom, leading to the formation of the desired complex. This synthesis is a more controlled and modular approach. It entails the addition of more and more ligands one after the other while maintaining precise control over the MPc structure and properties. The step-by-step

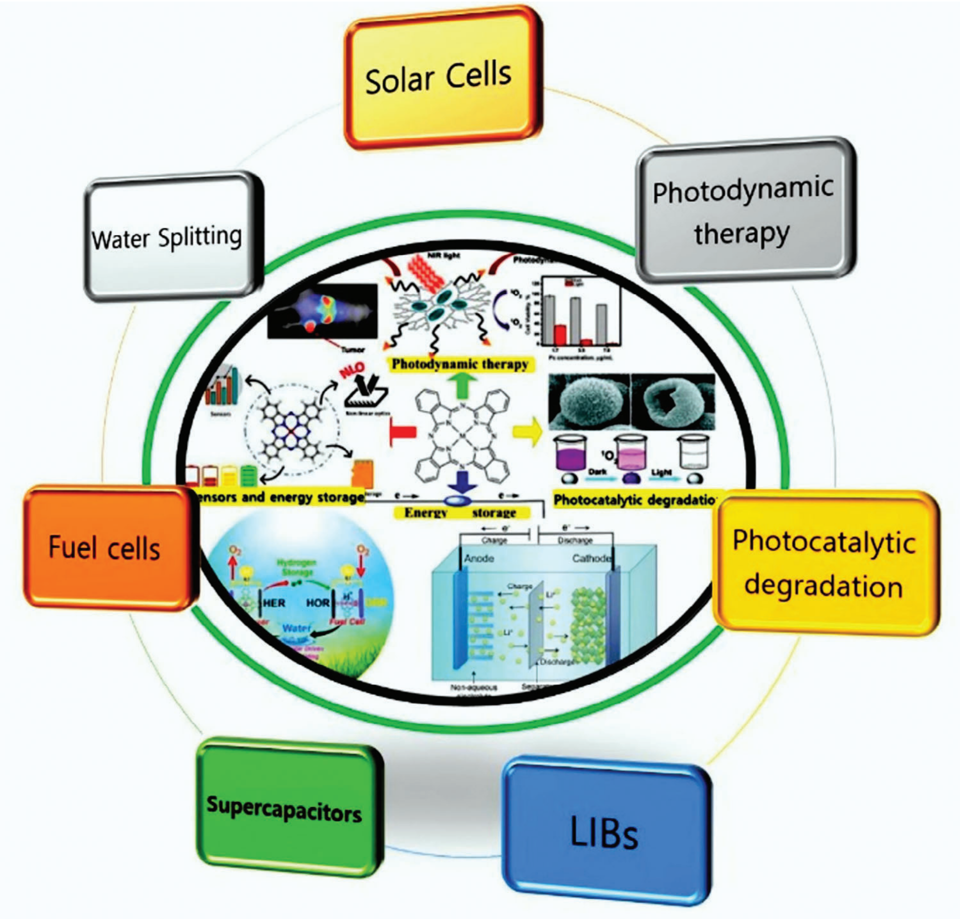

Figure 8. General applications of MPcs in different fields.

approach empowers the fine-tuning of the MPc structure, impacting properties like solvability, electronic characterization, and reactivity. The ligand-based synthesis also provides more control over the final design, permitting the chemist to tailor properties accurately. This technique is especially beneficial and has more advantages during the synthesis of specific structure with unique properties as well as electrochemically active metal frameworks or designs. In the condensation process, metal salt or metal oxide sources are used with mostly phthalonitrile derivatives. Condensation reactions are suitable for large-scale synthesis due to their versatility. The addition of more valuable groups or ligands to the existing Pc structure is part of the functionalization process. This methodology is employed during the combination or altering the structure or post-synthesis structural modifications. Adding functional groups to MPcs makes them more flexible by the improvement of properties like reactivity, electronic properties, and solubility.[68–71]

2.4. Applications

MPcs are a versatile class of electrocatalysts used in various scientific and modern sensor applications. **Figure** 8 highlights the general applications of MPcs across different fields and illustrates their versatility and importance in various technological and scientific endeavours. In solar cell technology, MPc serves as active materials or sensitizers for converting solar energy into electrical energy through the photovoltaic process. Moreover, in photodynamic therapy, MPcs produce reactive oxygen species (ROS) that induce cell death and lead to tumor regression. In the realm of electrochemistry, MPcs function as catalysts in water splitting and fuel cells and catalyze various electrochemical reactions. MPcs can act as anode or cathode active materials in the battery field and are capable of storing and releasing lithium ions during charge and discharge cycles and storing electrical energy through electrostatic double-layer capacitance or fast surface redox reactions. MPcs offer high specific capacitance, rapid charge-discharge rates, and long life-spans, making them desired and promising candidates for energy storage devices in portable electronic devices. MPcs also play a crucial role in electrochemical sensors due to their extraordinary sensitivity and selective properties, attributed to their macrocyclic structure with an active metal core. These sensors aid in the continuous monitoring of natural pollutants, including nitrite, nitrate, phosphate, ammonium, etc. In addition, the biocompatibility of MPcs' expands their utility in biological applications, where they play a crucial role in

Table 2. Comparison between MPcs and other electroactive materials.

Property	Metal Phthalocyanines (MPcs)	Metal Oxides	Carbon-based materials	Conducting polymers
Structure	Macrocyclic, planar structure with metal center	Crystalline or amorphous structure	sp^2 hybridized carbon atoms arranged in hexagonal patterns	Organic polymers with conjugated backbone
Catalytic activity	Excellent redox activity via metal centers.	Active for redox reactions, especially in oxygen reduction or pollutant degradation	Moderate; enhanced when functionalized with metal/organic groups	Moderate to high depending on the polymer; enhanced by doping
Thermal stability	High thermal stability	Very high thermal stability	Extremely high thermal stability	Limited thermal stability
Sensitivity	High sensitivity due to the coordination with metal centers and planar structure	High sensitivity in oxidation-reduction reactions	High sensitivity, especially when the surface area is large and functionalized	Moderate to high sensitivity, especially in flexible sensors
Selectivity	High selectivity for specific analytes, especially gases like NO_2, CO, and biomolecules like glucose	Moderate selectivity, often used in specific gas sensors	High selectivity when functionalized with specific groups	Moderate selectivity, enhanced by doping and functional groups
Detection limits	Low detection limits due to strong binding affinity with analytes	Low detection limits in specific redox reactions	Low detection limits, especially in gas sensors and biosensors	Moderate detection limits, improved by adding nanomaterials
Ease of functionalization	Easily functionalized through peripheral groups or metal center substitution	Limited functionalization possibilities	High potential for functionalization with oxygen-containing groups, nanoparticles	Easily modified with dopants, polymers, or nanoparticles
Cost	Moderate (depends on the metal used; transition metals are affordable)	Low-cost, widely available	High cost (especially for high-quality CNTs and graphene)	Low cost, but synthesis and doping can increase expenses
Environmental impact	Generally low; some metal centers (e.g., Co, Ni) may be toxic	Potential toxicity depending on the metal used	Low, but manufacturing can be energy-intensive	Low; disposal of dopants and polymer degradation may pose issues
Advantages	High sensitivity, selectivity, and electrochemical stability; customizable with various metals and ligands	High redox activity and stability in extreme environments	High surface area, fast electron transfer, and excellent stability	Flexible, low-cost, and versatile; high conductivity when doped
Disadvantages	Moderate conductivity without composites; can be expensive with certain metals (e.g., Pt, Au)	Low conductivity and selectivity in some cases	Expensive, challenging to process and functionalize	May degrade over time; moderate sensitivity compared to other materials

determining biomolecules like dopamine in natural fluids and provide augmented information on neurochemical processes relevant to biomedical assessments.[72–75]

In the present scenario, MPc-based sensors are utilized for real-time testing and monitoring of hazardous substances and guaranteeing worker safety and health. Moreover, MPcs have been used as catalysts for detecting various chemical processes and facilitating the integration of materials and mixtures with anticipation of novel electrical, optical, and reactive properties in materials research for broadening their applications. Additionally, MPcs serve as catalysts for various chemical processes and enhance the efficiency of photovoltaic devices, enabling the development of electrochemical cells that are both sustainable and biocompatible for energy applications.[76] **Table 2** compares MPcs with various other electroactive materials in literature, such as metal oxides, carbon materials, and conducting polymers.

The unique physicochemical properties of MPcs, including their planar structure, extended π-conjugation, the capacity to organize with different metal ions, redox activity, stability, and specificity, make them exceptionally significant in electrochemical applications. These properties collectively contribute to upgraded electron transfer properties, superior redox performance, and high stability, making MPcs excellent candidates for use in electrochemical sensors, energy storage systems, and catalysis.[73]

3. MPcs for Detection of Bio-Molecules, Environmental Pollutants, and Pharmaceutical Molecules

MPcs have attracted much interest in electrochemical sensors, especially because of their selectivity, sensitivity, and stability. As a result of their unique features and electrocatalytic properties, they show great promise in fabricating simple and sensitive sensors for a wide range of analytes. **Figure 9** illustrates the process of electrode modification and the localization and detection of various analytes of environmental and biological interest.

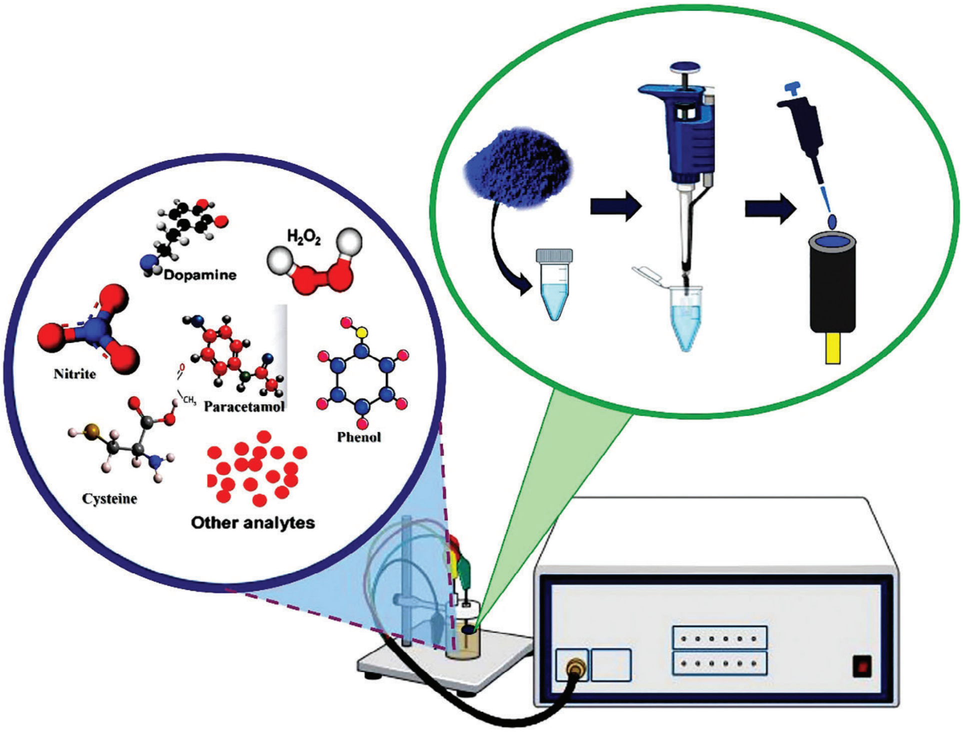

Figure 9. Schematic representation of the modification of an electrode as well as the location and detection of molecules of pharmaceutical and biomolecular interest.

The schematics present a visual guide to the experimental procedure involved in adjusting the instruments and electrodes, localizing target molecules, and in turn detection of desired molecules.

3.1. Dopamine

MPc-based sensors play a crucial role in distinguishing neurochemicals due to their versatility. Their electrocatalytic properties and unique behavior enable them to perceive the neurotransmitter dopamine with excellent selectivity, distinguishing them from other species that could cause interference. Dopamine is essential for frontal cortex abilities and is associated with neurological conditions like schizophrenia and Parkinson's disorder. Detailed and precise dopamine recognition is crucial in understanding neurochemical circuits and diagnosing related disorders. MPc-based dopamine sensors are beneficial for neurochemical detection due to their biocompatibility and ability to recognize dopamine species in trace levels as they undergo facile interaction with MPcs during redox processes.

It is essential to develop a sensitive and selective sensor with superior response for clinical diagnostics, particularly for the early detection of dopamine-related disorders. The goals of research in this field include enhancing sensor execution, analyzing implantable and miniaturization of sensor arrangements, and expanding continuous real-time measurements. **Table** 3 provides a comprehensive summary of the performance of MPcs in sensing and detecting dopamine. It highlights various key parameters and characteristics associated with the sensing capacity of MPcs, including electrode materials, methods, wide linearity, Low LOD, sensitivity, and stability.

Our group has designed a cobalt (II) tetra [β-N-(4-nitrophenyl) benzamide] phthalocyanine (CoTNBAPc) complex, which was then reduced to amine phthalocyanine (CoTABAPc).[77] The benzamide aminephthalocyanine derivative showed a redox peak with a small shoulder-like peak for amine oxidation. The amine of the phthalocyanine initiates oxidative polymerization on cycling in DMSO and forms a polymeric film on the electrode surface. The polymeric film was used for the voltammetric and amperometric detection of dopamine (DA), as shown in **Figure** 10. The voltammetric method showed a linear response in the range of 100–4000 nmol L^{-1}, while the amperometric method showed a linear dynamic range of 100–1000 nM with a correlation coefficient (R^2) of 0.999, LOD of 20 nmol L^{-1}, and sensitivity was 0.024 μA nmol L^{-1} for DA. The developed sensor was also employed for the amperometric detection of dopamine in the real sample. Other co-existing species didn't show interfering peaks during oxidation sensing of dopamine.

Diab et al. developed an electrochemical dopamine-detecting surface using graphene sheets and cobalt tetrasulfonated phthalocyanine on a polished glassy carbon electrode (GCE) (CoTSPc/Gr-GC).[78] DPV was used to detect dopamine, and the electrode was found to be effective in detecting dopamine in high concentrations of ascorbic acid (AA) and uric acid (UA), with a LOD of 0.87 nM over a unique linear range of 20–220 nM. Mounesh et al. successfully combined cobalt (II) tetracarboxylic acid phthalocyanine (CoTCAPc) through amide linkage to form tetra8[(E)(4methoxybenzylidene)amino] naphthalene 1-amine cobalt (II) phthalocyanine (CoTMBANAPc), which revealed

Table 3. Summary of the performance of metal phthalocyanine electrodes in dopamine sensing.

