

Electrochemical Detection of Free Chlorine in Ballast Water Management System

Pil Ju Park, Won Jin Jang, Dong Jun Lee, Tae Jung Park,* and Soo Young Kim*

Ballast water, which is seawater taken onboard ships to ensure stable and maneuverable sailing, can pose a significant threat to marine ecosystems and human health when discharged owing to the presence of undesirable organisms. To mitigate this risk, ballast water treatment methods such as electrochlorination are employed, where oxidants such as hypochlorite are generated to effectively eliminate marine microorganisms. The effectiveness of an electrochlorination-based ballast water management system (BWMS) depends on the maintenance of optimal concentrations of total residual chlorine (TRC). However, excessive levels of free chlorine (Cl) can result in corrosion and environmental damage, rendering the accurate monitoring of TRC levels crucial for the safe discharge of ballast water. This review focuses on recent advancements in electrochemical sensors for free Cl measurement in BWMS. The process of free Cl generation, techniques for electrochemical detection, and factors influencing sensor performance are elucidated. In addition, materials and strategies for improving the performance of the sensors are described. Finally, perspectives on the current issues and future challenges that must be overcome to effectively utilize electrochemical detection in BWMS are discussed, thereby offering new directions for advancing this technology.

In 2022, the global maritime trade volume reached 12027 million tons, representing roughly a threefold increase in the volume of cargo transported via shipping over the last 40 years.^[2,3] However, with the growth of the shipping industry, environmental problems caused by ballast water have gradually become an emerging issue. Ballast water is seawater loaded into the ballast tank to maintain the stability and maneuverability of the ship throughout a voyage and therefore is essential. However, numerous marine species and aquatic microorganisms contained inside the ballast water are transferred to different oceans, hence resulting in major biological invasions.^[4,5] The amount of ballast water discharged through maritime trade reaches more than 10 billion tons every year, and more than 10 000 marine species are introduced to other marine environments.^[6] Marine bioinvasion has been known as one of the four greatest threats to the world's oceans, not only

1. Introduction

Seaborne transportation plays a pivotal role in world trade and the global economy. According to statistics, almost 90% of the global merchandise is transported overseas through shipping.^[1]

its effects on the ecology of ocean nature but also on the global economy and human health. The harmful impacts of invasive species on the marine environment include predation, disturbance, and the spread of diseases virtually irreversibly affecting the natural habitat and population ecology.^[7] The direct economic impact of currently known marine bioinvasion is estimated to exceed US\$100 billion per year, including costs from disruption in fisheries and aquaculture industry, physical impacts on coastal infrastructure, loss of income from the shipping industry, and impacts on tourism.^[8]

In order to prevent the bioinvasion of harmful marine alien species and regulate discharges of ballast water, the Ballast Water Management Convention (BWM Convention) was adopted by consensus of the International Maritime Organization (IMO) in 2004.^[9] After Finland signed the BWM Convention, a total of 30 countries representing 35% of the gross tonnage of the world's merchant shipping have ratified the Convention, which entered into force in 2017.^[9] Hence, all ships built before 2017 September 8 are imperative to be equipped with an approved Ballast Water Management System (BWMS), until 2024 September 7, to manage the disinfection of ballast water before discharging according to the BWM Convention ballast water performance standard (Regulation D-2).^[9] Apart from the BWM Convention, the United States has implemented strong federal regulations and therefore only ships installed with BWMS that have been type-approved by

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Table 1. Discharge standard of IMO and USCG; cfu, colony forming unit.

Organism category	IMO D-2 Regulation BW performance standard	USCG Regulation BW discharge standard
Organisms size $\geq 50 \mu\text{m}$ in min. Dimension	<10 viable organisms/ m^3	<10 living organisms/ m^3
Organisms size $10\text{--}50 \mu\text{m}$ in min. Dimension	<10 viable organisms/mL	<10 living organisms/ m^3
Toxicogenic <i>Vibrio cholerae</i> (O1 and O139)	<1 cfu/100 mL, or <1 cfu/g (wet weight) zooplankton samples	<1 cfu/100 mL
<i>Escherichia coli</i>	<250 cfu/100 mL	<250 cfu/100 mL
Intestinal <i>Enterococci</i>	<100 cfu/100 mL	<100 cfu/100 mL

the United States Coast Guard (USCG) are allowed to discharge ballast water in US oceans.^[10] The comparison between the ballast water performance standard by IMO and ballast water discharge standard by USCG is shown in Table 1. Also, Vessel General Permit (VGP) was issued by the U.S. Environmental Protection Agency (USEPA) to regulate several vessel discharge categories including ballast water.^[11] To meet such strict discharge limits for each category of live organisms with various size classes stated in Regulation D-2 and USCG regulation, several methods have been developed and applied to BWMS to disinfect organisms in ballast water. A number of disinfection technologies such as UV radiation, chemical injection, and ozone treatment have been applied to BWMS to effectively eliminate any marine species.^[12,13] However, these methods are accompanied by challenges, including cumbersome disinfection processes, high costs, and safety issues due to harmful hazards.^[14]

Electrolysis or electrochlorination method has been adopted in wastewater treatment industries due to its effectiveness in removal of organisms and other several advantages such as low price, low footprint, safety, requiring less power and no need for chemical reagents, and long-term stability.^[15] Owing to its advantages, a number of BWMS have adopted the same method and so far, roughly 30% of BWMS types approved by USCG include the electrolysis method therefore being one of the most used system types applied to BWMS to date.^[16] Electrolytic treatment adopted in BWMS effectively disinfects any marine species in ballast water using an oxidizing agent generated through simple electrolysis of seawater such as chlorine, sodium hypochlorite, and hypochlorous acid.^[17] These oxidants act as a powerful biocide, effectually killing aquatic microorganisms inside ballast water. The total sum of these free chlorine and the combined available chlorine residual is termed as the total residual chlorine (TRC) and the total residual oxidant (TRO) is expressed for a broader definition of TRC.

The sterilization performance of the electrochlorination-based BWMS depends on the TRC concentration. The sufficient concentration of TRC for effective disinfection is found to require at least 5 mg L^{-1} . However, corrosion of the ballast water tank could occur when TRC concentration exceeds 10 mg L^{-1} and discharge of electrolytically-treated ballast water with TRC concentration higher than 15 mg L^{-1} could lead to severe threat to the ocean ecosystem.^[18] Therefore, a neutralization process must be needed to maintain optimal TRC concentration ranging at nearly 5 mg L^{-1} for ballast water and less than 0.1 mg L^{-1} TRC concentration for discharged de-ballast water.^[19] Moreover, chlorination treatment can generate disinfection by-products (DBPs), partic-

ularly trihalomethanes, halogenated acetic acids, and bromate, having potential ecotoxicity to de-ballast water when discharged without further removal of DBPs.^[20] On account of such reasons, self-monitoring of ballast water with continuous TRC measurement is included in essential requirement by USEPA VGP for BWMS type adopting electrolysis method.^[11] Accordingly, a precise sensing method for TRC is crucial for the efficient on-site operation of BWMS to continuously control the TRC concentration, so as to meet the regulation requirements.

The colorimetric method using N,N-diethyl-p-phenylenediamine (DPD) reagents, known as the DPD method is the current gold standard for free chlorine (Cl) measurement used in aqueous system. The DPD method utilizes a chemical reaction between free Cl and the DPD reagent. Through redox reaction between chlorine and the DPD reagent, colorless DPD can be oxidized to a radical form of $\text{DPD}^{\bullet+}$ by electron transfer.^[21] $\text{DPD}^{\bullet+}$ radical is stabilized by resonance and acquires a fairly stable magenta color with an absorbance wavelength of 551 nm, which is quantitatively proportional to the concentration of the TRC in the sample.^[22] The DPD colorimetric method provides a fast response and high consistency under various conditions, making it the most commonly applied TRC measurement method in BWMS. However, there are several shortcomings associated with the DPD method such as generating waste stream due to usage of the toxic chemical reagent and requiring periodic replacement of the reagent.^[23]