Electrode materials	Method	Linearity [μм]	LOD [μм]	Sensitivity [μA μм$^{-1}$ cm^{-2}]	Reference
Poly(CoTABAPc)	CV	0.1–4	0.03	16	[77]
	Amperometry	0.1–1	0.02	24	
CoTSPc/Gr	DPV	0.02–0.22	0.0087	–	[78]
CoTMBANAPc/MWCNT	Amperometry	7.5–67.5	6.6	0.14	[79]
GCE/MnPc	DPV	1.13–10.98	0.0146	6.05	[80]
GCE/ZnPc	DPV	0.021–7.441	0.0105	9.54	
ZnPc-P8BT-Pdots	Photoelectrochemical sensors	0.0025–17.5	0.00169	–	[81]
GCE/CNP-FeTCAPc	CV	0.10–1.0	0.02	0.042	[82]
GCE/ CNP-polyFeTBImPc	CV	0.10–1.00	0.02	0.067	
CoTGPc	DPV	2–12	1.2	2.91	[83]
Au-PEA-CoTCPhOPc	CV	5–10	1.32	0.49	[84]
CoPc/GQDs	DPV	2.91–33.38	0.021	2.78	[85]
ITO/(PEI/Na+MMT/PEI/NiTsPc)	DPV	5–150	1	–	[86]
AgNPs/CuMAPA/GCE	DPV	0.01–10	0.0007	14.43	[87]
GCE/rGO–Zn(II)TPEBiPc	DPV	0.05–0.8	0.0016	24.86	[88]
GCE/PANI/TA-CoPc hybrid	CV	20–200	0.064	1.21	[89]
GCE/poly-3N–CoPc	DPV	3.83–19	3.76	3.12	[90]
GCE/poly-3N–CuPc	DPV	3.71–19	2.6	2.53	
SiO2/C/CuPc	Amperometry	10–140	0.6	0.63	[91]
CoPc-modified carbon paste electrode (CoPc-CPE)	Electrochemiluminescence	0.5–50	0.0088	–	[92]
N-G/NiTsPc/GCE	CV	0.1–200	0.1	0.93	[93]

excellent solubility in aprotic solvents.[79] The modification of the electrode and sensing is shown in **Figure 11**. The modified electrode was used to simultaneously detect AA and DA using CV, DPV, and amperometric techniques. The modified GC electrode was highly stable, reproducible, and sensitive for the micromolar estimation of AA and DA.

Demir et al. synthesized tetra-substituted MPcs with 4-methoxyphenylthiazole-2-thio-units and characterized them using essential techniques such as NMR, FT-IR, and UV–vis spectroscopy.[80] Redox-dynamic metal centers and electropolymerizable substituents were introduced to increase redox properties and electrochemical polymerization capacity. These MPcs were electropolymerized on polished GCE and used as an electrochemical sensor to detect AA, DA, and UA using the DPV method which displayed highly selective and sensitive detection and identification of AA, DA, and UA. Peng et al. developed a method to create photoelectrochemical (PEC) sensors using phthalocyanine polymer dots. The zinc phthalocyanine was dipped into a poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzothiadia-zol-4,8-diyl)] (P8BT) and characterized using various techniques.[81] Repeated immersion of indium tin oxide (ITO) electrode in the solution produced the resulting ultrasensitive PEC sensor for DA sensing. Here, the authors strategically orchestrated the phthalocyanine polymer dabs (Pdots), with zinc phthalocyanine

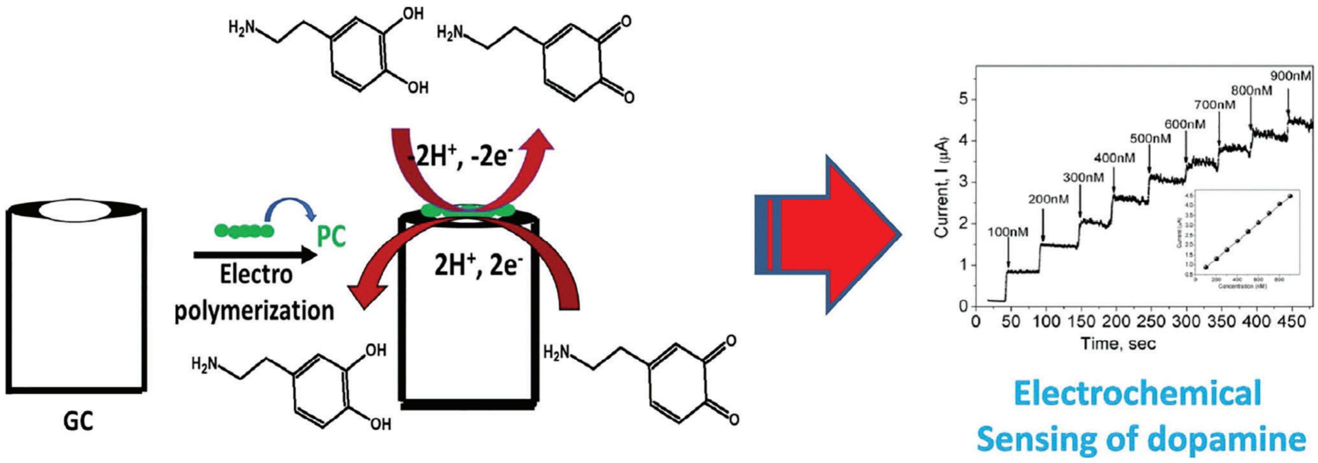

Figure 10. Schematic representation of dopamine sensing at poly-CoTABAPc. Reproduced with permission.[77] Copyright 2019, Elsevier.

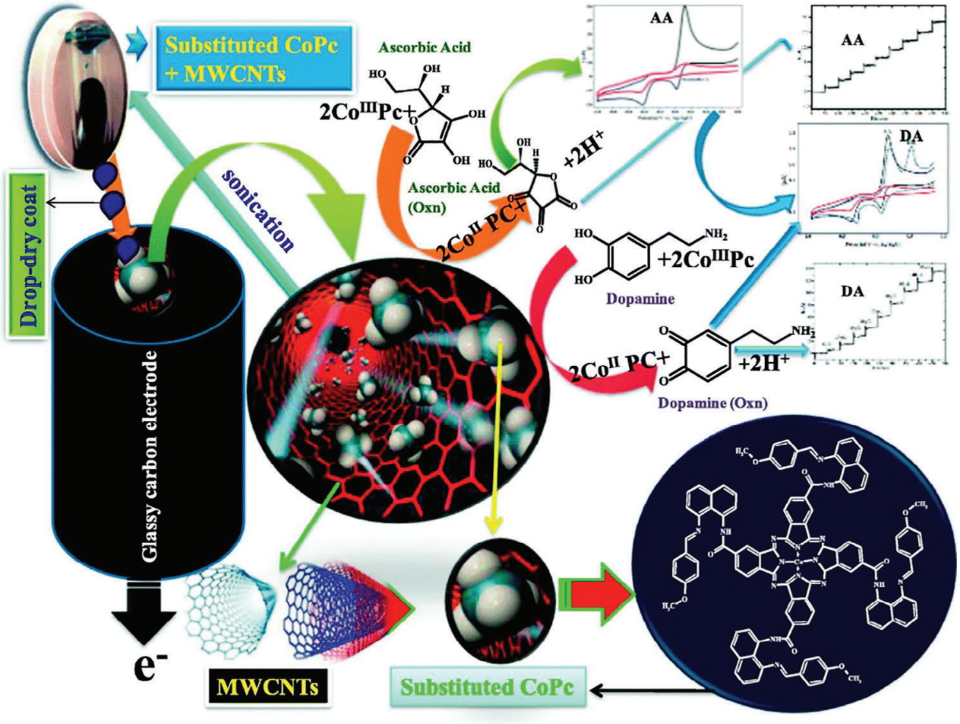

Figure 11. Schematic representation of dopamine sensing at CoTMBANAPc. Reproduced with permission.[79] Copyright 2019, Elsevier.

(ZnPc) doping into poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzothiadia-zol-4,8-diyl)] (P8BT). The photocurrent intensity of the ZnPc-P8BT-Pdots/ITO sensor increased as the concentration of DA increased under blue light irradiation. Under optimal conditions, the PEC sensor could accurately locate DA in the range of 2.5 nM–125 μM with a LOD of 1.69 nM. The sensor also demonstrated high performance, responsiveness, quick response, and positive stability, indicating its potential as PEC sensor for pharmaceutical research and application. Semiconducting polymers with ZnPc-doped structures showed run-of-the-mill photocurrent decrease compared with the virgin polymers. As the photocurrent degraded, energy was transferred from the polymer to ZnPc. Additionally, the ZnPc-P8BT-Pdots/ITO sensor showed unrivaled PEC detection, high response, quick reaction, and positive response for DA.

Our group synthesized iron tetrabenzimidazole phthalocyanine (FeTBImPc) and iron tetracarboxylic acid phthalocyanine (FeTCAPc) and mixed them separately with CNP to fabricate GCE/CNP-FeTCAPc and GCE/CNP-polyFeTBImPc electrodes[82] and the schematic representation of the modification of electrode and sensing mechanism is illustrated in **Figure 12**. The composite was immobilized on the GCE using drop-casting or electropolymerization. The modified GCE/CNP-FeTCAPc electrode demonstrated superior electrocatalytic activity for dopamine oxidation, with linearity of 100–1000 nM and LOD of 22 nM. The GCE/CNP-polyFeTBImPc sensor displayed a dynamic range of 100–1000 nM with an LOD of 20 nM and sensitivity of 67.2039 mA nM^{-1} cm^{-2}. This electrode showed high stability and selectivity for dopamine recognition, and its practicality was explored through real sample investigation.

3.2. Cysteine

Cysteine is a non-essential amino acid known for producing proteins with other metabolic capabilities. It is tracked down in beta-keratin, nails, skin, and hair. Collagen is made by using cysteine. The cysteine sensors provide sensitive and explicit detection, which is essential for knowing metabolic cycles and perceiving related disorders. The remarkable electrocatalytic capacity of MPcs makes it possible to accurately evaluate cysteine in complex natural structures. MPcs are used in biomedical assessment to follow cysteine levels, which helps to understand issues associated with cysteine assimilation and offers information about cell abilities.

The unprecedented response and sensitivity of MPc-based sensors allow the identification of trace and lower amounts of cysteine in natural and biological systems. The unique electrocatalytic property of MPcs helps in the precise and trustworthy disclosure of cysteine in complex natural structures by not responding to other intruding species from interfering. **Table 4** provides a comprehensive summary of the performance parameters of MPcs in the sensing of cysteine related to electrode materials, methods, linear range, LOD, and sensitivity.

Our group has developed cobalt (II) tetra[4-(2-(E)- [(4-bromophenyl) imino]methylphenoxy)] phthalocyanine (CoTBrImPc) complex, which was analyzed using various spectroanalytical techniques such as IR, UV–vis, NMR, mass, powder X-ray diffraction, and thermogravimetric methods.[94] The complex was electrochemically active and used for the recognition of L-cysteine. The CoTBrImPc electrode was found to be a promising electrocatalyst for the oxidation of L-cysteine, with a

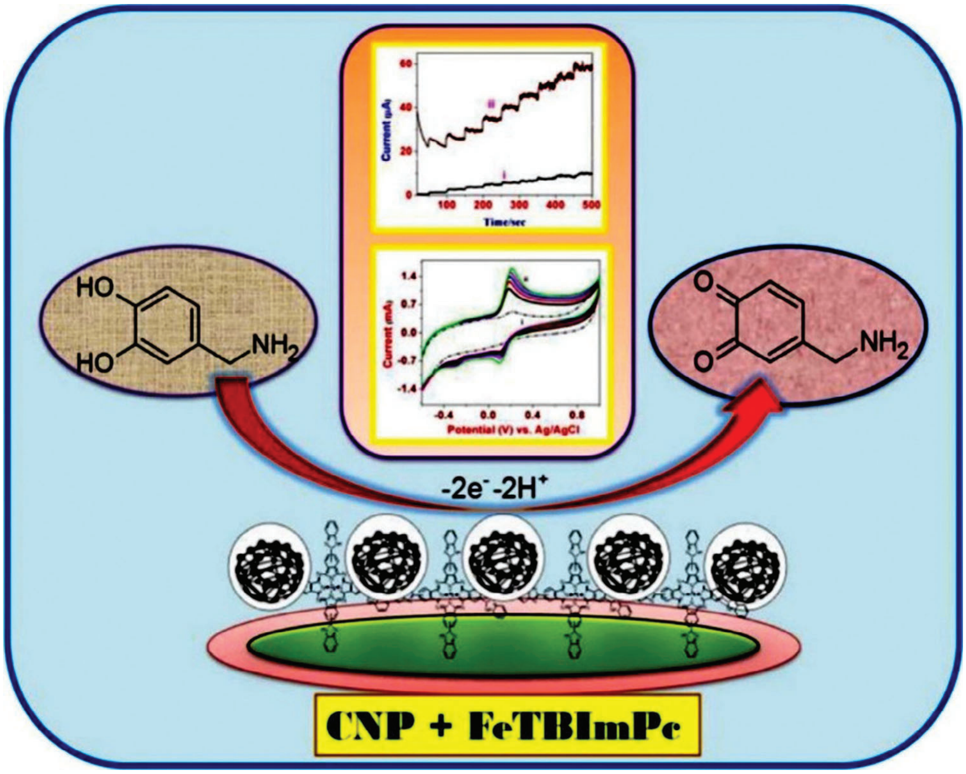

Figure 12. Schematic representation of GCE/CNP-polyFeTBImPc for dopamine sensing. Reproduced with permission.[82] Copyright 2019, Elsevier.

shift in the overpotential toward more negative potential with an enhancement in the peak current compared to the virgin GCE. The voltammetric sensor showed its applicability in lower concentration ranges. The amperometric sensor ensured LOD and LOQ values of 4 and 12 nM, respectively, with a sensitivity value of 10.81 μA nM^{-1} cm^{-2} for L-cysteine. The preparation of the modified electrode and sensing mechanism is demonstrated in **Figure 13**.

Shahrokhian et al. developed a cysteine-specific modified electrode using lead phthalocyanine (PbPc) as an ionophore.[95] The electrode was integrated into a plasticized polyvinyl chloride layer and coated on the outer layer of a graphite electrode. The electrode showed high selectivity for the detection of cysteine compared to the inorganic cations, salicylate, and amino acids. The sensor showed a wide range of cysteine detection between 1×10^{-6} and 5×10^{-2} M. The electrode had a quick response

Table 4. Summary of metal phthalocyanines performance in cysteine sensing.

Electrode materials	Method	Linearity [μM]	LOD [μM]	Sensitivity [μA μM^{-1} cm^{-2}]	Reference
GCE/CoTBrImPc	CV	0.01–0.100	0.003	0.00299	[94]
	Amperometry	0.01–0.08	0.003	0.01081	
CoPc-SPEs	CV	5–200	3.8	0.78	[96]
Au NPs–FePc	DPV	50–1000	0.27	57.2	[97]
FeTSPc/MWCNTs	Amperometry	10–200	1	0.176	[98]
NiTsPc	CV	1000–7000	–	233	[99]
(OMo(V)(OH)Pc)	CV	2000–20 000	0.1	–	[100]
RGO-pTACoPc	CV	0.05–2.0	0.018	10.19	[101]
FePc-based SAM	CV	4–100	2	–	[102]
CoTPC/poly-L-lysine	CA	0.50–216	0.15	0.157	[103]
CoOBTPc SAM	CV	0.5–10	0.31	–	[104]
CoOHETPc	CV	–	0.52	–	[105]
Electropolymerized (CoTAPc)	CV	–	120	–	[106]
CoPc	CV	1–12	0.2	8.89	[107]

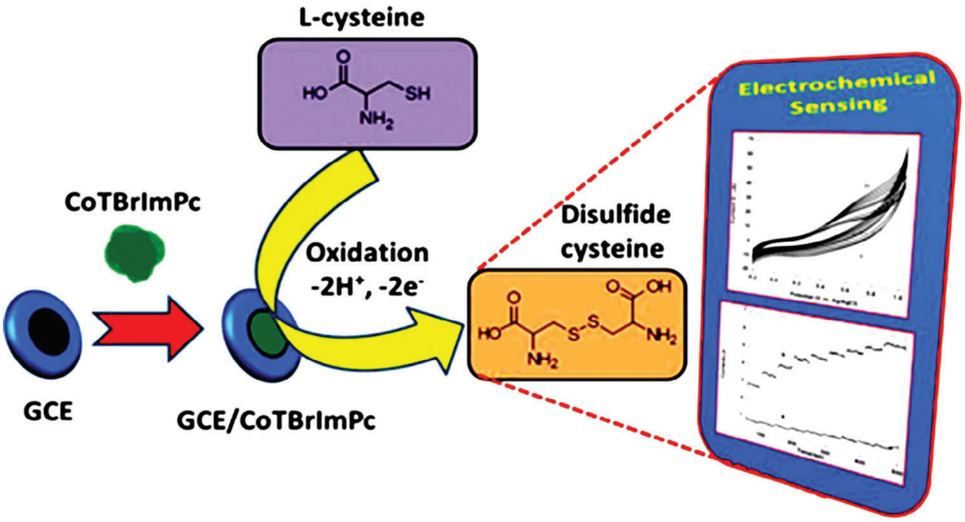

Figure 13. Schematic representation of cysteine sensing at CoTBrImPc. Reproduced with permission.[94] Copyright 2019, Elsevier.

and excellent long-term stability. The electrode was applied for cysteine sensing in a synthetic human serum sample which achieved excellent recovery results.

Dispensable Co(II)-phthalocyanine screen-printed graphite electrode (CoPc-SPE) sensor has been fabricated for the electroanalytical detection of L-cysteine.[96] Cyclic and squarewave voltammetric (SWV) techniques showed impressive electrocatalytic action toward the oxidation of L-cysteine at CoPc-SPEs under optimum neutral pH. The SWV displayed a linear range of 2.6–200 μM, with a low sensitivity of 0.78 μA μM^{-1} cm^{-2} for detecting L-cysteine. The reproducibility and repeatability of L-cysteine determination using CoPc-SPE presented RSD of 3% and 0.4%, respectively. The proposed L-cysteine electrochemical sensor is applied for the evaluation of L-cysteine in a complex embryo cell culture medium.

Abbas et al. have developed an electrochemical sensor for the precise quantification of cysteine using gold nanoparticle (AuNP)-iron (III) phthalocyanine (FePc)-modified graphite paste electrode.[97] The sensor characteristics were understood using SEM, TEM, CV (cyclic voltammetry), and EIS (electrochemical impedance spectroscopy). CV of cysteine at the AuNP-FePc-modified graphite paste electrode showed significant improvement in the electrochemical behavior compared to the unmodified and FePc-modified graphite paste electrode. The sensor, containing 0.055 wt% AuNPs, demonstrated excellent response in the analytical range of 50–1000 mM and a LOD of 0.27 mM. Devasenathipathy et al. have constructed an iron tetrasulfonated phthalocyanine (FeTsPc)-designed MWCNT composite modified electrode for L-cysteine sensing.[98] Surface morphological investigations revealed uniform coverage of the FeTsPc at the outer layer of MWCNT. MWCNT-FeTsPc composite decorated on GCE showed improved electrocatalytic oxidation of L-cysteine with two oxidation peaks related to FeTsPc-intervened electrocatalysis. The overpotential of the oxidation peak extraordinarily shifted to −0.1 and +0.22 V. The amperometric sensor of MWCNT-FeTsPc showed a wide linear range of 10 μM–0.2 mM and an exceptionally low LOD (1 μM). The functional practicality of the sensor was assessed for the determination of cysteine in human urine. The designed sensor showed excellent stability, repeatability, and reproducibility results.

The substituted nickel phthalocyanine (NiTsPc) chemically immobilized on silica gel-modified carbon paste showed a redox behavior with a midpoint potential of 0.44 V vs. saturated calomel electrode (SCE).[99] The NiTsPc-modified silica showed enhanced stability even in acidic media with an excellent ability to catalyze the electro-oxidation of cysteine at 0.5 V versus SCE. The oxomolybdenum(V) phthalocyanine (OMoOH)Pc) embedded into graphite powder was used to catalyze the oxidation of cysteine.[100] A significant decrease in the overpotential for cysteine oxidation was observed at 0.26 and 0.28 V versus Ag/AgC1 at (OMoOH)Pc and [OMo(OH)TSPc] separately, while 0.77 V versus Ag/AgCl was noticed at CoPc electrode. The anodic peak of cysteine showed linearity in the concentration range of 0.02–0.08 mol dm^{-3} and 0.008–0.02 mol dm^{-3} for [OMo(OH)TSPc]$^{4-}$ and OMoPc, respectively.

3.3. Nitrite

Nitrite is commonly found in the environment, as well as produced by various industrial processes. It can originate from natural sources, such as microbial activities in soil and water, as well as from anthropogenic sources like sewage, fertilizers, and industrial waste, posing critical risks to the environment and human health. Nitrite is highly toxic, causes hypotension, and limits oxygen transport and delivery in the body through the formation of methemoglobin. Hence for its detection, several analytical methods have been developed to detect and quantify nitrite in different grids, including water, soil, and biological samples ranging from conventional colorimetric examinations to advanced sensor innovations. Colorimetric examinations, such as the Griess response, offer simplicity and cost-effectiveness but may require high sensitivity and selectivity. Electrochemical sensors influence nitrite's redox properties for quantitative recognition, providing a fast and versatile solution for on-site analysis with minimal sample preparation.

Table 5. Summary of different metal phthalocyanine-based sensor performance for nitrite sensing.

Electrode material	Method	Linearity [μM]	LOD [μM]	Sensitivity [μA μM^{-1} cm^{-2}]	Reference
(CoTsPc/PDDA-Gr)n/GCE	CV	2–36	0.084	5.30	[108]
PEDOT/FePc/MWCNT/SPCF	CV	2.5–25	0.71	0.64	[109]
CoTM-QOPc/ CNP/GCE	CV	0.2–200	0.06	2.30	[110]
	DPV	0.2–225	0.06	1.03	
SiO2/C/MnPc	CV	0.79–15.74	0.02	17.3	[111]
FeMAPc/AuNPs/GCE	CV	1.9–2000	0.21	0.015	[112]
GCE/CoPc	CV	–	0.18	58.8	[113]
GCE/CuPc	CV	–	0.67	51.7	
GCE/MnPc	CV	–	0.2	32	
GCE/NiPc	CV	–	1.77	11.5	
Poly(TazoCoPc)/CNP/GCE	Amperometry	0.02–1	0.006	0.1372	[114]
Alternated FeT4MPyP/CoTSPc layers/GCE	Amperometry	0.2–8.6	0.04	0.37	[115]
Pt-1/a-FePc/GCE	Amperometry	0.5–30	0.1	1.2	[116]
Pt-2/a-FePc/GCE	Amperometry	–	0.06	1.4	
FePc(tBu)4/GCE	Amperometry	2–26	0.63	0.36	[117]
Au/FePc(tBu)4/GCE	Amperometry	20–120	0.35	0.46	
Pd/CoPc	DPV	0.2–50	0.1	0.01	[118]
PA-TaCoPc@ZnO	CV	–	0.00021	6.36	[119]
CoPc@SWCNTs	CV	–	1.01	3.16	[120]
Chit-TsCuPc/GCE	DPV	0.2–6.3	0.012	–	[121]
CoTMePhCAPc/MWCNT/ GCE	CV	50–750	10.5	0.00037	[122]
	DPV	50–750	10.5	0.000043	
	Amperometry	50–500	6	0.000033	

MPc-based composite electrochemical sensor systems standout from other electrocatalysts due to their ability to react and interact with nitrite. The unique electrochemical properties of MPcs facilitate the selective and sensitive response for nitrite monitoring in various samples. The ongoing studies on MPc-based nitrite sensors aim to improve sensor performance, overcome limitations in sensing, and investigate how MPc-based sensors can be connected to different coherent systems. **Table 5** provides a comprehensive summary of the performance of MPcs in the sensing and detection of nitrite. Table highlights various electrochemical parameters and characteristics associated with the sensing of nitrite including electrode materials, methods, linearity, LOD, sensitivity, and stability.

Cui et al. designed a novel composite film of graphene/cobalt phthalocyanine composite on GCE for sensing nitrite.[108] Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images provided the parity between the graphene/cobalt phthalocyanine in the film, and it was found that the composite film had extraordinary synergist activity toward the oxidation of the nitrite sample. This film not only displayed greater synergist catalysis but also long-term stability for more than 70 days, which can be credited to the dispersion of electroactive cobalt phthalocyanine on immobilized graphene. The sensor had a LOD of 0.084 μM at a signal-to-noise proportion of 3 (S/N = 3). Similarly, Lin et al. explored the oxidative electrochemistry of nitrite on poly(3,4-ethylenedioxythiophene)/iron phthalocyanine/multi-walled carbon nanotubes (PEDOT/FePc/MWCNT) modified screen-printed carbon electrode (SPCE).[109] The designed electrode showed increased anodic peak current and reduced anodic peak potential for PEDOT-charged SPCE. The heterogeneous electron transfer rate constant increased by 7.8 times on the addition of MWCNT. The SPCE of PEDOT/FePc/MWCNT fundamentally diminished the overpotential and improved the peak current density. The sensor had a lower detection limit than other electrodes and was applied for nitrite detection in various water samples.

Jilani et al. integrated cobalt (II) tetramethylquinoline oxy-bridged phthalocyanine (CoTMQOPc) and studied its properties utilizing different analytical techniques.[110] The schematic illustration of their work is presented in **Figure 14**. The GCE, coated with CoTMQOPc/ carbon nanoparticles (CNP) composite, served as a sensing element for nitrite detection. The composite film is carefully fabricated on the GCE through drop coating while ensuring uniform coverage and adhesion to the electrode surface. The pure CoTMQOPc modified electrode displayed a linear range of 0.3–120 μmol L^{-1} with a lower LOD for nitrite whereas the hybrid composite of CoTMQOPc/CNP/GCE demonstrated a linear range of 0.2-200 by CV, 0.2-225 by differential pulse voltammetry (DPV), 0.1-350 μmol L^{-1} by chronoamperometry (CA), a LOD of (0.06, 0.06, 0.033 μmol L^{-1} by CV, DPV and CA respectively), and sensitivity of (2.298, 1.031, 1.237 μA μM^{-1}.cm^{-2} by CV, DPV and CA respectively). The composite-modified electrode showed superior electrocatalytic behavior and high selectivity even in the presence of other interfering ions like carbonate, ascorbic acid, urea, phosphate, and glucose. The better voltammetric response observed is due to the integration of CoTMQOPc with CNP,

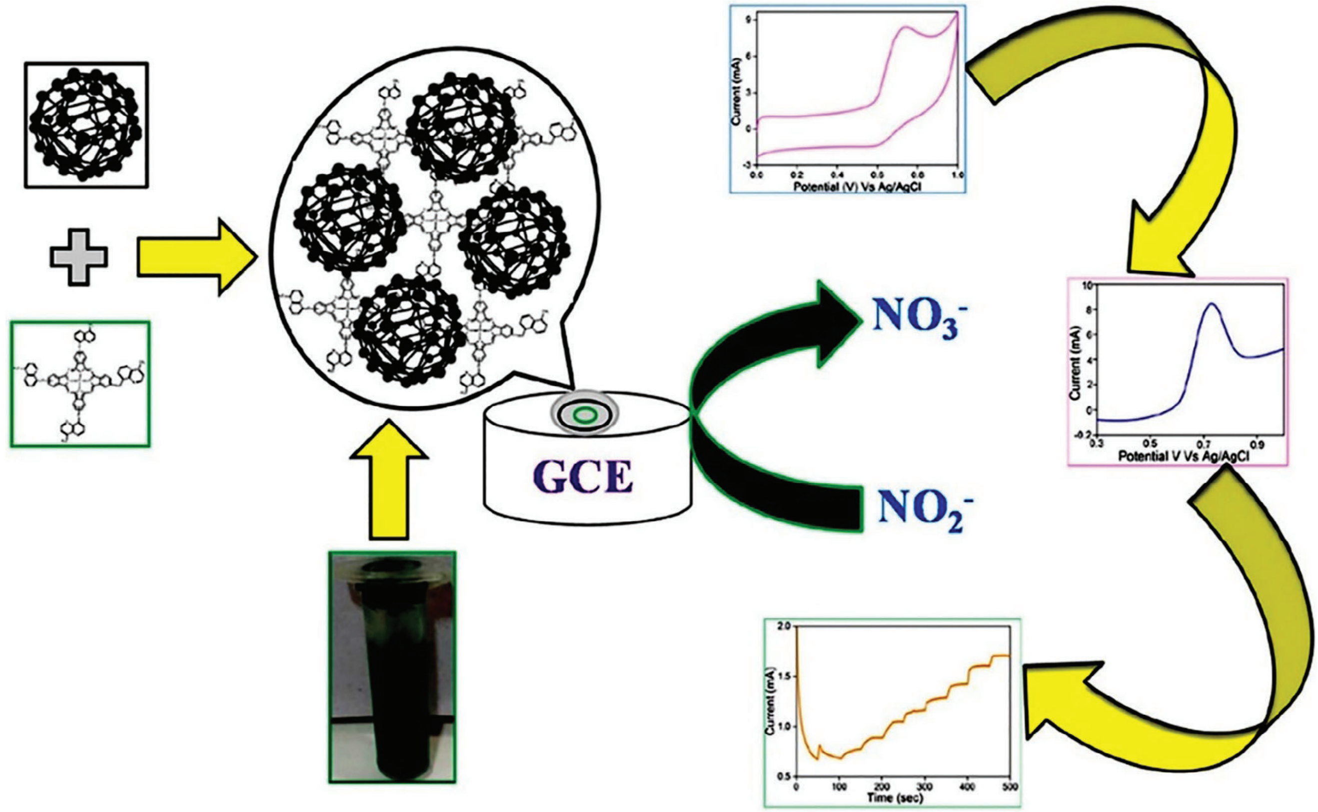

Figure 14. Schematic representation of the fabrication of CoTMQOPc/CNP/GCE and nitrite sensing. Reproduced with permission.[110] Copyright 2020, Elsevier.

which increased the surface area and conductivity of the electrode.

Rahim et al. prepared mesoporous carbon ceramic lattice SiO_2/50 wt% C and characterized the materials utilizing N_2 sorption isotherms (SBET = 170 m^2 g^{-1}), SEM, and conductivity measurements.[111] Then MnPc was immobilized and XPS was used to determine the Mn/Si nuclear characteristics and composition of the MnPc-modified materials. The sensor showed a linear range, limit of detection (LOD), quantification limit, and sensitivity of 0.79–15.74, 0.02, 0.79 µmol L^{-1}, and 17.31 µA L $µmol^{-1}$, respectively. The repeatability of the proposed sensor was found to be within the standard deviation of 1.7%. The sensor was applied to real samples to determine nitrite levels in sausage meat, streams, and lake water.

Saeed et al. electrodeposited gold nanoparticles onto GCE, followed by 3-mercaptopropionic acid to empower the connection of an iron (III) monoamino-phthalocyanine (FeMAPc) via amide bond arrangement.[112] They examined the modified electrode for SEM, energy dispersive X-ray (EDX), and UV spectroscopy for surface characterization, while CV and electrochemical impedance spectroscopy (EIS) procedures were applied to understand the electrochemical characteristics. The electrochemical activity of nitrite at GCE, AuNPs/GCE, FeMAPc/GCE, and FeMAPc-MPA/AuNPs/GCE was assessed utilizing DPV in a phosphate buffer solution (0.1 м PBS, pH 5.8). FeMAPc-MPA/AuNPs/GCE yielded a significant sensitive response of 14.5 nA $µм^{-1}$, which was twofold better than that of AuNPs/GCE, 2.4 times FeMAPc/GCE, and 3.5 times at bare GCE, with a linear range of 1.9 µм–2.04 mм (PBS, pH 5.8) and a LOD of 0.21 µм. The FeMAPc-MPA/AuNPs/GCE showed specificity in the presence of interfering anions and demonstrated its practical capacity in real water analysis.