Hence lately, electrochemical sensing technologies have been applied in order to overcome such limitations of the current DPD method based-TRC sensor installed in BWMS. Electrochemical sensors are well established in a number of industries for water quality monitoring, providing high sensitivity and accuracy for the detection of free Cl. In addition to such benefits, electrochemical sensors provide wider detection ranges, fast response, low footprints, reagent reagent-less detection method which make them attractive candidates for TRC sensor in BWMS.^[24] Yet, there are several challenges to overcome when TRC sensors are to be applied in BWMS. The sensing environment in ballast water differs significantly from other aqueous systems like pools, rivers, or wastewater treatment plants due to the unique characteristics of ballast water and its regulatory requirements. Ballast water often includes a mixture of freshwater and seawater, with high variability in salinity, turbidity, and the presence of organic material, sediments, and potential contaminants.^[25] Also, the sensing environment in ballast water is more challenging for continuous monitoring systems due to factors like biofouling, the confined nature of ballast tanks, and dynamic conditions

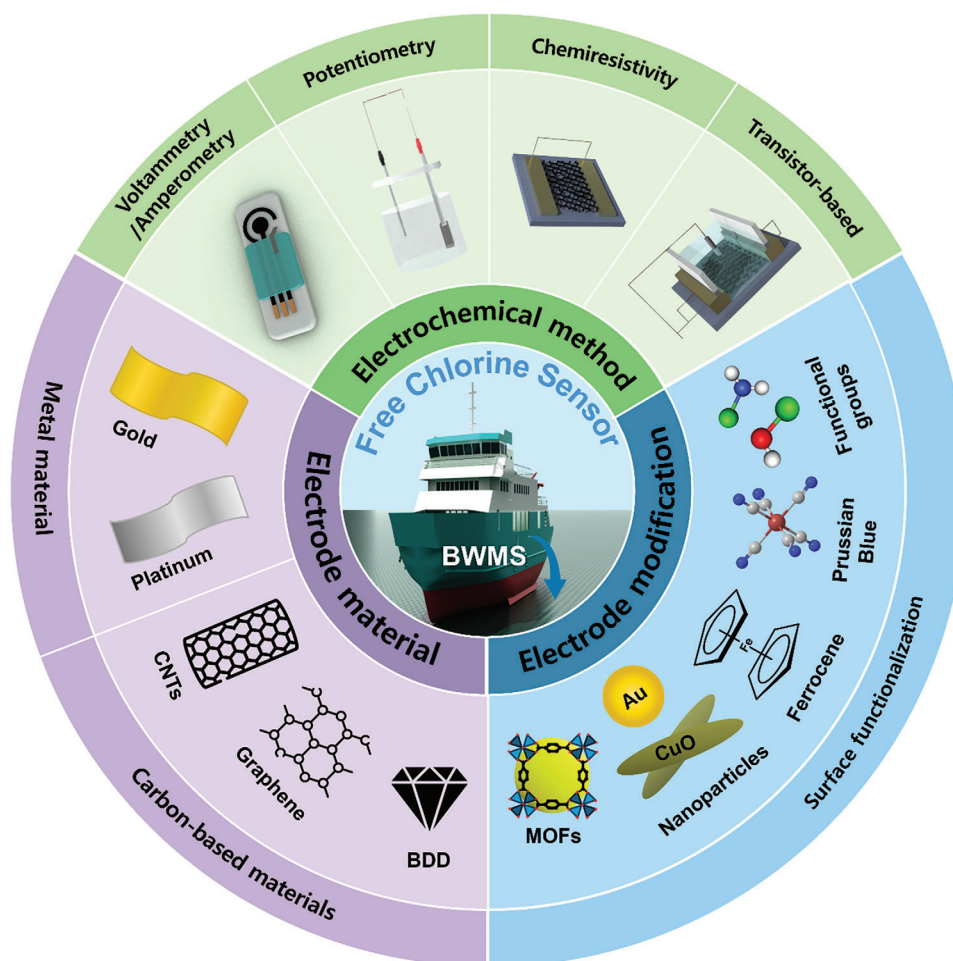


Figure 1. Schematic representation of electrochemical free Cl sensor in BWMS.

during voyages.^[26] Thus, TRC sensors for BWMS need to be robust and stable to endure harsh conditions and require high specificity and sensitivity. Besides, TRC measurements in BWMS mainly focus on specific periods, especially during ballasting for tracking treatment dose and de-ballasting process for monitoring residual concentrations, which occur intermittently and are dependent on vessel cargo operations.^[24] Therefore, TRC sensors for BWMS should be operated with minimal maintenance and high stability since any technical support is almost unavailable during shipping. Furthermore, the requirement to manage invasive species and disinfection reagents inside ballast water in accordance with international regulations adds a layer of complexity to the TRC sensors utilized for BWMS.

A number of review papers have been published, addressing different types of sensors for free chlorine measurement.^[27] Banna et al. reviewed general sensing methods for measurement of water quality parameters.^[28] Kruse reviewed various types of water quality monitoring sensors, focusing on compiling and tabulating the various types of sensors.^[29] Qin et al. provided with a detailed review about microfabricated electrochemical-free Cl sensors.^[30] However, to the best of our knowledge, electrochemical-based TRC sensors particularly applied for BWMS have not yet been precisely reviewed. Herein,

this review focuses on recent advances on electrochemical sensors for free chlorine measurement and highlights some of promising fabrications that could be applied to TRC sensor in BWMS. Finally, future perspectives on improvement of performance of electrochemical sensors in order to address the difficulties of applying in BWMS are discussed. An overview of this review is depicted in **Figure 1**.

2. Basic Principles for Electrochemical Detection of Free Chlorine

2.1. Ballast Water Treatment

Ballast water is essential for maintaining a ship's stability and maneuverability and is achieved by storing seawater in ballast tanks when the ship is not loaded. However, invasive species introduced into foreign ecosystems through ballast water can cause serious ecological and economic damage. Therefore, all ships are required to comply with the BWMS adopted by the IMO. Ballast water treatment involves filtration and secondary treatment, which includes mechano-physical and chemical processes, and disinfection.^[31,32] Mechano-physical treatments typically include UV, heat treatment, ultrasound, cavitation, and electric pulses.

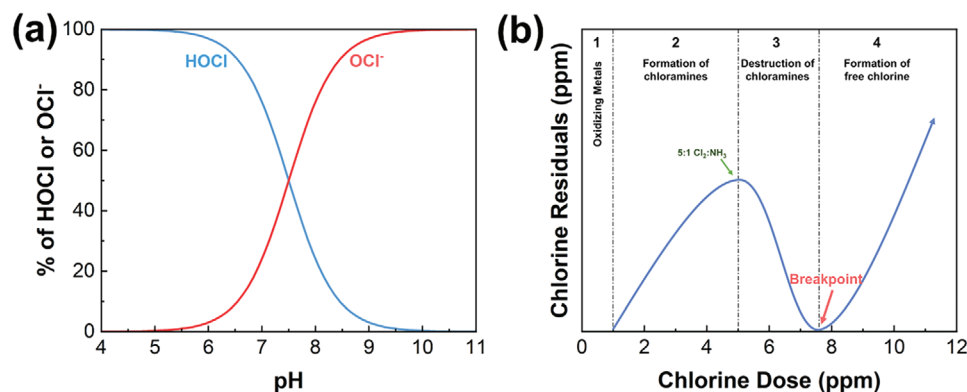
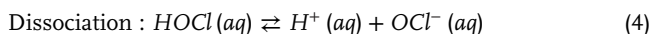
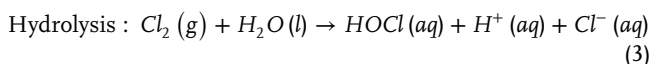
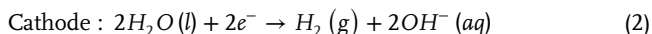
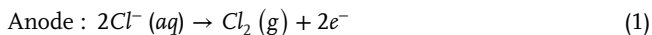


Figure 2. a) Distribution of HOCl and OCl[−] depending on pH variation. b) The formation of residual Cl in seawater.

However, most ships rely on chemical treatments, including biocides, Cl, electrolytic Cl, ozone, and deoxygenation. Cl-based disinfection is particularly prevalent in ballast water treatment, and electrochlorination is the most widely used technique. In this section, we explain the principles governing the generation of free Cl during ballast water treatment, as well as the formation of residual Cl.

2.1.1. Free Cl Generation During Ballast Water Treatment

Cl is a powerful oxidizing agent that is commonly used in ballast water treatment. It effectively eliminates microorganisms by destroying cell membranes, inactivating enzymes, and damaging nucleic acids.^[33] Although Cl gas or hypochlorite salts can be directly incorporated into a system by installing a chlorinator, this approach can result in storage and corrosion issues. Moreover, the effectiveness of Cl disinfection is highly influenced by factors such as temperature, pH, Cl concentration, organic matter content, type and quantity of microorganisms, and exposure time.^[34] Electrochlorination is a cost-effective and widely applied disinfection technology for ballast water treatment systems.^[35] Seawater typically contains $\approx 19 \text{ g L}^{-1}$ chloride, which facilitates efficient electrochemical disinfection.^[36] The process of electrochlorination of seawater involves passing an electric current through the seawater in an electrolytic cell, producing hypochlorous acid (HOCl) and OCl[−], which effectively eliminate microorganisms and contaminants in the water.



The above reaction equation explains the electrochemical chlorination process in seawater.^[37] Seawater and chloride ions undergo electrochemical oxidation reactions to produce oxygen, Cl gas, and hydrogen ions. Subsequently, Cl gas reacts with water to form OCl[−] and hypochlorous acid. Real-time generation of

hypochlorous acid eliminates the need to store highly concentrated OCl[−] solutions, thereby rendering the process economical, safe, and capable of providing rapid disinfection.^[38] However, it is sensitive to pH and depends on factors such as salinity, temperature, and reaction time. As shown in **Figure 2a**, HOCl and OCl[−] are pH-sensitive, with HOCl being dominant at pH levels below 7.5 and OCl[−] becoming predominant at pH levels above 7.5. As HOCl is 80–200 times more potent as a disinfectant than OCl[−], the disinfection efficiency of the electrochlorination system decreases at higher pH levels.^[39] In addition, a lower salinity results in a reduced amount of Cl gas being generated during the electrochlorination process, which can decrease the disinfection efficiency. In contrast, at lower temperatures, the Cl concentration is maintained for a longer period, potentially increasing the disinfection efficiency.^[40] The presence of other naturally occurring organic matter or halide ions in seawater can facilitate the formation of disinfection by-products, such as trihalomethanes, haloacetic acids, or hypobromous acid. These by-products can diminish the effectiveness of the disinfection process and pose risks to marine ecosystems.^[41]

2.1.2. Residual Free Chlorine Formation

Figure 2b shows the residual Cl formation process. The X-axis represents the Cl dosage (ppm) added to the seawater, and the Y-axis shows the residual Cl concentration (ppm). The formation of residual Cl occurs through four distinct stages following the introduction of Cl into seawater.^[42] In the first stage, Cl is consumed as it reacts with substances such as iron (Fe²⁺), manganese (Mn²⁺), and hydrogen sulfide (H₂S) in the seawater, leaving minimal to no free Cl. Once the reactions with these metals are complete, residual Cl begins to form. In the second stage, Cl reacts with ammonia and reactive organics to form combined free Cl in the form of chloramines.^[43] (Equation 5) At this point, any unbound free ammonia is completely converted. In the third stage, with the further addition of hypochlorous acid, as the Cl₂:NH₃ weight ratio reaches 5:1, no free ammonia remains. Consequently, the amount of monochloramine decreases as it reacts with free Cl to form dichloramine. (Equation 6) Although chloramines are less effective as disinfectants compared to OCl[−], they still function as sanitizing agents. When sufficient Cl is added, and the Cl₂:NH₃ weight ratio reaches approximately 7.6:1, which

Table 2. Comparison of electrochemical methods, monitored electrical properties, and electrode configurations.

Electrochemical methods	Monitored electrical properties	Electrode configuration
Voltammetry	Current as a function of applied potential	3 electrodes
Amperometry	Current at a fixed potential	3 electrodes
Potentiometry	Potential at zero current	2 electrodes
Chemiresistivity	Resistance or conductance	2-terminal device
Transistor-based	Current or voltage as applied V_{SD} at fixed V_G	3-terminal device

can vary between 8:1 and 10:1 depending on factors such as pH, temperature, and the presence of reducing agents, a breakpoint occurs.^[44] At this breakpoint, free Cl ($HOCl$, OCl^-) becomes the predominant form of free Cl, thus marking the beginning of effective disinfection. After the breakpoint, chloramines are nearly eliminated and the available residual free Cl becomes dominant, continuing to provide disinfection. Therefore, the continuous monitoring of the Cl dosage and free Cl concentration before discharge is crucial to ensure regulatory compliance, highlighting the importance of electrochemical sensors in the process.



2.2. Electrochemical Sensors

Electrochemical sensors are crucial tools for the real-time, precise measurement of substance concentrations in various environmental and industrial applications. Comprising an active sensing material (receptor) and a signal transducer, these sensors detect and convert interactions with analytes into measurable energy, which is then transformed into an analytical signal.^[45] This facilitates accurate detection and quantification of specific analytes. Electrochemical sensors offer significant advantages over colorimetric, fluorometric, and luminometric sensors for the continuous monitoring of Cl concentrations, leading to extensive research in this field.^[46–48]

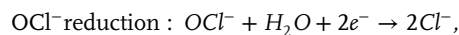
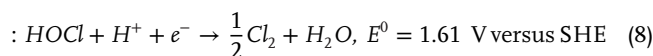
Electrochemical sensors can be classified into voltammetry-, amperometry-, potentiometry-, chemiresistivity-, and transistor-based sensors, depending on the monitored electrical properties; their specific characteristics are detailed in Table 2. These sensors typically employ either a two-electrode or a three-electrode configuration.^[49]

The surface of the working electrode (WE) facilitates electrochemical reactions with the analyte, resulting in current generation. The reference electrode (RE) provides a stable potential, thereby ensuring the accuracy and reproducibility of measurements, whereas the counter electrode (CE) completes the electrical circuit and maintains the electrical balance of the system. In this system, free Cl is detected at the electrode surface where it undergoes reduction or oxidation reactions, generating a current that is detected by the sensor. The irreversible reduction reactions of free Cl, along with their reduction potentials (E^0) at 1 atm and

25 °C, are detailed in Equations (7–9).^[50,51]



$$E^0 = 1.48 \text{ V vs SHE} \quad (7)$$



$$E^0 = 0.90 \text{ V versus SHE} \quad (9)$$

This process facilitates the real-time monitoring and management of ballast water, with the data processing unit optimizing the Cl disinfection efficiency based on the detected current. In this section, we discuss measurement methods using electrochemical sensors and explore the different operating principles of various electrochemical sensors.

2.2.1. Cyclic Voltammetry

Cyclic voltammetry (CV) is an extensively used electrochemical technique for studying the reduction and oxidation reactions of analytes driven by electron transfer.^[52–54] In CV, the potential applied to the WE is linearly swept over time relative to the RE and then reversed to create a cyclic loop during which the resulting current is measured. Peak currents are obtained when oxidation or reduction reactions occur at the surface of the electrode. These peaks are influenced by the concentration of the analyte and the rate of charge transfer. This relationship is expressed as the Nernst equation (Equation (10)), which elucidates the correlation between the electrode potential and the concentrations of oxidized (Ox) and reduced (Red) species in a system at equilibrium.

$$E = E^0 + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]} \quad (10)$$

where E^0 is the standard potential of the analytes, F is Faraday's constant, R is the gas constant, n is the number of electrons, and $[Ox]$ and $[Red]$ are the concentrations of the oxidized and reduced analytes, respectively. In CV experiments, the current density represents the number of redox species, whereas the peak potential reflects the characteristics of the electron transfer rate for the corresponding redox reaction. Figure 3a shows a typical CV curve, where the oxidation and reduction peak potentials (E_{pa} and E_{pc}), peak currents (i_{pa} and i_{pc}), and the differences between the peak potentials can be observed. CV facilitates the detailed analysis of redox reactions as a function of the electrode material, electrode size, and scan rate. Notably, the scan rate is a crucial variable that influences the size of the diffusion layer and the magnitude of the redox peak currents. According to the Randles–Sevcik equation for reversible processes, the peak current increases linearly with the square root of the scan rate^[55] (Equation 11).

$$i_p = (2.69 \times 10^5) n^{\frac{3}{2}} A D_0^{\frac{1}{2}} C_0 v^{\frac{1}{2}} \quad (11)$$

where, i_p is the peak current, n is the number of electrons in the reaction, A is the surface area of the WE, D_0 is the diffusion