Ndebele et al. utilized a new series of MPcs with Cu, Mn, and Ni as focal metals (CuPc, MnPc, and NiPc) with tetrasubstituted chalcone ligands, which were coated on polished carbon electrodes and used as electrocatalysts for the nitrite sensor in pH 7 phosphate-cushioned saline.[113] The detection limit ranged between 0.18 and 1.77 µм with a high sensitivity rate of 58.8 µA $mм^{-1}$ for CoPc. Compared to other electrodes, the CoPc showed the best and NiPc displayed poor electrocatalytic activity for nitrite detection. Shambhulinga et.al. synthesized a novel terrazzo-cobalt phthalocyanine polymer [poly(TazoCoPc)] using an oxy-bridge to increase the conjugation and delocalized π electron impact on the phthalocyanine moiety.[114] Poly (TazoCoPc) and CNP were combined to create an electrochemical voltammetric and amperometric nitrite sensor, as represented in **Figure 15**. The composite showed improved electrocatalytic activity for nitrite oxidation compared to pristine poly(TazoCoPc). The amperometric sensor demonstrated excellent performance for nitrite detection in 20 nм–1 µм range, with a LOD of 6 nм (S/N = 3) and a sensitivity of 0.137 mA $µм^{-1}$. The composite electrode was highly specific and did not interfere with other co-existing species.

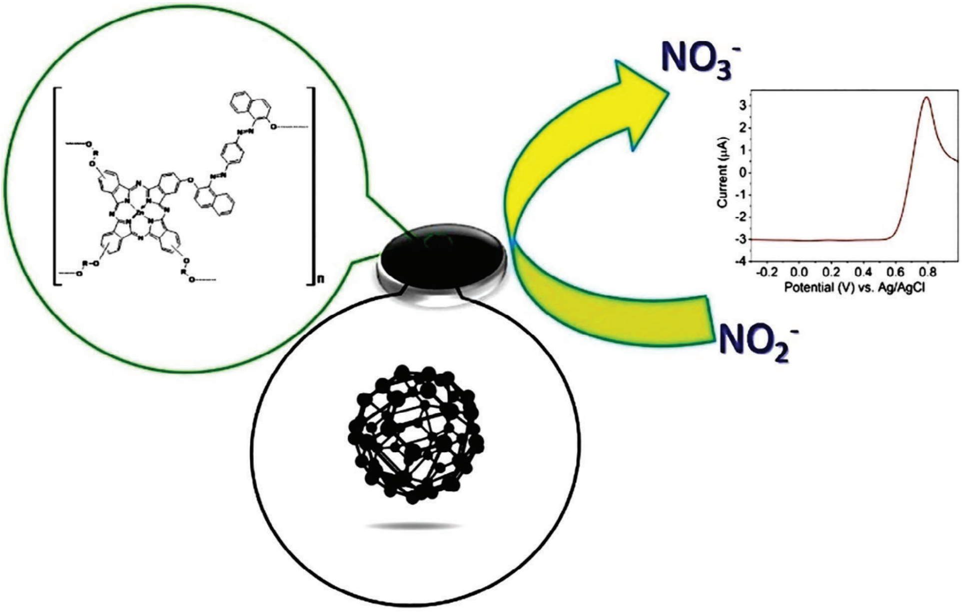

Figure 15. Schematic representation of nitrite sensing using poly(TazoCoPc) electrode. Reproduced with permission.[114] Copyright 2019, Elsevier.

3.4. Phenols

Phenols are a class of organic compounds that contain a hydroxyl (-OH) group connected to the aromatic benzene ring. They are known for their active role in drugs and biomolecules but can also be toxic with significant impacts on the environment and human health. Phenols are often found in industrial wastewater from various sources, such as chemical manufacturing, refineries, and agricultural runoff. These phenol-based pollutants can enter water bodies through improper disposal practices or accidental spills, and once in the environment, they can persist for significant periods due to their stability and non- degradation. Phenols are poisonous and can irritate the skin, eyes, and respiratory system upon contact or inhalation. Systemic toxicity can result from prolonged or high-level exposure to phenols, affecting the nervous system, kidneys, and liver. Also, phenols can present dangerous situations to the environment and humans through bioaccumulation and biomagnification in the food chain. Due to these environmental and health concerns, there is a need for effective methods to sense and detect the phenols in water samples. The electrochemical sensors offer a promising solution for the detection of phenols due to their sensitivity, selectivity, and potential for portability. MPc-based sensors are very crucial in the detection of phenols even in complex systems. MPc systems exhibit excellent electrochemical activity toward the oxidation of phenols by enhancing their response in addition to selectivity and sensitivity.[123] These sensors are ideal for assessing phenol levels in water bodies and effluents, making them applicable to regular monitoring and assessment.

Table 6 provides an extensive literature on the MPc-based sensors in the detection of phenols. Our group has developed a novel cobalt (II) tetra-b-[N(2-(1,3-benzothiazole)) carboxamide] phthalocyanine (CoTBTCAPc) complex, which has been characterized using various physicochemical and analytical techniques.[124] CV studies revealed that the complex is redox-active, and its modification on GCE (GCE/CoTBTCAPc) showed an excellent charge transfer ability, while the composite hybrid of CoTBTCAPc with CNP covered on GCE (GCE/CNP-CoTBTCAPc) enhanced the charge transfer at the interface. The electrochemical oxidation of 4-aminophenol at nanomolar

Table 6. Summary of metal phthalocyanine based electrodes performance in sensing of phenols.

Electrode materials	Method	Linearity [μм]	LOD [μм]	Sensitivity [μA μм$^{-1}$cm^{-2}]	Reference
GCE/CNP-CoTBTCAPc	CV	0.04–0.8	0.011	8.2	[124]
	DPV	0.1–1.0	0.03	417.7	
	Amperometry	0.1–0.9	0.03	888.7	
GC/MWCNT/CoPc	Squarewave voltammetry (SWV)	0.99–8.30	0.63	–	[125]
CoPcNRs/FA-rGO/GCE	DPV	2–160	0.65	–	[126]
CoTSAPc-MWCNT-GCE	CV	0.1–30	0.03	56.03	[127]
	DPV	0.1–38	0.03	114.09	
	Amperometry	0.05–20	0.016	177.14	
(PAH/FeTsPc + DPPG/AgNp)5	CV	2–100	0.87	–	[128]

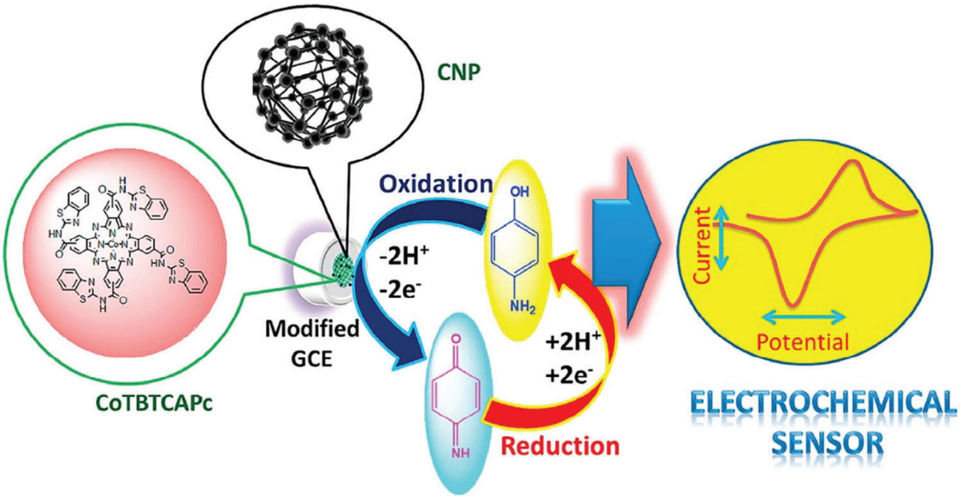

Figure 16. Schematic representation for the construction of GCE/CNP-CoTBTCAPc electrode for 4-aminophenol sensing. Reproduced with permission.[124] Copyright 2019, Elsevier.

concentration was noticed in phosphate buffer of pH 7.0 electrolytic media. DPV and amperometric sensors showed a wide linear response for 4-aminophenol oxidation in different concentration ranges as represented in **Figure 16**. The GCE/CNP-CoTBTCAPc displayed selectivity for 4-aminophenol, even in the presence of mixture of organic and inorganic species. The proposed sensor offers potential for sensitive electrochemical detection of 4-aminophenol in real-world applications like Paracetamol tablets.

Cesarino et al. developed a sensitive electrochemical sensor using MWCNT and CoPc modified on smooth carbon electrodes to identify the side effects of benzene electrolysis.[125] The sensor showed a response for sequence of phenols' such as catechol, hydroquinone, resorcinol, phenol, and 1,4-benzoquinone using squarewave voltammetry (SWV). The sensor was successfully used to ensure the total amount of phenols produced after benzene oxidation, and the results were in full agreement with the HPLC analysis. The results for the individual phenols formed i.e., catechol (15.62 μg L^{-1}), hydroquinone (17.91 μg L^{-1}), resorcinol (46.12 μg L^{-1}), phenol (58.83 μg L^{-1}) and 1,4-benzoquinone (13.75 μg L^{-1}) were also determined.

Zhang et al. developed a novel nanocomposite fulvic acid reduced graphene oxide (FA-rGO) and Co-phthalocyanine nanorods (CoPcNRs) for synchronous detection of catechol, hydroquinone, phenol, and p-nitrophenol. FA was used as a reductant, and CoPcNRs were synthesized using a surfactant-assisted ultrasonic technique.[126] The microstructure and morphologies of the materials were studied using SEM, XRD, and UV–vis spectrophotometer. DPV was used to explore the electrochemical oxidation of catechol (CC), hydroquinone (HQ), phenol (PN), and p-nitrophenol (p-NP). The FA-rGO/CoPcNRs electrode showed improved electrochemical catalytic activity toward the synchronous reduction of these compounds. The nanocomposite showed great selectivity, response, and stability. The study also investigated their application in real samples indicating the potential of the developed senor as an ideal platform for simultaneous detection of these compounds in natural samples.

Jilani et al. have developed a novel cobalt tetra-substituted sorbaamide phthalocyanine (CoTSAPc) sensor for electrochemical oxidation of 2-amino phenol (2-AP).[127] The CoTSAPc with multiwalled carbon nanotubes-based sensor demonstrated excellent electron transfer capacity with an increase in surface area on GCE. The sensor was able to detect 2-AP in a wide range of concentration (0.1–30 by CV, 0.1–38 by DPV, and 0.05–20 μmol L^{-1} by CA), LOD of (0.03 by CV, 0.03 by DPV, 0.016 μmol L^{-1} by CA) and sensitivity of (56.03 by CV, 114.09 by DPV, 177.14 μA.μ$M^{-1}cm^{-2}$ by CA). The MWCNT-CoTSAPc/GCE sensor demonstrated excellent electrocatalytic activity compared to the CoTSAPc modified sensor, showcasing remarkable repeatability, dependability, and high selectivity even in overabundance of o-nitrophenol, p-nitrophenol, bisphenol A, aniline, and hydroquinone. The schematic representation of the modification of MWCNT-CoTSAPc/GCE and the detection mechanism is shown in **Figure 17**.

3.5. Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a crucial component of various natural and modern cycles, and its detection provides a better understanding of different natural and industrial processes. MPc-based H_2O_2 sensors offer several benefits, including low LOD, high sensitivity, and ensure precise and reliable H_2O_2 detection by preventing interference from other species. MPc-based sensors are versatile and suitable for monitoring H_2O_2 concentrations in various natural and artificial systems. They are used in biological processes to monitor H_2O_2 levels and to obtain information on oxidative stress and related cell processes. MPc-based sensors are also employed for continuous monitoring of H_2O_2 in environmental systems.[56] **Table 7** provides a comprehensive summary of the performance of MPcs in sensing H_2O_2.

Sudhakara et al. used cobalt phthalocyanine, which is known to be a better electrocatalyst for a wide variety of natural, inorganic, and biomolecular analytes.[135] Using an amide bridge, they

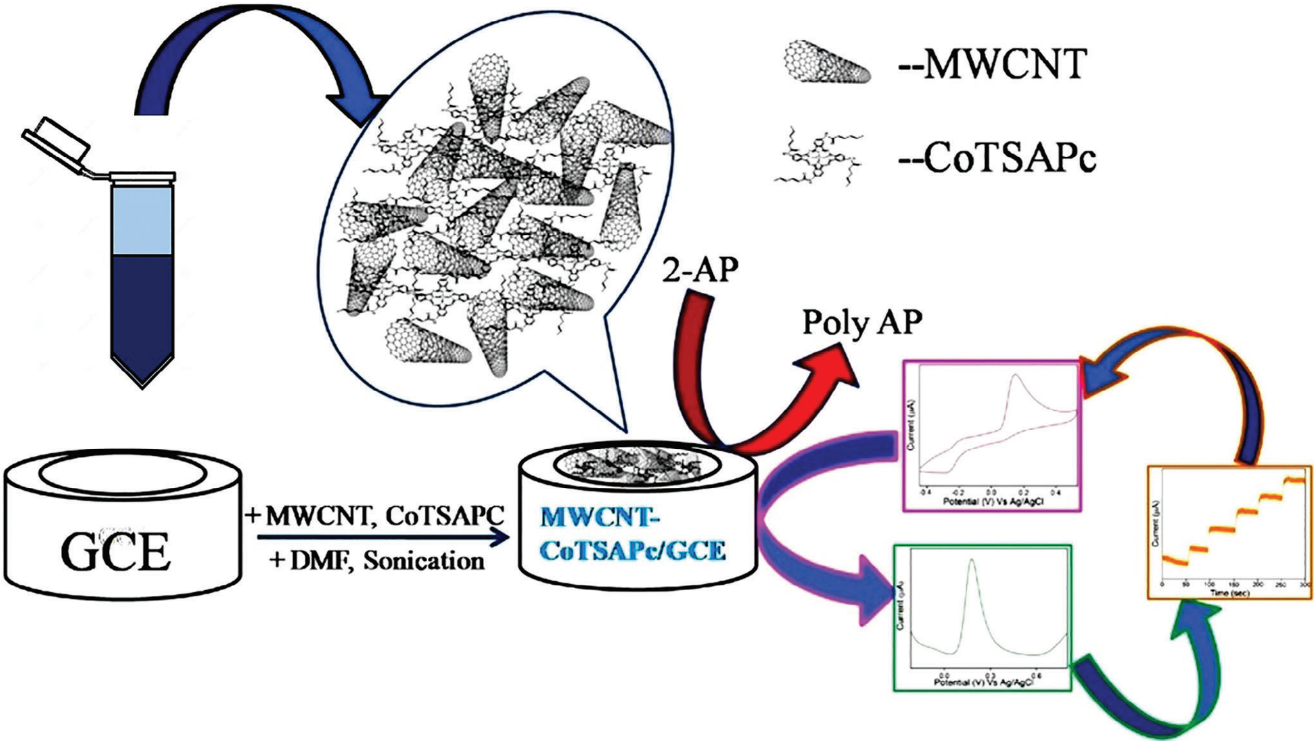

Figure 17. Schematic representation of a modification of MWCNT-CoTSAPc/GCE and sensing of 2-amino phenol. Reproduced with permission.[127] Copyright 2019, Elsevier.

covalently bonded tetracarboxy cobalt phthalocyanine (TCCoPc) with polyaniline (PANI). The linear sweep voltammetry (LSV) and CA methods were employed for the quantification of H_2O_2, as illustrated in **Figure 18**. The activity of the TCCoPc –PANI for H_2O_2 detection may be due to the synergetic impact of the pendanted macrocyclic Pc with the redox-dynamic attitude of the core cobalt metal and the PANI units.

Lokesh et.al. have developed a supramolecular self-assembled monolayer of polymeric phthalocyanine (poly(CuPc)) on a gold substrate.[130] The process involves the interaction of the cyano group of poly(CuPc) and Au surface. The functionalized gold substrate was characterized using Raman spectroscopy, X-ray diffraction, XPS, AFM, and electrochemical techniques. The results showed that the cyano groups of CuPc firmly bind with the gold surface with uniform distribution. The modified gold surface exhibited a reversible redox nature and acted as an electronic mediator for fast electron movement. The modified electrode successfully catalyzed H_2O_2 reduction, showing a synergist current that grows with the peroxide concentration. In another study, Lokesh et al. developed a layer-by-layer assembly of water-soluble cobalt tetrasulfophthalocyanine on a gold substrate pre-modified with poly(diallyldimethylammonium

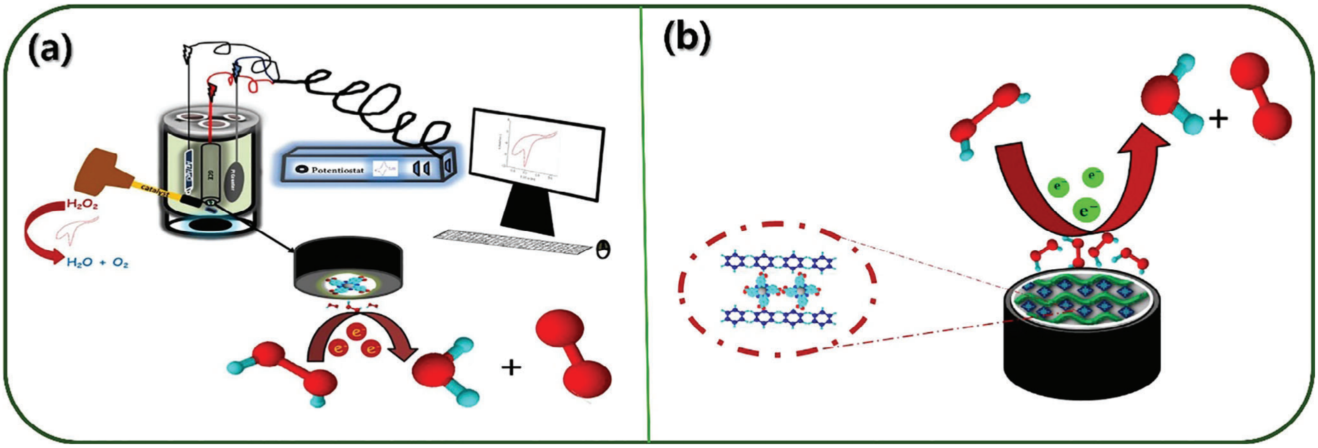

Figure 18. A) Schematic representation of H_2O_2 sensing and, B) reduction of H_2O_2 on the TCCoPc-PANI modified electrode. Reproduced with permission.[129] Copyright 2021, Elsevier.

Table 7. Summary of Metal Phthalocyanine based sensor performance for hydrogen peroxide sensing.

Electrode materials	Method	Linearity [μM]	LOD [μM]	Sensitivity [μA μM^{-1} cm^{-2}]	Reference
CoTMePhCAPc/MWCNT/GCE	CV	50–750	12.5	0.000529	[91]
	DPV	50–750	11.2	0.000049	
	Amperometry	50–500	5.5	0.00004	
TCClCoPc-PANI/GCE	Amperometry	0.2–52	0.05	2.32	[129]
poly (CuPc)	CV	0.35–70	0.25	–	[130]
CoTSPc	Amperometry	1–20	0.4	–	[131]
GO/poly(CoTBIPc)	CV	2–300	0.5	0.34	[132]
	Amperometry	2–200	0.6	1.0004	
CNT/Poly(CoTBImPc)	CV	0.01–0.1	0.005	–	[133]
	Amperometry	0.01–.01	0.002	–	
CoTLMethPc/MWCNTs/GCE	CV	0.1–0.8	0.01	–	[135]
	DPV	0.05–0.750	0.025	–	
	Amperometry	0.05–0.500	0.022	–	
SPAuE-PA-MnTAPc	Amperometry	1–30	0.117	150	[136]
SPAuE-PA-SWCNT-MnTAPc	Amperometry	1–30	0.442	2790	
SPAuE-PA-CoTAPc	Amperometry	1–30	0.582	190	
SPAuE-PA-SWCNT-CoTAPc	Amperometry	1–30	0.643	5160	
CoTCAPc	Amperometry	100–25 000	8.4	0.0075	[137]
$(OEt)_8$CoPc	Amperometry	£4000	3	–	[138]
CoPc	Amperometry	£4000	3	–	
CoPC	Amperometry	200–5000	0.2	1.12	[139]
Nano-CoPc	CV	20–18 000	5	7.7	[140]
FePc-CP NS	CV	0.1–1000	0.017	97000	[141]
CoTTBMPPc	Amperometry	0.01–0.2	0.004	0.00038	[142]
GCE-PolyCoTAPc	Amperometry	0.50–4.46	0.15	15 400	[143]
GCE-PolyMnTAPc	Amperometry	0.50–3.85	0.11	7400	
Nano CoPc-Gr/GCE	Amperometry	14–630	10	–	[144]
rGO/CoPc-COOH	CV	100–12 000	60	14 500	[145]

chloride).[131] The assembled film was characterized using UV–vis, Raman spectroscopy, ellipsometry, contact angle, AFM, and electrochemical techniques. The results ensured complete coverage of phthalocyanine film on the gold surface, with a reversible redox behavior for the electrochemical sensing of hydrogen peroxide in pH 7.0 phosphate buffer electrolyte. The H_2O_2 spiked pond water yielded a recovery of 94%, demonstrating the efficiency and practical applications of the developed sensor.

In another study, our group synthesized cobalt phthalocyanine with tetrabenzimidazole (CoTBIPc) moieties using tetracarboxylic acid phthalocyanine. The resulting compound was stable up to 500 °C and showed an amorphous nature.[132] The CoTBIPc complex was analyzed by CV and showed redox characteristics corresponding to the central metal (Co^{+2}/Co^{+1}) of the CoTBIPc and Pc macrocycle. The auxiliary amine of the benzimidazole ring initiated the electropolymerization on the polished GCE during potential cycling. The electropolymerized film was used for H_2O_2 detection, and the same is illustrated in **Figure** 19. Further, electropolymerization was also performed on graphene oxide (GO) covered GCE to improve the surface area, conductivity, and sensitivity. The poly(CoTBIPc) and GCE/GO/poly(CoTBIPc) demonstrated H_2O_2 sensing in the range of 3 to 140 μM and 2 to 200 μM, respectively. The amperometric sensor GCE/poly(CoTBIPc) and GCE/GO/poly(CoTBIPc), showed better LOD, reproducibility, repeatability, and high stability.

Cobalt tetrabenzimidazole phthalocyanine (CoTBImPc) and its polymer (poly(CoTBImPc)) were synthesized.[133] The CV technique confirmed the redox nature of the poly(CoTBImPc). To enhance conductivity, surface area, and responsiveness, CNTs were functionalized on GCE before electropolymerization. The resulting CNT/poly(CoTBImPc) amperometric sensor showed a direct relation in 10–100 nM H_2O_2 concentration range. The sensor displayed remarkable reproducibility, repeatability, and high stability without losing synergistic properties. **Figure** 20 represents a detailed illustration of the sensing mechanism of H_2O_2 detection and electrochemical behavior of the CNT/poly(CoTBImPc) electrode.

Mashazi et al. used metallo-tetra-amino phthalocyanine (MTAPc, M = Co and Mn) polymer films on gold and lustrous carbon electrode surfaces to detect and quantify H_2O_2.[134] The AFM study of the polymeric Pc electrode showed a polymeric rough film on ITO surface. The electrocatalytic response for H_2O_2 was significantly greater on the lustrous carbon polymer-modified electrode compared to its gold counterpart.

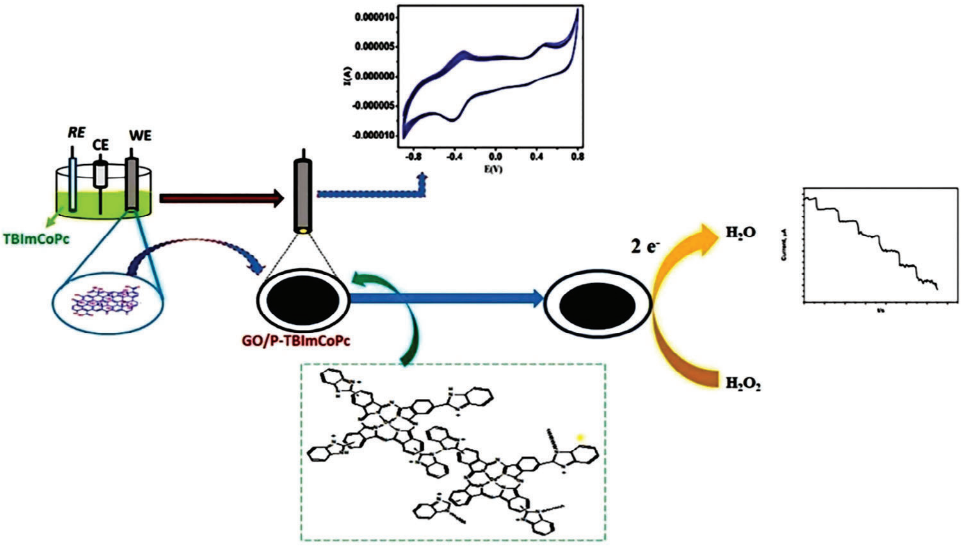

Figure 19. Schematic representation of H_2O_2 sensing at GCE/GO/poly(CoTBIPc). Reproduced with permission.[132] Copyright 2018, Elsevier.

3.6. Paracetamol

Paracetamol is a crucial drug molecule known for its potency as a painkiller. MPcs provide a platform for paracetamol detection due to their versatile behavior and offer several benefits, including better response for lower concentration, selectivity, and sensitivity. These sensors are particularly suitable for drug-specific applications, such as medication quality control and biological monitoring to assess the effects of environmental changes on the medication storage. The goals of MPc-based paracetamol detection are focused on sensor execution, fabrication of flexible and compact sensor systems, and scope of steady-state and real-time monitoring applications. The adaptability and capability of MPc-based sensors make them significant tools for addressing the logical issues associated with the detection of paracetamol in both regular and medication platforms. **Table** 8 provides a comprehensive summary of the comparison of the performance of MPcs in the sensing of paracetamol.

Our group has developed a novel thio-bridged cysteine ligand and its corresponding cobalt phthalocyanine complex (CoTATPAPc) to enhance the stability and compatibility of phthalocyanine with biomolecules during detection and to overcome the electrode fouling effects.[146] The synthesized complex was characterized using various spectroscopic methods, including TGA, FT-IR, UV–vis, mass, and NMR spectroscopy. The resulting GCE/CoTATPAPc showed excellent electrocatalytic performance for the simultaneous detection of paracetamol (PA) and 4-aminophenol (4-AP). This sensor demonstrated a linear response in the range of 20–360 nᴍ with LOD of 4.2 and 4.1 nᴍ for 4-AP and PA, respectively. The DPV procedure exhibited LODs of 6.1 and 6.3 nᴍ with a sensitivity of 0.2211 and 0.0197 nᴍ$^{-1}$ cm^{-2} for 4-AP and PA, respectively. The sensor demonstrated excellent response, reproducibility, repeatability, high selectivity, and stability for recognizing PA and 4-AP, even at high concentrations. **Figure** 21 presents the proposed mechanism for the electrocatalytic oxidation of the PA and 4-AP compounds.

Luhana et al. have developed a touchy, quick, cost-effective, and eco-friendly electrochemical sensor for biomedical, natural, and pharmaceutical applications. They used graphene oxide to form electrochemically reduced graphene oxide on GCE (GCE-ERGO). Cobalt (II) tetra-aminophthalocyanine was electropolymerized onto the GCE consequently creating a stable GCE-ERGO/polyCoTAPc electrode.[147] The detecting surface, GCE-ERGO/polyCoTAPc was characterized using CV and EIS

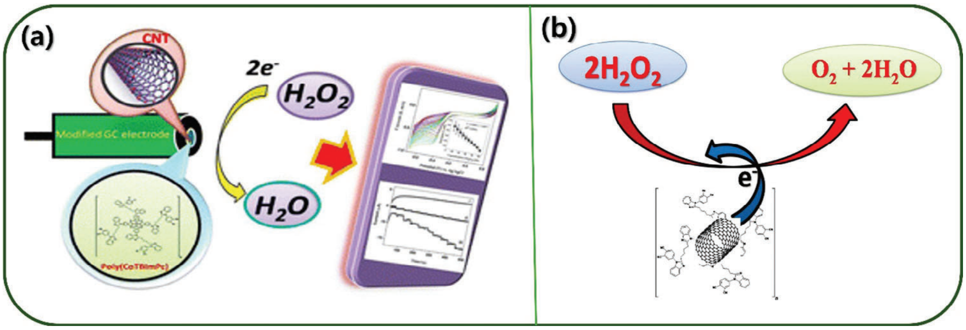

Figure 20. A) Schematic representation of H_2O_2 sensing, B) Mechanism of H_2O_2 reduction at the CNT/poly(CoTBImPc) electrode.[133]

Table 8. Summary of Metal Phthalocyanine electrodes performance in Paracetamol sensing.

Electrode materials	Method	Linear [µм]	LOD [µм]	Sensitivity [µA µм$^{-1}$ cm^{-2}]	Reference
GCE/CoTATPAPc	CV	0.020–0.380	0.007	0.00019	[146]
	DPV	0.020–0.340	0.0063	0.00025	
	Amperometry	0.020–0.360	0.0041	0.00302	
GCE-ERGO/polyCoTAPc	DPV	7.0–90	0.104	1.32	[147]
CoTBPCAPc/MWCNTs/GCE	CV	0.05–0.5	0.019	0.00008	[148]
	DPV	0.05–0.75	0.017	0.0007	
	Amperometry	0.05–0.5	0.014	0.00012	
FeTClBCTCAPc@MWCNTs/GC	CV	0.05–0.5	0.0205	–	[149]
	DPV	0.05–0.5	0.015	–	
	LSV	0.05–0.5	0.0155	–	
	Amperometry	0.05–0.9	0.0185	–	
1.0SiO2- CS/CuPc	CV	39.8–458	0.513	146	[150]
	DPV	19.9–385	0.564	173	
4-CuIITAPc SAM modified GCE	DPV	5–1400	0.0304	–	[151]

methods. The modified surface was characterized and confirmed using infrared spectroscopy and energy-dispersive X-ray spectroscopy. The fabricated electrode was used for ultrasensitive simultaneous recognition and assurance of dopamine (DA) and paracetamol (PA). The electrocatalytic peak current for DA and PA was significantly improved, with an oxidation potential difference of 264 mV, wide enough for concurrent and simultaneous detection of the analytes. The sensor showed excellent sensitivity of 8.39 µA.µм$^{-1}$ cm^{-2} for DA and 1.32 µAµм$^{-1}$ cm^{-2} for PA. The ultrasensitive electrochemical sensor was effectively used for DA and PA determination in synthetic urine with excellent recovery.