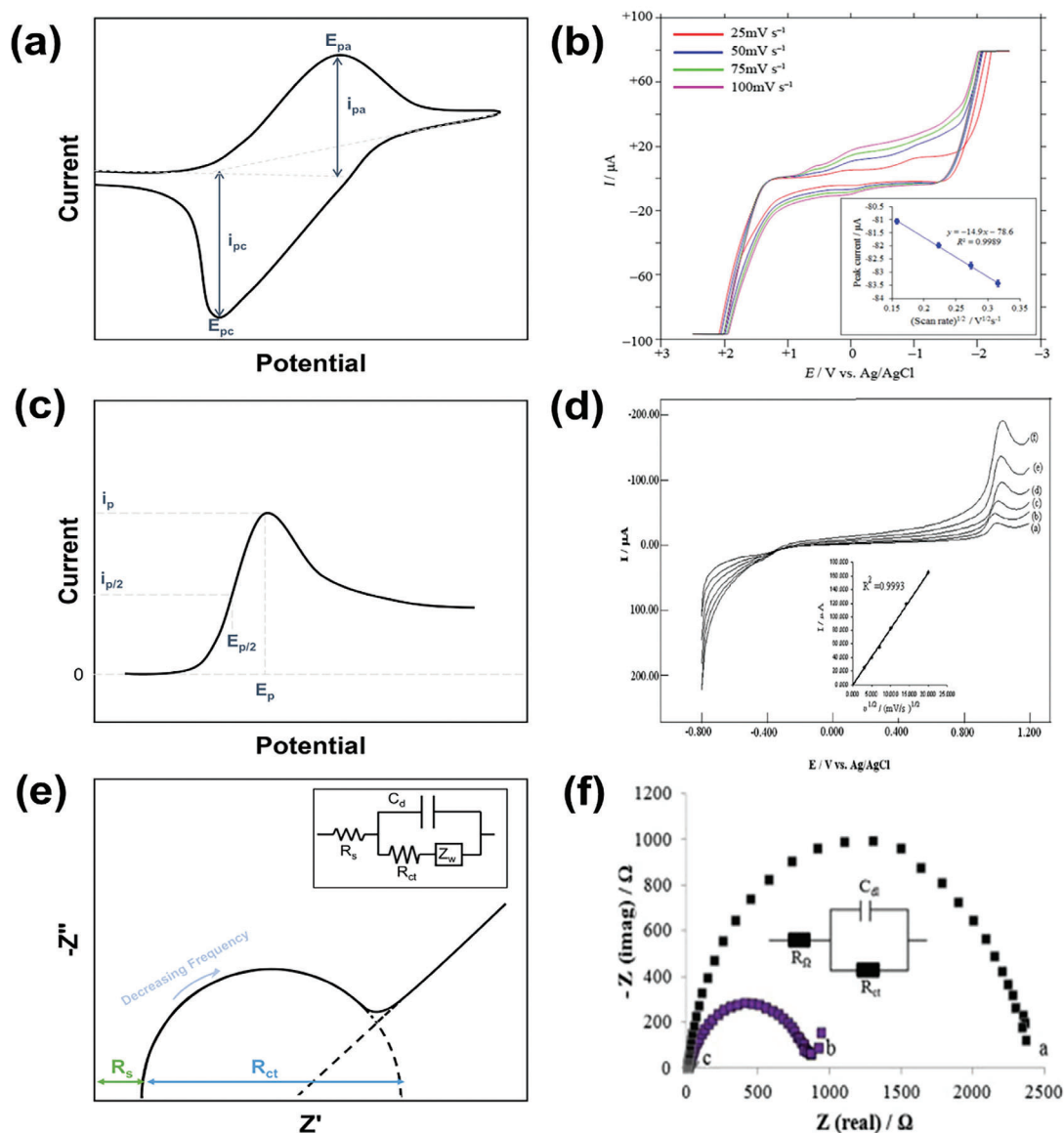


Figure 3. a) Examples of cyclic voltammograms showing the oxidation and reduction peak potentials (E_{pa} , E_{pc}), peak current (i_{pa} , i_{pc}). b) CV voltammograms of the chlorinated seawater solution for the free Cl concentration of 0.06 mol L^{-1} in the various scan rate (25, 50, 75, and 100 mV s^{-1}) at a GEC electrode. The inset illustrates the relationship between current and the square root of the scan rate. Reproduced under terms of the CC-BY license.^[59] Copyright 2024, The Authors, published by Elsevier. c) Representative linear sweep voltammetry result showing redox peak potential (E_p) and peak current (i_p). d) Linear sweep voltammograms for a solution containing $50 \text{ mg dm}^{-3} \text{ OCl}^-$ in $0.1 \text{ mol dm}^{-3} \text{ KNO}_3$ using a graphite electrode. The initial and final potentials were set at -0.800 and $+1.200 \text{ V}$, respectively. Scan rates were: (a) 10 mV s^{-1} , (b) 25 mV s^{-1} , (c) 50 mV s^{-1} , (d) 100 mV s^{-1} , (e) 250 mV s^{-1} , (f) 400 mV s^{-1} . The inset displays a Randles-Sevcik plot of anodic peak current versus the square root of the scan rate. Reproduced under terms of the CC-BY license.^[66] Copyright 2008, The Authors, published by National Science Foundation of Sri Lanka. e) Nyquist plot of the impedance spectrum recorded for the system. In the corresponding Nyquist plot, the R_s value at the starting point on the left represents the solution resistance, while the diameter of the semicircular curve reflects the R_{ct} . The curvature of the semicircle is influenced by the C_d , and the linear portion at low frequencies indicates the diffusion resistance associated with W_d . The inset displays ideal Randles equivalent circuit model used for fitting. f) Electrochemical impedance spectra for nanocomposite electrodes: (a) raw MWCNTs, (b) CuO-NPs@MWCNTs, and (c) bulk CuO-NPs, measured in a 0.1 M KCl solution containing $0.01 \text{ M } [\text{Fe}(\text{CN})_6]^{3-/4-}$. The inset illustrates the equivalent circuit model applied for fitting the impedance data. Reproduced with permission.^[75] Copyright 2015, Elsevier.

coefficient of the analyte, C_0 is the concentration of the analyte, and ν is the scan rate. This equation plays a critical role in analyzing the characteristics of the electrode and kinetics of the reaction.^[56–58] Figure 3b illustrates the hydrogen oxidation peak currents for a graphite-epoxy composite (GEC) electrode

at various scan rates (25, 50, 75, and 100 mV s^{-1}) in seawater containing 0.06 mg L^{-1} of free Cl. As evident, the peak current increased linearly with the square root of the scan rate, indicating that the reaction was diffusion controlled. In addition, the GEC electrode demonstrated a very high correlation coefficient

(R^2) of 0.9998, indicating the reliability of the experimental results.^[59]

2.2.2. Linear Sweep Voltammetry

Linear Sweep Voltammetry (LSV) is an electrochemical technique wherein the potential applied to an electrode is linearly increased along one direction over time and the resulting current is measured.^[60,61] During this process, redox reactions occurring at the electrode surface generate a peak current, which is determined by the characteristics of the analyte and electron transfer kinetics.^[62] In contrast to CV, LSV is characterized by a unidirectional change in the potential. Figure 3c illustrates a typical LSV curve. In LSV, the potential increases linearly from an initial value E_i over time, as defined by Equation (12).

$$E(t) = E_i - vt \quad (12)$$

As the potential increases, redox reactions occur at the electrode surface, expressed as Equation (13).



This results in the appearance of a peak current and corresponding peak potential, which are observed as analytes are consumed and new analytes diffuse to the electrode surface, a process that is governed by Fick's first law.^[63] Following the peak, the current decreases with the expansion of the diffusion layer, thereby limiting the supply of reactants to the electrode surface. The LSV characteristics are influenced by several factors, including the electron transfer rate, chemical reactivity of the analyte, and scan rate.^[64–66] A higher electron transfer rate typically facilitates a higher and sharper peak current. In addition, a faster scan rate, which underlies the diffusion phenomenon described by the Randles–Sevcik equation, results in higher current peaks, whereas a slower scan rate allows the current to spread over a wider potential range, resulting in broader peaks. These factors are crucial for understanding the electrochemical behavior of the analytes during LSV measurements.

Figure 3d presents the LSV curves for a OCl^- concentration with the graphite electrode, obtained by linearly varying the potential from -0.8 to $+1.2$ V at different scan rates (10, 25, 50, 100, 250, and 400 mV s^{-1}).^[66] At lower scan rates between 10 – 50 mV s^{-1} , the peak potential gradually shifted along the positive direction, and the peak current increased. At higher scan rates, the peak current continued to increase, while the peak potential remained constant at $+1.040$ V. In addition, the inset shows a Randles–Sevcik plot, which demonstrates a high linearity between the peak current and the square root of the scan rate, with an excellent R^2 of 0.9993.