Mounesh et al. developed an electrochemical sensor for the sensing of PA and DA. They mixed substituted CoPc

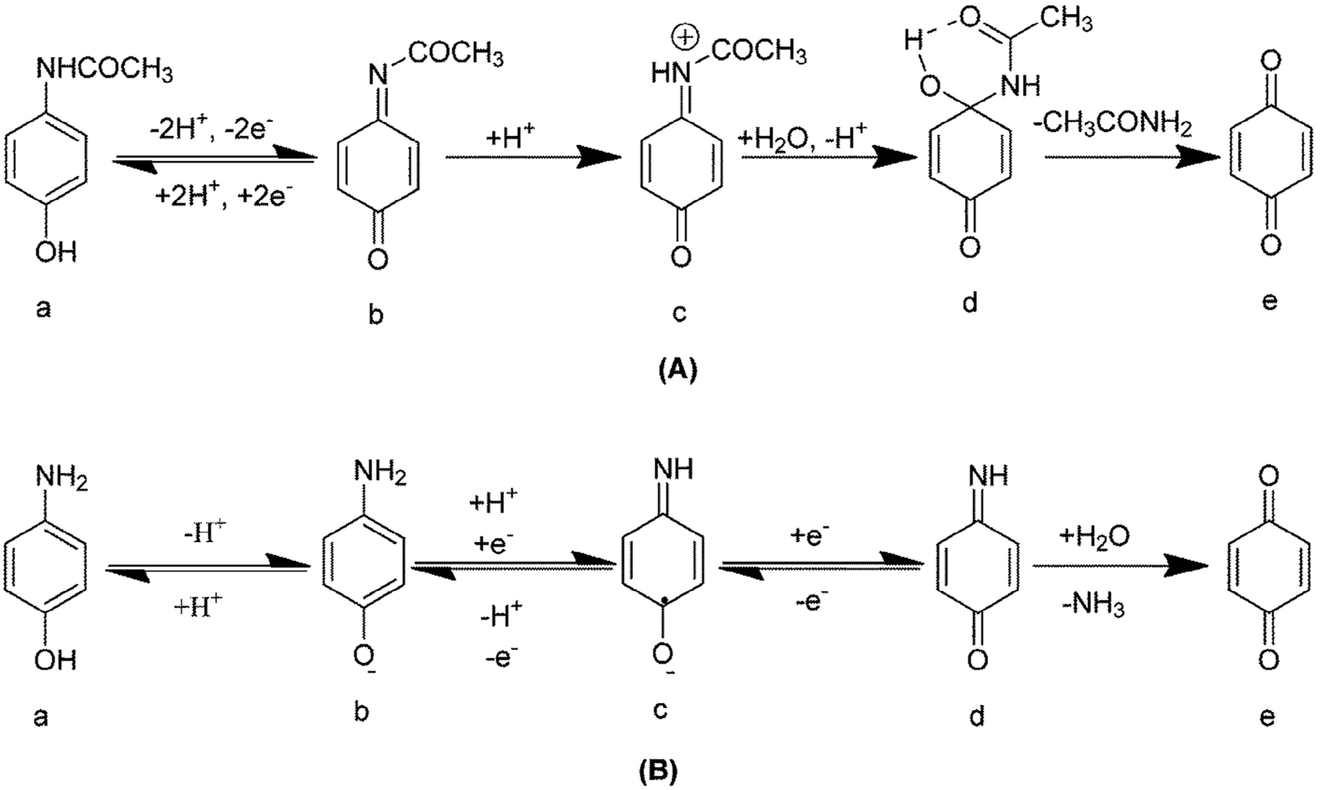

Figure 21. Proposed mechanism for the electrocatalytic oxidation of the compound A) PA and B) 4-AP. Reproduced with permission.[146] Copyright 2022, RSC Publications.

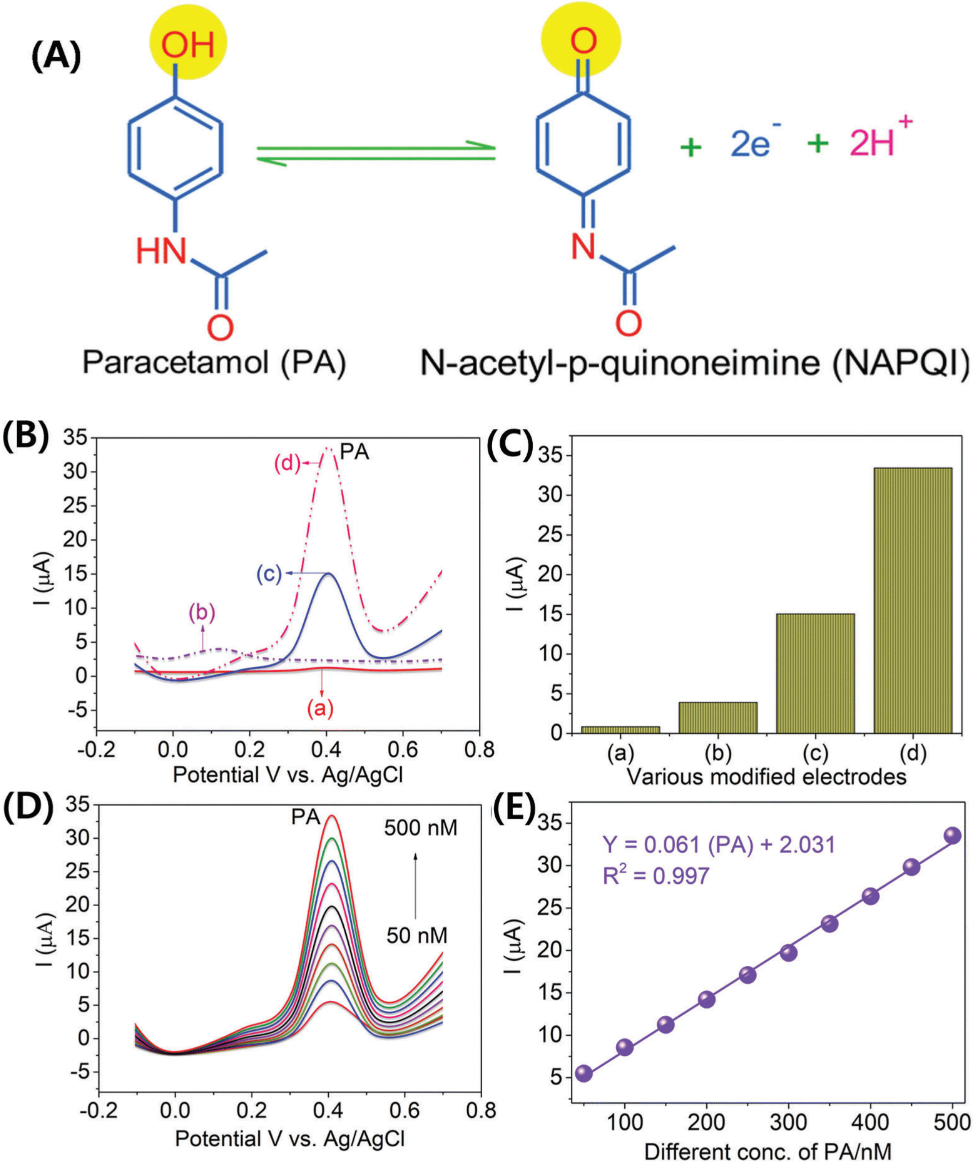

Figure 22. A) Electrochemical mechanism for the oxidation of paracetamol (PA), DPV plot for (B) (a) bare GCE, (b) FeTClBCTCAPc/GC, (c) 200 nM PA at FeTClBCTCAPc/GC and (d) 200 nM PA at FeTClBCTCAPc@MWCNTs/GC electrode in PBS (pH 7) solution at a scan rate of 50 mV s^{-1}, (C) Peak current for different electrodes, (D) different concentrations (50–500 nM) of PA at FeTClBCTCAPc@MWCNTs/GC electrode and (E) linear plot of oxidation peak currents versus concentration of PA. Reproduced with permission.[149] Copyright 2022, RSC Publications.

(CoTBPCAPc) with MWCNTs and deposited them on the GCE and applied CV, DPV, CA, and EIS to analyze the concentration of PA and DA.[148] The sensor demonstrated excellent performance in identifying PA and DA in concentrations of 50 to 750 nmol L^{-1}, with LOD of 17 and 19 nmol L^{-1} and high reproducibility with 5.1% relative standard deviation. The sensor constructed was simple, and delicate for the quantitative analysis and screening of PA and DA and was successfully applied in the analysis of commercial urine samples. The same group has also developed a novel tetra-substituted Schiff base iron (II) phthalocyanine (FeTClBCTCAPc) complex and characterized using IR, ^{1}HNMR, mass spectroscopy, XRD, TGA, and UV–vis spectroscopy.[149] The composite of FeTClBCTCAPc with MWCNTs was applied for the electrochemical detection of PA as represented in **Figure 22**. The FeTClBCTCAPc@MWCNTs/GC electrode showed superior electrocatalytic action for the oxidation of PA which exhibited lower oxidation potential and larger peak current. This nanocomposite electrode can be used as an improved detecting stage for the electrochemical detection of PA by LSV. The proposed strategy was effectively applied to the identification and sensing of PA in commercially available tablet samples, confirming its suitability for practical examination.

Ramos et al. have developed a mesoporous and thermally stable chitosan/silica (SiO_2-CS) bioinorganic hybrid material using the sol–gel technique.[150] The material has explicit surface

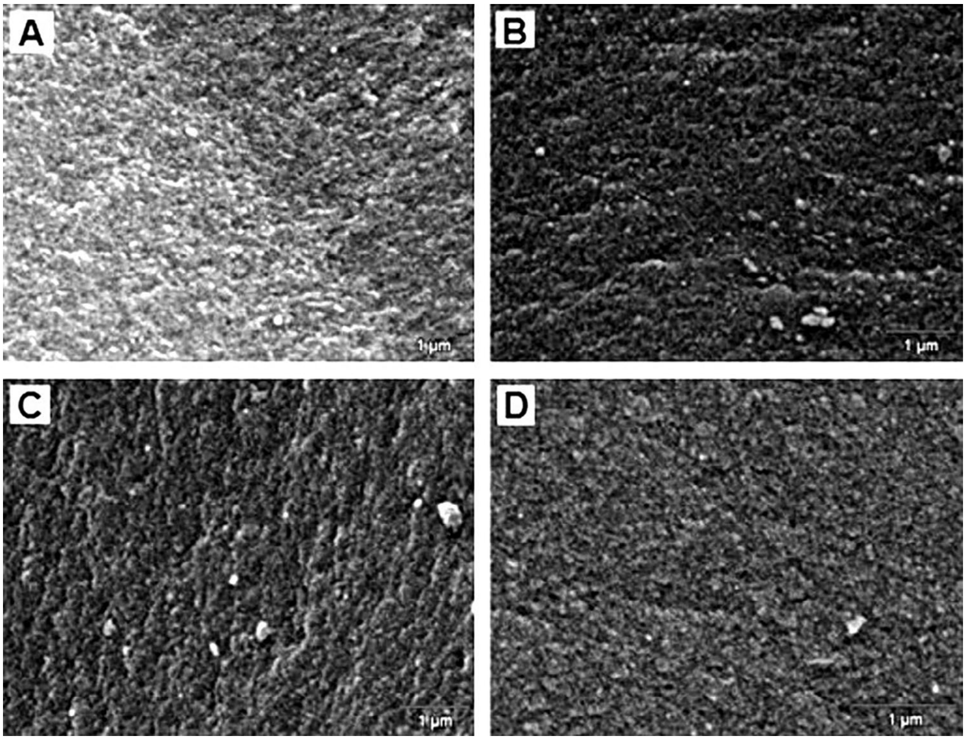

Figure 23. SEM images of hybrid material A. 0.5 SiO_2-CS, B.1.0 SiO_2-CS, C. 2.0 SiO_2-CS, D. 4.0 SiO_2-CS (magnification 20,000x). Reproduced with permission.[150] Copyright 2019, Elsevier.

regions and mesopore widths allowing the immobilization of the electroactive species, copper (II) tetrasulfonic phthalocyanine, on the outer layer. The material was applied to the carbon paste electrode, which showed good electrocatalytic activity for the redox response of paracetamol. The modified electrode with 1% w/w chitosan/silica showed a higher reaction current, and further CV studies showed that the paracetamol oxidation-reduction process is constrained by a diffusion-limited mass transfer process. CV and DPV techniques demonstrated a low LOD and high sensitivity. The electrode was also applied for paracetamol detection in the presence of dopamine, which ensured excellent selectivity, and reproducibility. The designed electrode is suitable for paracetamol detection independently as well as simultaneously with paracetamol and dopamine. **Figure** 23 shows the SEM images of hybrid material which revealed a rough surface for all the samples, and the images are comparable inferring that the insertion of various amounts of chitosan does not create huge morphological changes at the integrated composite.

4. Advantages and Disadvantages of MPc-Based Sensors

4.1. Advantages

4.1.1. Catalytic Activity

MPcs exhibit excellent catalytic activity due to their capacity to facilitate reversible redox reactions.

4.1.2. Tunable Redox Properties

The redox properties of MPcs can be customized by changing the central metal ion and functional groups attached to the phthalocyanine ring.

4.1.3. Stability

MPcs are chemically and thermally stable, which makes them suitable for long-term sensing applications. Their resistance to oxidation and degradation ensures their durability, even in extreme conditions and environments, such as high pH or high temperatures.

4.1.4. Selectivity

MPcs can be designed to have selective interactions with molecules, such as gases, biomolecules, or environmental pollutants. This selectivity, combined with their catalytic properties, allows MPc-based sensors to provide precise detection, reducing cross-sensitivity and improved sensor precision.

4.1.5. Modification

MPcs can be functionalized with different functional groups or integrated into nanocomposites like carbon nanotubes, nanoparticles, graphene, reduced graphene oxide, or conducting polymers. This hybridization can enhance their conductivity, surface area, catalytic effectiveness, and overall performance in electrochemical detecting applications.

4.1.6. Biocompatibility

Certain MPcs are biocompatible, making them appropriate for biosensing applications such as distinguishing the biological molecules in medical diagnostics (e.g., glucose, dopamine).

4.2. Disadvantages

4.2.1. Slow Response Time

MPc-based sensors may occasionally display slower response times compared to other materials, such as graphene-based sensors. This is due to the slower electron transfer kinetics of MPcs, which might restrict their application in rapid detection situations.

4.2.2. Limited Conductivity

Pure MPcs have lower electrical conductivity compared to other electroactive materials such as graphene or conductive polymers. This can reduce their efficiency in electrochemical analysis, unless they are modified or utilized as composite with more conductive materials.

4.2.3. Cost of Synthesis

The synthesis of some MPcs, particularly those incorporating rare or expensive metals (e.g., ruthenium, platinum), can be costlier. This increases the overall expense of producing MPc-based sensors, making them less economically viable for large-scale commercial applications.

4.2.4. Sensitivity to Environmental Conditions

MPc-based sensors can be affected by environmental factors such as humidity or temperature changes, which can alter their performance. This can lead to decreased accuracy or the need for calibration to maintain sensor reliability.

4.2.5. Limited Dynamic Range

MPc-based sensors offer various benefits, like high catalytic activity, stability, selectivity, and tunability, making them promising materials for different electrochemical applications. However, challenges such as slower response times, lower conductivity, and higher synthesis costs should be addressed through further material engineering and optimization process to enhance their performance and make them more commercially viable.

5. Challenges, Concluding Remarks, and Future Directions

While discussing the limitations and challenges of existing research on MPcs, it would be of great importance to consider various dimensions, related to theoretical gaps, experimental shortcomings, technological issues, and application-specific barriers.