2.2.3. Impedance Analysis

Impedance analysis, commonly known as electrochemical impedance spectroscopy (EIS), is a powerful technique that is widely used to study electrochemical processes occurring at the electrode/electrolyte interface.^[67,68] EIS measurements involve

the application of a small sinusoidal alternating current (AC) voltage to the system and the measurement of the resulting voltage and current responses. The impedance of the system is calculated from the relationship between these two quantities. Impedance is a critical parameter for assessing the resistance and reaction kinetics within an electrochemical system, enabling a detailed analysis of the electrical behavior of the system across a spectrum of frequencies.^[69] Impedance can be categorized into Faradaic and non-Faradaic components. The Faradaic component is related to the current generated via electron transfer during redox reactions at the electrode/electrolyte interface, involving charge transfer resistance (R_{ct}). It influences the reaction kinetics and is essential for understanding the efficiency of electron transfer at the electrode surface. In contrast, the non-Faradaic component pertains to the current owing to the charging of the double-layer capacitance (C_d) at the electrode surface, where no chemical redox reactions occur, and charge accumulation occurs without electron transfer. In EIS, the measured data are visually represented via a Nyquist plot (Figure 3e), which depicts the resistive (real component, Z') and reactive (imaginary component, $-Z''$) properties of the system, exhibiting an increasing impedance pattern with a decrease in the frequency.^[70] The inset graph in Figure 3e illustrates the ideal Randles equivalent circuit, which is commonly used for EIS analysis. This circuit comprises the electrolyte resistance (R_s), R_{ct} between the electrode and electrolyte, C_d formed at the electrode surface, and diffusion resistance owing to mass transport (Warburg impedance, W_d).^[71] Impedance analysis aids in gaining a deep understanding of the reaction mechanisms and performances of electrochemical sensors. It facilitates the optimization of sensor performance metrics, such as sensitivity, selectivity, and limit of detection (LOD).^[72–74]

Figure 3f shows the EIS results of a modified nanocomposite electrode incorporating CuO nanoparticles (NPs) for the detection of free Cl. This analysis assessed the ohmic resistance (R_Ω) and R_{ct} of three different electrodes: (a) raw multi-walled carbon nanotubes (MWCNT)/epoxy, (b) CuO-NPs/MWCNT/epoxy, and (c) CuO-NPs/MWCNT/epoxy.^[75] The impedance spectra were interpreted using the equivalent circuit model ($R_\Omega \cdot (R_{ct} \cdot C_d)$), as presented in the inset of Figure 3f. The incorporation of CuO-NPs, serving as electron mediators, significantly reduced the R_Ω values, which were dependent on ionic concentration. The reduction observed was from 126.7Ω in the original MWCNT/epoxy to 92.6Ω in CuO-NPs/MWCNT/epoxy, and further to 13.7Ω in CuO-NPs/MWCNT/epoxy. In addition, the R_{ct} values, related to electron transfer, were notably reduced from 2360.3Ω in the original MWCNT/epoxy to 976.4Ω in CuO-NPs/MWCNT/epoxy, and further to 84.9Ω in CuO-NPs/MWCNT/epoxy. These findings suggest that CuO-NPs/MWCNTs play a pivotal role in enhancing electron transfer, thereby significantly improving the sensitivity and response speed for the detection of free Cl.

2.2.4. Voltammetric Sensors

A voltammetric sensor functions via the application of a variable voltage to the electrode system and leveraging the electrochemical reactions occurring at the electrode surface to quantify the concentration and determine the characteristics of the analyte.

Typically, this sensor utilizes a three-electrode configuration (Figure 4a), wherein a variable voltage is applied between the WE and RE, and the resultant variations in current are recorded.^[76,77] Analytes such as free Cl are selectively detected at specific redox potentials. Various voltammetric techniques, including LSV, CV, differential pulse voltammetry, square-wave voltammetry, and cathodic stripping voltammetry, offer high sensitivity and selectivity while minimizing signal noise.^[78–80] These sensors are particularly well suited for real-time monitoring of free Cl, with sensitivity that can be tailored based on the electrode material, electrolyte composition, and measurement conditions.

Ko et al. conducted CV measurements with a platinum (Pt) disk electrode as the WE to measure the concentration of free Cl in ozonated seawater.^[81] As shown in Figure 4b, the CV experiments conducted with different seawater electrolytes revealed that the current at Peak 2 was proportional to the concentration of free Cl in all electrolytes. This finding was based on the principle that free Cl promoted the oxidation of hydrogen molecules, demonstrating that the current at Peak 2 could be used to accurately measure the concentration of free Cl in seawater. Figure 4c presents a linear regression line illustrating the relationship between the free Cl concentration and current at Peak 2. This relationship exhibited linearity in the range of 0.02–0.4 mg L^{−1} with a correlation coefficient (R^2) of 0.9982. From this data, the following linear regression equation was derived: $I_{p2}(\mu A) = (-81.259 \pm 5.748) [\text{free Cl}] (\text{mg L}^{-1}) - (131.34 \pm 1.47)$.

In this equation, the slope of $-81.259 \mu A \text{ mg L}^{-1}$ indicated the sensitivity of the electrode. The LOD for free Cl was calculated to be $1.2 \times 10^{-2} \text{ mg L}^{-1}$ using the formula $\frac{3\sigma}{S}$ (where 3 is the S/N ratio, σ is the standard deviation of the current, and S is the sensitivity of the electrode). Consequently, it was concluded that the Pt disk electrode offered higher sensitivity and a lower LOD than the other electrodes.

2.2.5. Amperometric Sensors

Amperometric sensors measure the current generated when an analyte undergoes a redox reaction at the electrode surface.^[82,83] This sensor operates via the application of a constant potential to the WE and the detection of the current produced in direct proportion to the concentration of the analyte undergoing selective oxidation or reduction. Amperometric sensors are typically configured using a three-electrode system. However, in recent years, cost-effective and mass-producible screen-printed electrodes (SPEs) have been widely adopted.^[84–86] (Figure 4d) Chronoamperometry (CA), an essential technique in amperometric measurements, records the current over time to analyze the concentration and diffusion coefficient of the analyte. Figure 4e illustrates a typical chronoamperometric experiment. The experiment began at an initial potential E_i , and at $t = 0$, the potential was switched to a new value E_1 . This change induced a redox reaction of the analyte, and the resulting current was recorded as a function of time.^[87,88] Initially, the capacitive current, which is associated with the formation of an electrical double layer, was dominant. This current, known as the non-Faradaic current, occurs without any electrochemical reaction and decreases exponentially over time. As time progressed, the analyte diffused to the electrode surface, and the Faradaic cur-

rent became dominant. This current is proportional to the analyte concentration and inversely proportional to the square root of time, as described by the Cottrell equation (Equation 14).^[89]

$$i(t) = \frac{nFD^{1/2}CA}{\pi^{1/2}t^{1/2}} = kt^{-1/2} \quad (14)$$

where n is the number of electrons ($n = 2$ for the reduction of free Cl), F is Faraday's constant, D is the diffusion coefficient of analyte (1.0×10^{-9} – $2.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 25 °C for free Cl), C is the concentration of analyte, and A is the surface area of the electrode.^[90,91] Through this equation, both the concentration and diffusion coefficient of the analyte can be determined. Salazar et al. developed a sensor utilizing surfactant-modified Prussian blue (PB) screen-printed carbon electrodes (SPCEs/PB-BZT) to establish a linear relationship between the free Cl concentration and current. Subsequently, they calculated the diffusion coefficient of free Cl using CA.^[92] Figure 4f presents the current versus time graph obtained from the PB sensor in the absence of free Cl across the concentration range of 0–180 ppm. The graph demonstrated that the current increased linearly with free Cl concentration, which is consistent with the Cottrell equation. The current exhibited a high R^2 of 0.999, with the relationship expressed as $I(\mu A) = 0.028 [\text{free Cl}] (\text{ppm}) + 0.001$. Based on this, the diffusion coefficient of free Cl was calculated to be $1.26 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. This value aligned with values reported in the literature, thereby confirming the superior performance of the sensor.

Several key considerations must be considered when employing amperometric sensors. First, the measurement duration necessitates careful attention. Short measurement times may result in inaccuracies owing to the charging process of the electrical double layer at the electrode surface. Conversely, prolonged measurements can introduce natural convection effects caused by temperature and concentration gradients, which may result in mass transport that is not diffusion-controlled, thereby compromising data reliability.^[93] Second, the selection of the applied potential is critical. Although amperometric sensors exhibit high selectivity at specific potentials, the application of an excessively extreme potential (either highly positive or negative) can result in the oxidation or reduction of additional species, thereby diminishing selectivity for the target analyte. To mitigate such interferences, it is advisable to use a low potential range, typically between -0.2 and 0.2 V . Moreover, as the potential is fixed in amperometric methods, the applied potential for measuring the analyte's current should slightly exceed the potential at which the peak current is observed in the voltammogram, and measurements should be conducted in a region with minimal residual current.^[94] Third, the sensitivity of the sensor may gradually decrease owing to the adsorption of reaction products on the electrode surface, which can interfere with electron transfer because of the heterogeneous electrochemical reactions occurring at the interface between the electrode surface and solution.^[95] To address this issue, pulse voltammetry can be employed to measure the current over short sampling intervals. Else, larger negative or positive potentials can be applied to regenerate the electrode surface. These techniques enhance the sensor performance and minimize potential issues that may arise during long-term measurements.

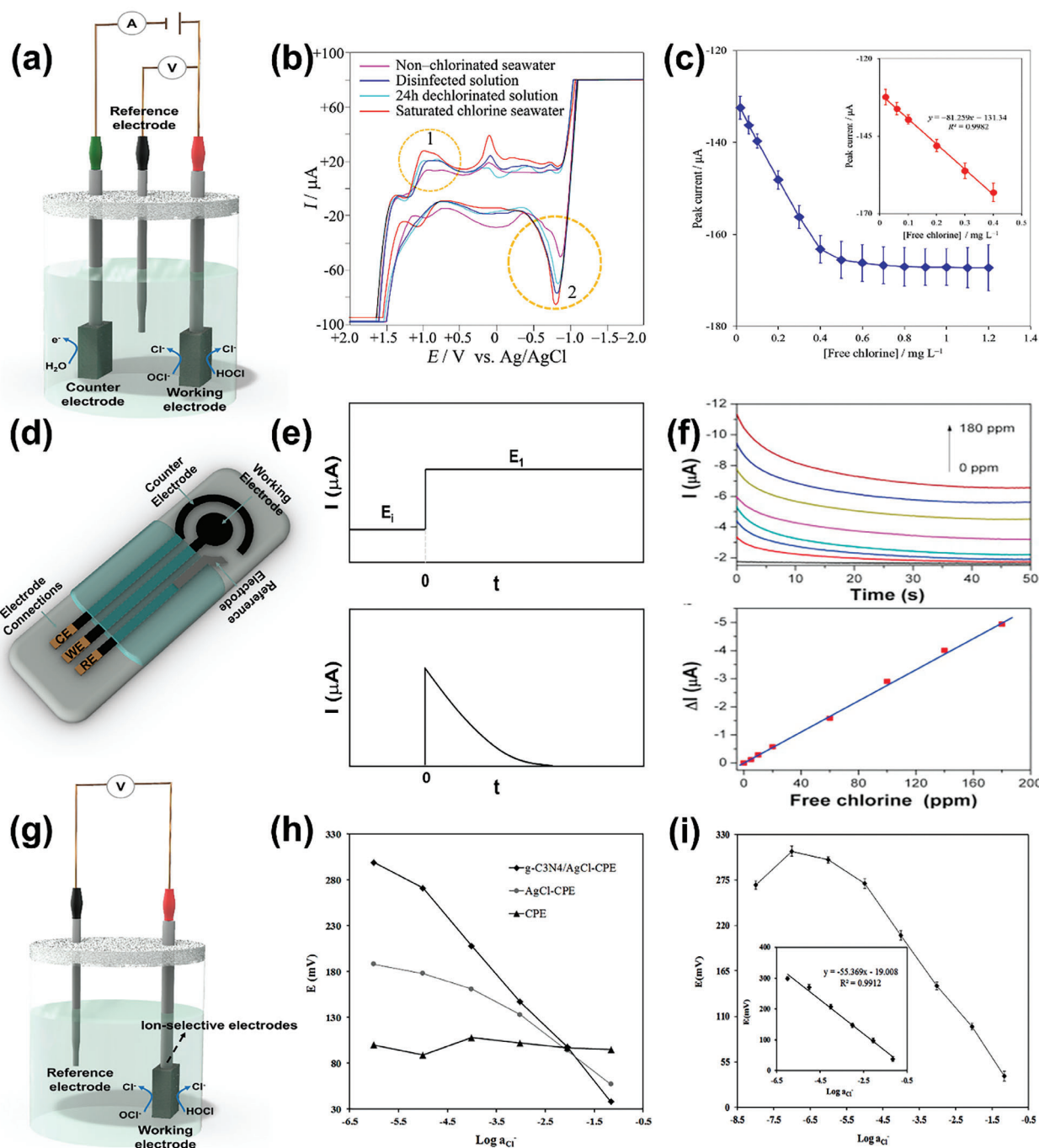


Figure 4. a) Schematic representation of the voltammetric sensor setup featuring a three-electrode configuration: WE, RE, and CE. b) Cyclic voltammograms recorded in four different seawater solutions using a bare Pt disk electrode at a scan rate of 100 mV s^{-1} . Reproduced with permission.^[81] Copyright 2022, Elsevier. c) Correlation between peak current (I_{p2}) and free Cl concentrations ranging from 0.02 to 1.2 mg L^{-1} . Inset: Calibration curve for free Cl concentrations from 0.02 to 0.4 mg L^{-1} , with error bars representing the standard deviation ($n = 5$). Reproduced with permission.^[81] Copyright 2022, Elsevier. d) Schematic illustration of the screen-printed electrode configuration used in the amperometric sensor, featuring the WE, RE, and CE. e) Potential step applied at $t = 0$ during chronoamperometry measurements, and the corresponding current response as a function of time. f) Chronoamperograms of a PB-BZT sensor at varying free Cl concentrations (0, 5, 10, 20, 60, 100, 150, and 180 ppm) in PBS, with an applied potential of -0.15 V. and the calibration curve derived from the data of the upper graph. Reproduced with permission.^[92] Copyright 2015, Elsevier. g) Schematic of the two-electrode system used in the potentiometric sensor, comprising a WE and a RE. h) Comparison of potentiometric responses to Cl^- ($\text{pH} = 3.5$) using $\text{g-C}_3\text{N}_4/\text{AgCl-CPE}$, AgCl-CPE , and CPE electrodes. Reproduced with permission.^[109] Copyright 2022, Elsevier. i) Calibration curve for free Cl activity measurement using the $\text{g-C}_3\text{N}_4/\text{AgCl-CPE}$; the inset shows the linear dynamic range of the calibration curve. Measurement conducted at $\text{pH} = 3.5$. Reproduced with permission.^[109] Copyright 2022, Elsevier.

2.2.6. Potentiometric Sensors

A potentiometric sensor is a two-electrode system (Figure 4g) that measures the open-circuit potential between two-electrodes to detect the concentration of specific ions in a solution.^[96,97] The potential difference is generated with the variation of the potential of the WE according to the concentration of the target ion, whereas the RE, typically Ag/AgCl, maintains a stable potential. The measured potential difference is directly related to the ion concentration via the Nernst equation (Equation (10)). A logarithmic relationship is prevalent between the potential difference and ion concentration, facilitating the potentiometric sensor in effectively detecting the variations in ion concentration.^[98]

Ion-selective electrodes (ISEs) are commonly used to accurately measure target ions while minimizing interference from other ions. Their performance is evaluated using a selectivity coefficient.^[99] Carbon paste electrodes (CPEs) are widely used as ISEs owing to their compatibility with various materials, ease of fabrication, reusability, stable electrochemical performance, and structural flexibility.^[100–103] The sensitivity of potentiometric sensors for detecting free Cl can be diminished by characteristics such as weak basicity, large ionic size, spherical shape, and low charge density of free Cl. Moreover, because of the low exchange current density of free Cl, electrode finds it difficult to reach electrochemical equilibrium and achieve a stable potential. The high oxidative power of free Cl can also passivate the electrode surface, thereby degrading the electrode performance. To address these issues, Zhang et al. improved the selectivity and sensitivity of free Cl detection using ferrocene-based CPE electrodes, which exhibited a high exchange current density and low reactivity with the electrode surface.^[19]