5.1. Theoretical Gaps

Many models have been proposed to understand MPcs' electronic, optical, and magnetic properties, but are still too simplistic to capture the complexity of real systems, especially under varying external conditions like temperature or pressure. Further, discrepancies in reported data (e.g., in optical absorption spectra or catalytic activity) often arise due to differences in experimental conditions or synthetic methods, complicating the development of universally applicable theories. The interaction between MPcs and substrates or guest molecules is often insufficiently understood in fields like catalysis or sensors. This hinders progress in optimizing MPc-based materials for specific applications.

5.2. Experimental Challenges

The synthetic procedures for producing MPcs often lead to variability in terms of purity, crystallinity, and morphology. This can make reproducibility across different laboratories difficult. While MPcs show promise in laboratory-scale applications, scaling up the production for industrial applications remains a challenge. This is especially critical for catalysis and electronic applications, where cost efficiency is important. Although advanced techniques exist for characterizing MPcs, many are still not fully optimized for in-situ measurements, which are crucial for understanding their behavior in real-time operational environments (e.g., in catalysis or sensor applications).

5.3. Technological Barriers

One of the major challenges in MPc-based research is integrating these compounds into practical devices (like transistors, photovoltaic cells, or sensors) without significantly losing performance. Issues like poor charge mobility and instability under operational conditions limit their use in commercial devices. Many MPcs are prone to degradation when exposed to environmental factors such as humidity, light, or oxygen, which limits their longevity and reliability in practical applications. While MPcs are relatively easy to synthesize, the cost of high-purity materials and the lack of efficient, large-scale production methods can make them less appealing for commercial purposes. MPcs are being explored for use in organic photovoltaic cells, but their relatively low efficiency compared to other materials (e.g., perovskites, silicon) remains a significant hurdle. While they show promise as catalysts, their activity and selectivity need to be improved for widespread applications in industrial catalysis. The challenge lies in fine-tuning the central metal and substituents to achieve high efficiency for specific reactions. Although MPcs have potential as therapeutic agents (e.g., photodynamic therapy), issues related to biocompatibility, toxicity, and efficient delivery mechanisms remain unresolved.

In conclusion, the in-depth exploration of phthalocyanine-based catalysts in electrochemical sensors revealed a promising prospect with the potential to advance sensors for commercialization. Through meticulous explanation of material properties and fundamentals of sensor mechanism, detailed insights into the feasibility of MPcs in sensing applications have been discussed. The inherent versatility of MPc-based catalysts because of their structural tenability and desired characteristics have positioned them as promising candidates for various photo and electrochemical applications. Their robust light absorption properties across UV–vis and IR regions coupled with redox-active sites facilitate the charge transfer and in turn enhance catalytic activity and energy storage. Moreover, their capacity to self-assemble or form parity with other conjugated materials during integration enhances their applicability across diverse sensor platforms. This comprehensive review of MPc-based electrochemical sensors sheds light not only on the remarkable efficacy of these materials but also on the boundless possibilities they hold for shaping the future of sensor technology. As researchers continue their efforts to advance sensor research technology, exploring phthalocyanine chemistry promises a future of exciting innovations, discovery, and transformative impacts with diverse catalyst materials.

Looking forward, the prospects for phthalocyanine-based electrochemical sensors are bright and promising. From environmental monitoring to healthcare diagnostics, these sensors are imperative to unlock transformative solutions to societal challenges. Advanced materials engineering, the integration of emerging technologies, and the pursuit of multifunctional sensor platforms stand as pillars upon which future advancements will be built. The following criteria can be considered for the research in this field:

1) Materials Engineering: Materials science is continuously evolving and offers new avenues for tailoring the properties of phthalocyanine-based catalysts. Advanced synthetic techniques, such as molecular self-assembly, hydrothermal/solvothermal, CVD, and bottom-up fabrication methods enable precise control over the structural morphology and chemical composition of these materials. By exploring novel synthetic routes and leveraging cutting-edge characterization techniques, researchers can engineer phthalocyanine-based catalysts with tailored functionalities optimized for specific sensing applications. The combining of nanotechnology and sensor technology presents a bundle of opportunities for advancing MPc-based electrochemical sensing capabilities and practical applications. Nanoscale fabrication methods, such as nanoimprint lithography and chemical vapor deposition (CVD) techniques architect the precise patterning of MPc-based catalysts onto sensor substrates, enhancing the surface area and electrochemical reactivity. Additionally, it is capable of real-time data analysis and adaptive sensing protocols, further enhancing sensor performance and usability.
2) Multifunctional sensor platforms: The development of multifunctional sensor platforms represents a shift in sensor design, enabling simultaneous detection of multiple analytes with high sensitivity and selectivity. MPc-based catalysts, with their versatile chemical properties and tunable electronic structures, are ideally suited for integration into multifunctional sensor arrays. Researchers can address complex analytical challenges in diverse fields ranging from environmental monitoring to biomedical diagnostics by designing sensor platforms capable of multiplexed sensing.
3) Environmental and healthcare applications: The applications of MPc-based electrochemical sensors in environmental monitoring and healthcare diagnostics hold immense promise for addressing the impetus of societal challenges. In environmental monitoring, these sensors can be utilized for the detection of pollutants, heavy metals, and toxic chemicals in air, water, and soil samples with high sensitivity and specificity. In healthcare, MPc-based sensors offer potential applications in disease diagnosis, biomarker detection, and drug screening, enabling early disease detection and personalized treatment strategies.
4) Commercialization and industrial adoption: The successful translation of research findings into practical applications and commercial products is essential for realizing the full impact of MPc-based electrochemical sensors. Collaboration efforts between academia, industry, and regulatory bodies are necessary to navigate the complexities of technology transfer, scale-up, and market penetration. Through the partnership between researchers, manufacturers, and end-users, researchers can accelerate the commercialization and industrial adoption of MPc-based sensor technologies, bringing tangible benefits to society and the economy.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

S.A. and K.C.P. contributed equally to this work.

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[1] Y. Yang, W. Gao, *Chem. Soc. Rev.* **2019**, *48*, 1465.
[2] 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, *J. Ind. Eng. Chem.* **2022**, *109*, 21.
[3] G. Chen, X. Xiao, X. Zhao, T. Tat, M. Bick, J. Chen, *Chem. Rev.* **2022**, *122*, 3259.
[4] P. Mulimani, M. P. Bhat, P. Patil, S. Aralekallu, R. Kapavarapu, J. Yu, M. Kurkuri, R. G. Kalkhambkar, *J. Water Process Eng.* **2024**, *59*, 105030.

[5] N. Jadon, R. Jain, S. Sharma, K. Singh, *Talanta* **2016**, *161*, 894.
[6] D. W. Kimmel, G. LeBlanc, M. E. Meschievitz, D. E. Cliffel, *Anal. Chem.* **2012**, *84*, 685.
[7] R. Ramachandran, T.-W. Chen, S.-M. Chen, T. Baskar, R. Kannan, P. Elumalai, P. Raja, T. Jeyapragasam, K. Dinakaran, G. P. Gnana kumar, *Inorg. Chem. Front.* **2019**, *6*, 418.
[8] S. Aralekallu, G. Kuntoji, M. Nemakal, I. Mohammed, L. K. Sannegowda, *Surfaces and Interfaces* **2019**, *15*, 19.
[9] S. Aralekallu, L. K. Sannegowda, In *Handbook of Nanomaterials for Sensing Applications*, (Eds: C. M. Hussain, S. K. Kailasa), Elsevier, Amsterdam **2021**, pp. 589–629.
[10] S. Aralekallu, R. Thimmappa, P. Gaikwad, M. C. Devendrachari, A. R. Kottaichamy, S. P. Shafi, K. S. Lokesh, J. Sánchez, M. O. Thotiyl, *ChemElectroChem* **2017**, *4*, 692.
[11] B. J. Privett, J. H. Shin, M. H. Schoenfisch, E. Sensors, *Anal. Chem.* **2010**, *82* 4723.
[12] H. Karimi-Maleh, F. Karimi, M. Alizadeh, A. L. Sanati, *Chem. Rec.* **2020**, *20*, 682.
[13] X. Huang, M. Song, J. Zhang, T. Shen, G. Luo, D. Wang, *Nano-Micro Lett.* **2023**, *15*, 86.
[14] S. Sanati, A. Morsali, H. García, *Energy Environ. Sci.* **2022**, *15*, 3119.
[15] S. Kempahanumakkagari, K. Vellingiri, A. Deep, E. E. Kwon, N. Bolan, K.-H. Kim, *Coord. Chem. Rev.* **2018**, *357*, 105.
[16] Y.-H. Wang, K.-J. Huang, X. Wu, *Biosens. Bioelectron.* **2017**, *97*, 305.
[17] S. Dou, X. Wang, S. Wang, *Small Methods* **2019**, *3*, 1800211.
[18] S. Aralekallu, K. Sannegowda Lokesh, V. Singh, *Fuel* **2024**, *357*, 129753.
[19] S. Aralekallu, S. Hadimane, M. Shantharaja Nemakal, L. Koodlur Sannegowda, *Fuel* **2024**, *361*, 130736.
[20] S. Aralekallu, L. K. Sannegowda, V. Singh, *Int. J. Hydrogen Energy* **2023**, *48*, 16569.
[21] S. Aralekallu, V. A. Sajjan, M. Palanna, C. P. Prabhu, K. Hojamberdiev, M. Sannegowda, L. K., *J. Power Sources* **2020**, *449*, 227516.
[22] S. Hadimane, S. Aralekallu, K. P. Cp, M. Hojamberdiev, L. K. Sannegowda, *ACS Appl. Energy Mater.* **2021**, *4*, 10826.
[23] B. Çeken, M. Kandaz, A. Koca, *Synth. Met.* **2012**, *162* 1524.
[24] S. Lu, H. Jia, M. Hummel, Y. Wu, K. Wang, X. Qi, Z. Gu, *RSC Adv.* **2021**, *11*, 4472.
[25] O. Adeniyi, N. Nwahara, D. Mwanza, T. Nyokong, P. Mashazi, *Sens. Actuators, B* **2021**, *348*, 130723.
[26] Z. Zeng, X. Fang, W. Miao, Y. Liu, T. Maiyalagan, S. Mao, *ACS Sens.* **2019**, *4*, 1934.
[27] A. Ambrosi, C. K. Chua, A. Bonanni, M. Pumera, *Chem. Rev.* **2014**, *114*, 7150.
[28] A. A. Ensafi, K. Z. Mousaabadi, R. Fazel-Zarandi, In *Conductive Polymers in Analytical Chemistry*, Vol. *1405*, American Chemical Society, Washington, **2022**, pp. 185–217.
[29] A. J. Bandodkar, I. Jeerapan, J. Wang, *ACS Sens.* **2016**, *1*, 464.
[30] C. Yang, M. E. Denno, P. Pyakurel, B. J. Venton, *Anal. Chim. Acta* **2015**, *887*, 17.
[31] M. M. Shanbhag, G. Manasa, R. J. Mascarenhas, K. Mondal, N. P. Shetti, *Chem Eng J Adv* **2023**, *16*, 100516.
[32] A. J. Bard, L. R. Faulkner, H. S. White, *Electrochemical Methods: Fundamentals and Applications*, Wiley, Hoboken, New Jersey **2022**.
[33] I. I. Suni, *TrAC, Trends Anal. Chem.* **2008**, *27*, 604.
[34] C. Zhu, G. Yang, H. Li, D. Du, Y. Lin, *Anal. Chem.* **2015**, *87*, 230.
[35] K. S. Lokesh, A. Adriaens, *Dyes Pigm.* **2013**, *96*, 269.
[36] P. Gaikwad, M. Misal, S. Khaire, A. Raafik, S. Aralekallu, S. Varhade, Z. M. Bhat, A. R. Kottaichamy, M. C. Devendrachari, M. Gautam, M. O. Thotiyl, *Adv. Mater. Technol.* **2018**, *3*, 1700337.
[37] P. Gaikwad, K. Kadlag, M. Nambiar, M. C. Devendrachari, S. Aralekallu, A. R. Kottaichamy, Z. Manzoor Bhat, R. Thimmappa, S. P. Shafi, M. O. Thotiyl, *Anal. Chem.* **2017**, *89*, 7893.
[38] L. C. Lopes, A. Santos, P. R. Bueno, *Sens Actuators Rep* **2022**, *4*, 100087.
[39] Q. He, B. Wang, J. Liang, J. Liu, B. Liang, G. Li, Y. Long, G. Zhang, H. Liu, *Mater. Today Adv.* **2023**, *17*, 100340.
[40] P. C. Ferreira, V. N. Ataíde, C. L. Silva Chagas, L. Angnes, W. K. Tomazelli Coltro, T. R. Longo Cesar Paixão, W. Reis de Araujo, *TrAC, Trends Anal. Chem.* **2019**, *119*, 115622.
[41] T. Gebretsadik, T. Belayneh, S. Gebremichael, W. Linert, M. Thomas, T. Berhanu, *Analyst* **2019**, *144*, 2467.
[42] M. A. Mohamed, In *Electrochemistry*, Vol. *15*, (C. Banks, S. McIntosh), The Royal Society of Chemistry, United Kingdom **2018**, p. 0.
[43] R. Christie, A. Abel, *Phys. Sci. Rev.* **2021**, *6*, 391.
[44] M. A. Dahlen, *Ind. Eng. Chem.* **1939**, *31*, 839.
[45] B. N. Achar, K. S. Lokesh; *J. Organomet. Chem.* **2004**, *689*, 3357.
[46] R. Christie, A. Abel, In *Mixed Metal Oxide Pigments – Zinc Sulfide Pigments*, Vol. *3* (Eds: P. Gerhard), De Gruyter, Berlin, Boston, **2022**, pp. 1035–1040.
[47] K. P. C. H. Puttaningaiah, J. Hur, *Micromachines* **2024**, *15*, 1061.
[48] Y. Matsuo, K. Ogumi, I. Jeon, H. Wang, T. Nakagawa, *RSC Adv.* **2020**, *10*, 32678
[49] A. Aykanat, Z. Meng, G. Benedetto, K. A. Mirica, *Chem. Mater.* **2020**, *32*, 5372.
[50] D. Akyüz, T. Keleş, Z. Biyiklioglu, A. Koca, *J. Electroanal. Chem.* **2017**, *804*, 53.
[51] Z. Wang, Y. Wang, S. Yang, L. Xue, W. Feng, X. Liu, B. Li, M. Yin, J. Jiao, Q. Chen, *Talanta* **2021**, *226*, 122165.
[52] V. N. Carvalho da Silva, E. A. D. O. Farias, A. R. Araújo, F. E. Xavier Magalhães, J. R. Neves Fernandes, J. M. Teles Souza, C. Eiras, D. Alves da Silva, V. Hugo do Vale Bastos, S. S. Teixeira, *Biosens. Bioelectron.* **2022**, *210*, 114211.
[53] L. S. Porto, D. N. da Silva, M. C. Silva, A. C. Pereira, *Electroanalysis* **2019**, *31*, 820.
[54] H. Xu, J. Xiao, B. Liu, S. Griveau, F. Bedioui, *Biosens. Bioelectron.* **2015**, *66*, 438.
[55] S. Aralekallu, M. Palanna, S. Hadimani, C. P. K. Prabhu, V. A. Sajjan, M. O. Thotiyl, L. K. Sannegowda, *Dalton Trans.* **2020**, *49*, 15061.
[56] K. S. Lokesh, A. Shambhulinga, N. Manjunatha, M. Imadadulla, M. Hojamberdiev, *Dyes Pigm.* **2015**, *120*, 155.
[57] M. Palanna, S. Aralekallu, C. P. Keshavananda Prabhu, V. A. Sajjan, L. K. Mounesh Sannegowda, *Electrochim. Acta* **2021**, *367*, 137519.
[58] D. Mukherjee, R. Manjunatha, S. Sampath, A. K. Ray, In *Materials for Chemical Sensing*, (Eds. T. R. L. Cesar Paixão, S. M. Reddy), Springer International Publishing, Cham, **2017**, pp. 165–226.
[59] S. Pakapongpan, J. P. Mensing, D. Phokharatkul, T. Lomas, A. Tuantranont, *Electrochim. Acta* **2014**, *133*, 294.
[60] M. S. de Oliveira, E. A. d. O. Farias, A. M. S. de Sousa, N. A. Dionísio, P. R. S. Teixeira, A. S. do. N. M. Teixeira, D. A. da Silva, C. Eiras, *Surfaces and Interfaces* **2021**, *25*, 101245.
[61] C. R. Vanoni, J. P. Winiarski, G. R. Nagurniak, H. A. Magosso, C. L. Jost, *Electroanalysis* **2019**, *31*, 867.
[62] A. Sidorov, I. J. O. Kotlyar, *Opt. Spectrosc.* **1961**, *11*, 92.
[63] B. N. Achar, K. S. Lokesh; *J. Solid State Chem.* **1987**, *177*, 2004.
[64] K. P. C. Puttaningaiah, G. Kuntoji, S. Aralekallu, K. Shantharaja, K. Naseem, A. Chikkabasur Kumbara, L. K. Sannegowda, *ACS Appl. Nano Mater.* **2023**, *6* 8880.
[65] V. A. Sajjan, S. Aralekallu, M. Nemakal, M. Palanna, C. P. K. Prabhu, L. K. Sannegowda, *Inorg. Chim. Acta* **2020**, *506*, 119564.
[66] K. P. Cp, S. Aralekallu, V. A. Sajjan, M. Palanna, S. Kumar, L. K. Sannegowda, *Sustain. Ener. Fuels* **2021**, *5*, 1448.
[67] M. Nemakal, S. Aralekallu, I. Mohammed, S. Swamy, L. K. Sannegowda, *J. Electroanal. Chem.* **2019**, *839*, 238.
[68] A. B. Sorokin, *Chem. Rev.* **2013**, *113*, 8152.