Precipitate-based ISEs detect analyte concentrations by utilizing the precipitates formed via reactions between specific ions and the electrode material at the electrode surface.^[104,105] In these electrodes, the solubility product (K_{sp}) of the precipitate is inversely related to the LOD of the electrode. AgCl-CPE is commonly used to detect chloride ions because of its high selectivity for Cl ions, simple fabrication process, and stable potential.^[106–108] However, they have disadvantages such as high K_{sp} , uneven distribution within the electrode material, and reactivity with other halogen elements. Consequently, Alizadeh et al. developed a potentiometric sensor with a high selectivity and low LOD by combining graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) with AgCl in a CPE electrode.^[109] Figure 4h shows the potentiometric responses for free Cl detection using raw CPE, AgCl-CPE, and $g\text{-C}_3\text{N}_4/\text{AgCl-CPE}$. The $g\text{-C}_3\text{N}_4/\text{AgCl-CPE}$ electrode demonstrated more pronounced potential changes with varying Cl^- concentrations. This indicated the enhanced chloride ion detection capability. Figure 4i shows the results of the chloride ion concentration measurements using the $g\text{-C}_3\text{N}_4/\text{AgCl-CPE}$ electrode and the corresponding calibration curve in the inset graph. The sensor exhibited a linear response over a wide concentration range of 1×10^{-6} – 1×10^{-1} mol L^{-1} , with a slope of 55.7 mV/decade. Further, the LOD for chloride ions was as low as 4.0×10^{-7} mol L^{-1} . The $g\text{-C}_3\text{N}_4$ enhanced the crystal structure and particle size via strong bonding with Ag^+ , lowered the K_{sp} , and enabled uniform distribution. This resulted in high selectivity and effective detection even at low concentrations.

2.2.7. Chemiresistive Sensors

A chemiresistive sensor detects the concentration of specific analytes by changing the electrical resistance or conductivity through chemical interactions with the analyte.^[110,111] The transducing material, which is positioned between two-electrodes (source and drain) is the key component of such a sensor (Figure 5a). This transducing material undergoes a chemical reaction or exhibits changes in its electronic properties when the analyte comes in contact with or is adsorbed onto the sensor surface.

Free Cl functions as an oxidizing agent, inducing changes in the electronic state of the transducing material. During this process, free Cl accepts electrons from the transducing material, resulting in a charge transfer. This charge transfer can initiate oxidation reactions or alter the charge distribution on the sensor surface via electrostatic gating. These interactions modify the electron or hole density within the transducing material, which manifests as variations in electrical resistance or conductivity. The magnitude of these changes is proportional to the logarithmic scale of the free Cl concentration, which enables the sensor to precisely detect and quantify the concentration of free Cl. Specifically, materials such as phenyl-capped aniline tetramers (PCAT), single-walled carbon nanotubes (SWCNTs), poly(3,4-ethylenedioxythiophene) (styrenesulfonate) (PEDOT:PSS), and gold (Au) NPs can be easily oxidized by free Cl, causing significant changes in resistance.^[112–116]

Figure 5b illustrates a chemiresistive sensor based on graphene-like carbon (GLC). Thus, the sensor performance can be tuned according to the thickness of the GLC film.^[117] A thinner film provides higher sensitivity and a lower LOD, albeit with a restricted operational range. In contrast, a thicker film can detect a broader concentration range, but with lower sensitivity and a higher LOD. This phenomenon is attributed to the electrostatic gating effect, where the thinner films facilitate a stronger modulation of the charge distribution owing to interactions with the analyte, thereby maximizing the resistance change. However, the surface charge of the sensor saturates more easily, limiting its ability to detect a wide range of free Cl concentrations. Consequently, an optimal GCL thickness of 12 nm was selected, and the sensor's response was confirmed in the low concentration range of 0.01–0.2 ppm, as shown in Figure 5c, confirming the high sensitivity of the sensor. In addition, the sensor could detect very low concentrations (0.01 ppm), indicating a low LOD and high sensitivity.

The simple structure and high sensitivity of chemiresistive sensors render them particularly suitable for the real-time monitoring of free Cl in ballast water. These sensors can be manufactured at a low cost, easily miniaturized, and are reusable. This renders highly applicable in this specific field. However, chemiresistive sensors are sensitive to pH variations and oxidation–reduction potentials. This necessitates the careful adjustment of sensor sensitivity to optimize their performance in ballast water monitoring.^[118]

2.2.8. Field-Effect Transistor Sensors

Field-effect transistor (FET) sensors are three-terminal devices comprising source, drain, and gate electrodes.^[119,120] These

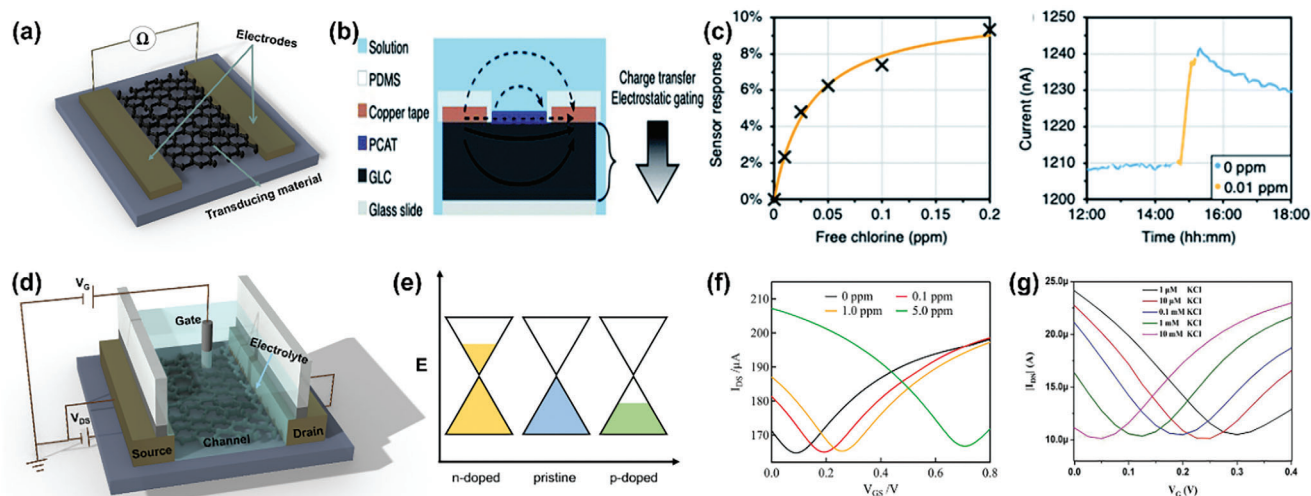


Figure 5. a) Schematic representation of a chemiresistive sensor utilizing graphene as the transducing material, highlighting the sensitive interaction between the graphene surface and free Cl, leading to measurable changes in resistance. b) Proposed mechanisms related to transducing film thickness of chemiresistive sensor. Solid arrows indicate current flow through the bulk of the GLC film, whereas dashed arrows represent the inhibited current paths through the analyte solution or PCAT molecular layers. The large arrow shows the diminishing charge transfer and electrostatic gating effects as they penetrate deeper into the bulk of the GLC. Reproduced under terms of the CC-BY-NC license.^[117] Copyright 2022, The Authors, published by The Royal Society of Chemistry. c) Sensor response of the PCAT-doped system to low concentrations of free Cl (applied potential: 100 mV, GLC thickness: 12 nm), along with an example of raw data corresponding to a 0.01 ppm free Cl measurement from one of the data points shown on the left. Reproduced under terms of the CC-BY-NC license.^[117] Copyright 2022, The Authors, published by The Royal Society of Chemistry. d) Schematic of a solution-gated graphene field-effect transistor (FET) sensor, highlighting the use of graphene as the conductive channel modulated by the electrolyte solution gate. e) Graphene's Dirac Cone showing the intersection of conduction and valence bands at the Dirac Point. The Fermi level aligns with the Dirac Point without an external field. f) Transfer curves of GFETs with Au gate electrodes at varying free Cl concentrations in 0.1 M PBS (pH 7). Reproduced with permission.^[119] Copyright 2024, The Royal Society of Chemistry. g) Transfer characteristics of an SGGT in a microchip, measured in KCl solutions with varying free Cl concentrations. Reproduced with permission.^[124] Copyright 2012, American Chemical Society.

sensors modulate the conductivity of the semiconductor channel through field effects. A voltage is applied between the source and drain, whereas the gate voltage is adjusted to control the current flow within the channel. Thus, the electron concentration is altered and the conductivity of solution-gated graphene field-effect transistors (GFETs) is changed to use an electrolyte to mediate the gate voltage, where the electric double layer formed at the electrolyte/graphene interface controls the conductivity of the channel.^[121] (Figure 5d) Graphene exhibits ambipolar behavior, which facilitates switching between n- and p-type conductivities through field-effect doping.^[122] The conductive properties of graphene are governed by the Dirac Point, where the conduction and valence bands intersect, thus minimizing the concentration of electric charge carriers. Figure 5e illustrates the Dirac Cone of graphene. As evident, without an external electric field, the Fermi level aligns with the Dirac Point. A negative field shifts the Fermi level below the Dirac Point, resulting in p-type behavior, whereas a positive field shifts the Fermi level above the Dirac point, leading to n-type behavior.