[69] N. Morlanés, W. Almaksoud, R. K. Rai, S. Ould-Chikh, M. M. Ali, B. Vidjayacoumar, B. E. Al-Sabban, K. Albahily, J.-M. Basset, *Catal. Sci. Technol.* **2020**, *10*, 844.

[70] W. M. Sharman, J. E. van Lier, *J. Porphyrins Phthalocyanines* **2000**, *4*, 441.

[71] D. Wöhrle, *Macromol. Rapid Commun.* **2001**, *22*, 68.

[72] C. G. Claessens, U. Hahn, T. Torres, *Chem. Rec.* **2008**, *8*, 75.

[73] K. P. Channabasavana Hundi Puttaningaiah, D. S. Ramegowda, J. Hur, *ACS Appl. Energy Mater.* **2024**, *7*, 6793.

[74] H.-G. Wang, Q. Wu, L. Cheng, L. Chen, M. Li, G. Zhu, *Energy Storage Mater.* **2022**, *52*, 495.

[75] A. Kumar, V. Kumar Vashistha, D. Kumar Das, *Coord. Chem. Rev.* **2021**, *431*, 213678.

[76] C. P. K. P. Naveen, K. R. Aralekallu, S. Shivalingayya, L. K. Sannegowda, *RSC Sustainability* **2023**, *1*, 128.

[77] V. A. Sajjan, I. Mohammed, M. Nemakal, S. Aralekallu, K. R. Hemantha Kumar, S. Swamy, L. K. Sannegowda, *J. Electroanal. Chem.* **2019**, *838*, 33.

[78] N. Diab, D. M. Morales, C. Andronescu, M. Masoud, W. Schuhmann, *Sens. Actuators, B* **2019**, *285*, 17.

[79] Mounesh, B. S. Jilani, M. Pari, K. V. Reddy, K. S. Lokesh, *Microchem. J.* **2019**, *147*, 755.

[80] F. Demir, H. Y. Yenilmez, A. Koca, Z. A. Bayır, *J. Electroanal. Chem.* **2019**, *832*, 254.

[81] J. Peng, X. Li, Y. Liu, W. Zhuge, C. Zhang, Y. Huang, *Sens. Actuators, B* **2022**, *360*, 131619.

[82] C. K. Prabhu, M. Nemakal, S. Aralekallu, I. Mohammed, M. Palanna, V. A. Sajjan, D. Akshitha, L. K. Sannegowda, *J. Electroanal. Chem.* **2019**, *847*, 113262.

[83] P. Malathesh, N. P. Kumara, B. S. Jilani, C. Mruthyunjayachari, K. V. Reddy, *Heliyon* **2019**, *5*.

[84] K. Tshenkeng, P. Mashazi, *Electrochim. Acta* **2020**, *5*, e01946.

[85] B. Wu, M. Li, R. Ramachandran, G. Niu, M. Zhang, C. Zhao, Z. Xu, F. Wang, *Adv Mater* **2023**, *10*, 2200738.

[86] N. C. de Lucena, C. M. Miyazaki, F. M. Shimizu, C. J. Constantino, M. Ferreira, *Appl. Surf. Sci.* **2018**, *436*, 957.

[87] Z. Fredj, M. B. Ali, M. N. Abbas, E. Dempsey, *Anal. Methods* **2020**, *12*, 3883.

[88] M. Pari, K. V. Reddy, K. Chandrakala, *Sens. Actuators, A* **2020**, *316*, 112377.

[89] S. M. Sudhakara, H. M. N. Kotresh, M. C. Devendrachari, F. Khan, *Electroanalysis* **2020**, *32*, 1807.

[90] D. Akyüz, Ü. J. Demirbaş, *J. Organomet. Chem.* **2022**, *982*, 122537.

[91] A. Rahim, S. B. Barros, L. T. Kubota, Y. J. Gushikem, *Electrochim. Acta* **2011**, *56*, 10116.

[92] Z. Dong, F. Du, T. H. Barkae, K. Ji, F. Liu, D. Snizhko, Y. Guan, G. J. Xu, *Electrochim. Acta* **2023**, *441*, 141774.

[93] H. Xu, J. Xiao, L. Yan, L. Zhu, B. J. Liu, *J. Electroanal. Chem.* **2016**, *779*, 92.

[94] C. K. Prabhu, N. Manjunatha, A. Shambhulinga, M. Imadadulla, K. Shivaprasad, M. Amshumali, K. S. Lokesh, *J. Electroanal. Chem.* **2019**, *834*, 130.

[95] S. J. Shahrokhian, *Anal. Chem.* **2001**, *73*, 5972.

[96] N. Hernández-Ibáñez, I. Sanjuán, M. Á. Montiel, C. W. Foster, C. E. Banks, J. Iniesta, *J. Electroanal. Chem.* **2016**, *780*, 303.

[97] M. N. Abbas, A. A. Saeed, B. Singh, A. A. Radowan, E. Dempsey, *Anal. Methods* **2015**, *7*, 2529.

[98] R. Devasenathipathy, V. Mani, S.-M. Chen, K. Kohilarani, S. J. Ramaraj, *Int. J. Electrochem. Sci.* **2015**, *10*, 682.

[99] E. F. Perez, L. T. Kubota, A. A. Tanaka, G. D. Neto, *Electrochim. Acta* **1998**, *43*, 1665.

[100] T. J. Mafatle, T. Nyokong, *J. Electroanal. Chem.* **1996**, *408*, 213.

[101] V. Mani, S.-T. Huang, R. Devasenathipathy, T. Yang, *RSC Adv.* **2016**, *6*, 38463.

[102] K. I. Ozoemena, T. Nyokong, *Electrochim. Acta* **2006**, *51*, 2669.

[103] R. d. C. S. Luz, A. B. Moreira, F. S. Damos, A. A. Tanaka, L. T. Kubota, *J. Pharm. Biomed. Anal.* **2006**, *42*, 184.

[104] K. Ozoemena, P. Westbroek, T. Nyokong, *Electrochem. Commun.* **2001**, *3*, 529.

[105] K. I. Ozoemena, T. Nyokong, P. Westbroek;, *Electroanalysis* **2003**, *15*, 1762.

[106] S. Griveau, M. Gulppi, J. Pavez, J. H. Zagal, F. Bedioui, *Electroanalysis* **2003**, *15*, 779.

[107] B. Filanovsky, *Anal. Chim. Acta* **1999**, *394*, 91.

[108] L. Cui, T. Pu, Y. Liu, X. He, *Electrochim. Acta* **2013**, *88*, 559.

[109] C.-Y. Lin, A. Balamurugan, Y.-H. Lai, K.-C. Ho, *Talanta* **2010**, *82*, 1905.

[110] B. J. M. C. P. Jilani, Mounesh, P. Malathesh, C. D. Mruthyunjayachari, *Mater. Chem. Phys.* **2020**, *239*, 121920.

[111] A. Rahim, L. S. Santos, S. B. Barros, L. T. Kubota, R. Landers, Y. Gushikem, *Electroanalysis* **2014**, *26*, 541.

[112] A. A. Saeed, B. Singh, M. N. Abbas, Y. M. Issa, E. Dempsey, *Electroanalysis* **2015**, *27*, 1086.

[113] N. Ndebele, T. Nyokong, *J. Electroanal. Chem.* **2022**, *926*, 116951.

[114] S. Aralekallu, I. Mohammed, N. Manjunatha, M. Palanna, Dhanjai, L. K. Sannegowda, *Sens. Actuators, B* **2019**, *282*, 417.

[115] W. J. R. Santos, A. L. Sousa, R. C. S. Luz, F. S. Damos, L. T. Kubota, A. A. Tanaka, S. M. Tanaka, *Talanta* **2006**, *70*, 588.

[116] S. Dorovskikh, A. Pelevina, D. Klyamer, V. Volchek, A. Sukhikh, E. Korotaev, N. Morozova, T. Basova, *Appl. Surf. Sci.* **2023**, *640*, 158300.

[117] S. I. Dorovskikh, D. D. Klyamer, A. D. Fedorenko, N. B. Morozova, T. V. Basova, *Sensors* **2022**, *22*, 5780.

[118] X. Song, L. Gao, Y. Li, L. Mao, J.-H. Yang, *Anal. Methods* **2017**, *9*, 3166.

[119] S. M. Sudhakara, M. C. Devendrachari, F. Khan, S. Thippeshappa, H. M. N. Kotresh, *Surfaces and Interfaces* **2023**, *36*, 102565.

[120] N. Ndebele, T. Nyokong, *Diamond Relat. Mater.* **2023**, *132*, 109672.

[121] A. Sudarvizhi, K. Pandian, O. S. Oluwafemi, S. C. Gopinath, *Sens. Actuators, B* **2018**, *272*, 151.

[122] M. Mounesh, M. J., V. Reddy, S. K., N. K., M. B., *Langmuir* **2023**, *39*, 1665.

[123] I. Mohammed, M. Nemakal, S. Aralekallu, V. A. Sajjan, T. R. Divakara, M. Palanna, C. P. Keshavananda Prabu, L. K. Sannegowda, *J. Electroanal. Chem.* **2020**, *871*, 114292.

[124] M. Nemakal, S. Aralekallu, I. Mohammed, M. Pari, K. V. Reddy, L. K. Sannegowda, *Electrochim. Acta* **2019**, *318*, 342.

[125] I. Cesarino, F. C. Moraes, T. C. Ferreira, M. R. Lanza, S. A. Machado, *J. Electroanal. Chem.* **2012**, *672*, 34.

[126] Y. Zhang, Q. Xie, Z. Xia, G. Gui, F. J. Deng, *J. Electrochem. Soc.* **2019**, *166*, B1293.

[127] B. S. Jilani, C. Mruthyunjayachari, P. Malathesh, T. Sharankumar, K. V. Reddy, *Sens. Actuators, B* **2019**, *301*, 127078.

[128] P. Alessio, C. S. Martin, J. A. De Saja, M. L. Rodriguez-Mendez, *Sens. Actuators, B* **2016**, *233*, 654.

[129] S. M. Sudhakara, M. C. Devendrachari, H. M. N. Kotresh, F. Khan, *Microchem. J.* **2021**, *161*, 105781.

[130] K. S. Lokesh, K. De Wael, A. Adriaens, *Langmuir* **2010**, *26*, 17665.

[131] L. S. Koodlur, *Bioelectrochemistry* **2013**, *91*, 21.

[132] I. Mohammed, M. Nemakal, V. A. Sajjan, D. B. Puttappashetty, L. K. Sannegowda, *J. Electroanal. Chem.* **2018**, *826*, 96.

[133] C. P. K. P. Naveen, S. Aralekallu, L. K. Sannegowda, *RSC Sustainability* **2023**, *1*, 128.

[134] J. Zhang, Z. Chen, H. Wu, F. Wu, C. He, B. Wang, Y. Wu, Z. Ren, *J. Mater. Chem. B* **2016**, *4*, 1310.

[135] K. V. Reddy Mounesh, *Anal. Chim. Acta* **2020**, *1108*, 98.

[136] P. Mashazi, T. Mugadza, N. Sosibo, P. Mdluli, S. Vilakazi, T. Nyokong, *Talanta* **2011**, *85*, 2202.

[137] P. N. Mashazi, K. I. Ozoemena, T. Nyokong, *Electrochim. Acta* **2006**, *52*, 177.
[138] F. Mizutani, S. Yabuki, S. Iijima, *Anal. Chim. Acta* **1995**, *300*, 59.
[139] E. Crouch, D. C. Cowell, S. Hoskins, R. W. Pittson, J. P. Hart, *Anal. Biochem.* **2005**, *347*, 17.
[140] K. Wang, J.-J. Xu, H.-Y. Chen, *Biosens. Bioelectron.* **2005**, *20*, 1388.
[141] W. Liu, H. Pan, C. Liu, C. Su, W. Liu, K. Wang, J. Jiang, *ACS Appl. Mater. Interfaces* **2019**, *11*, 11466.
[142] R. Mounesh, V. K., *Anal. Chem. Lett.* **2020**, *10*, 33.
[143] P. Mashazi, C. Togo, J. Limson, T. Nyokong, *J. Porphyrins Phthalocyanines* **2010**, *14*, 252.
[144] H. Wang, Y. Bu, W. Dai, K. Li, H. Wang, X. Zuo, *Sens Actuators B Chem* **2015**, *216*, 298.
[145] I. S. Hosu, Q. Wang, A. Vasilescu, S. F. Peteu, V. Raditoiu, S. Railian, V. Zaitsev, K. Turcheniuk, Q. Wang, M. Li, B. Rabha, S. Sabine, *RSC Adv.* **2015**, *5*, 1474.
[146] M. Palanna, I. Mohammed, S. Aralekallu, M. Nemakal, L. K. Sannegowda, *New J. Chem.* **2020**, *44*, 1294.
[147] C. Luhana, P. Mashazi, *Electrocatalysis* **2023**, *14*, 406.
[148] K. R. V. Mounesh Reddy, *New J. Chem.* **2020**, *44*, 16831.
[149] K. R. V. Mounesh Reddy, D. Yuvaraja, J. M. Manriquez, K. S. Lokesh, M. K. Amshumali, *React. Chem. Eng.* **2022**, *7*, 2550.
[150] J. V. H. Ramos, F. de Matos Morawski, T. M. H. Costa, S. L. P. Dias, E. V. Benvenutti, E. W. de Menezes, L. T. Arenas, *Microporous Mesoporous Mater.* **2015**, *217*, 109.
[151] A. J. Jeevagan, S. A. John, *Electrochim. Acta* **2012**, *77*, 137.

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