GFET sensors operate based on the principle that free Cl functions as an oxidizing agent at the electrode surface, interacting with the graphene channel and removing electrons, thereby modifying their electrical properties. Figure 5f illustrates the characteristic curve of the drain–source current (I_{DS}) versus gate voltage (V_G) for a GFET using an Au gate electrode.^[123] In this setup, free Cl functions as a p-type dopant by oxidizing graphene and removing electrons. Owing to the interaction of free Cl with graphene, the Fermi level shifts toward the valence band. With in-

creasing free Cl concentration, the Fermi level in graphene shifts further below the Dirac Point, thereby enhancing p-type doping and increasing V_G at the Dirac Point when using an Au electrode. This shift is attributable to the potential change induced by free Cl at the Au electrode. Conversely, with an Ag/AgCl electrode (Figure 5g), an increasing free Cl concentration results in the Ag/AgCl electrode potential shifting positively, according to the Nernst equation.^[124] This shift lowers the effective gate voltage applied to the graphene channel, causing the Dirac Point to shift toward a lower gate voltage. This effect occurs because the Ag/AgCl electrode adjusts its potential in response to changes in ion concentration. Although many studies have focused on the potential changes in the graphene active layer,^[125] potential changes at the gate electrode are equally crucial for sensing applications.^[126]

3. Materials for Working Electrode

Electrodes are among the most important considerations when constructing an electrochemical sensing system for free Cl detection. In particular, a WE that directly reacts with the target should exhibit high electrical conductivity, stability in the operating environment, and high reactivity toward the target substance. Furthermore, the electrode should have a high surface area to maximize the number of active sites, selectivity to minimize unwanted reactions, stability to facilitate measurements for as long as possible under operating conditions, economic feasibility, and biocompatibility.^[127,128]

In this section, the classification and characterization of representative materials used as WEs are discussed. We also review the electrical performance tests conducted on sensors that incorporate these materials. Subsequently, we address functionalization techniques that enhance critical parameters such as the sensitivity, selectivity, and stability of the electrodes. This section provides a theoretical and experimental foundation for the development of an efficient and environmentally friendly electrochemical monitoring system for the detection of free Cl in ballast water. **Table 3** summarizes the performances of the free Cl sensors.

3.1. Metals

Metals are preferred as basic electrode materials owing to their good electrical conductivity. In the electrochemical three-electrode sensor structure for free Cl detection, a non-polarizable silver (Ag)/silver chloride (AgCl) electrode is used as the RE because of its low resistance and high reproducibility. Whereas, Pt is used as the CE because of its inertness.^[129,130] Noble metals can also be used as WEs because they have high electrical conductivity, are easy to process, and can be used as nanostructures.^[131] Compared with other metal electrodes, Ag is inexpensive and can be fabricated into electrodes of various shapes through inkjet printing. However, owing to its narrow potential window and susceptibility to oxidation and sulfation, Ag has been rarely used as a WE.^[132]

Pt is a well-accepted material for electrodes in electrochemical sensors owing to its chemical stability.^[133] Ordeig et al. reported a Pt WE for the continuous monitoring of OCl^- in tap water.^[50] The current data of a Pt disk cathode based on the reduction reaction of free Cl indicate a fast response to OCl^- concentration changes within 30 s. Continuous OCl^- detection facilitates electrode passivation owing to the formation of an oxide layer on the Pt surface that can be removed electrochemically. However, the current generated by the reduction of dissolved oxygen degrades the accuracy of the test. Pt electrodes using oxidation currents generated by the anodic reaction of free Cl have yielded highly reproducible LSV results.^[134] A current below +800 mV, where the oxidation of free Cl occurs, indicates the lack of an oxidation reaction, because free Cl inhibits oxide layer formation. Consequently, current data with linear behavior was obtained for Cl concentrations of 0.1–12.0 mmol dm⁻³.

The advantages of the Au electrode, which exhibits a wide potential window and higher overpotential for oxygen reduction, render its use a dominant approach for amperometric sensors.^[135] Alam et al. designed a fabrication procedure for a thin-film Au-based free-Cl sensor.^[136] The simply fabricated sensor was integrated with a readout circuit to facilitate immediate sensing and demonstrated excellent reproducibility and high sensitivity in the HOCl concentration range of 0.8–5.5 ppm. The hysteresis, which represents the difference in the chronoamperometric response over a cycle of free Cl concentration, was negligible at 0.06 ppm. Au also exhibited a relatively weak pH dependence compared to other noble metals, such as Pt, in the pH range of ≈ 5 –8. Therefore, in the pH range of typical ballast water, the Au WE-based free Cl sensor can be operated simply and accurately without any calibration.^[137]

3.2. Carbon-Based Materials

Recent advancements in carbon-based materials are attributable to their exceptional electrical conductivity, cost-effectiveness, sustainability, high surface area, sensitivity, rapid response, reversibility, stability, and ease of modification into nanostructures.^[47,138,139] The exceptional electrical, chemical, and physical properties of carbon-based materials facilitate various electrocatalytic applications such as oxygen and hydrogen evolution reactions, carbon dioxide reduction, nitrogen reduction, and electrochemical sensing technologies.^[140–144]

Graphite has a layered structure, with carbon atoms arranged in a hexagonal lattice within each layer. The uniquely ordered crystal endows graphite with electrical conductivity, chemical stability, and a high surface area, rendering it an effective material for electrochemical sensors.^[145–148] **Figure 6a** shows a scanning electron microscopy (SEM) image of a pencil-drawn graphite electrode.^[149] The electrode was prepared by direct drawing on cellulose paper with a 6B pencil. In **Figure 6b**, the graphite electrode exhibited an anodic current response in 10 mM NaOCl added to 0.1 M phosphate buffer solution (PBS). The amperometric current was measured when a potential of 1.5 V was applied to the electrode in 1 mM NaOCl (**Figure 6c**). From the slope of the linear calibration curve shown in the inset, a sensitivity of $27 \pm 3.65 \mu\text{A mM}^{-1} \text{cm}^{-2}$ with a LOD of 88.9 μM was calculated.

Graphene and CNTs possess properties similar to those of graphite but have higher charge carrier mobilities because of their honeycomb network of sp² hybridized carbon atoms.^[150–154] **Figure 6d** shows a schematic of the improved flow-injection amperometry (FIA) system involving a three-way solenoid valve used to integrate the CNT composite amperometric sensor.^[155] The hydrodynamic curve for a composite electrode made of CNTs and epoxy resin, illustrating a plateau indicating free Cl reduction is shown in **Figure 6e**. The CV measurements in the inset revealed that the reduction current without overlap owing to dissolved oxygen was measured at a potential of ≈ -0.1 V. The amperometric measurement was conducted in a concentration range of 0–4 mg L⁻¹ in **Figure 6f**.

Carbon black (CB), which is a product of the incomplete combustion of hydrocarbons, can be readily prepared as an electrode through simple techniques such as drop casting owing to its high electrical conductivity and satisfactory dispersion in solvents.^[156,157] **Figure 7a** presents the CV of CB-SPE in 0.1 M PBS with 0.1 M KCl (pH 5.5). A higher current response was observed at lower potentials, which can be attributed to enhanced electrocatalytic activity.^[158] To assess the interference from ions other than free Cl, a mixture containing 2 ppm of free Cl along with 7.3 ppm NO_3^- , 13.5 ppm SO_4^{2-} , 11.3 ppm CO_3^{2-} , 14.5 ppm HCO_3^- , and 1.8 ppm Cl^- was tested. As shown in **Figure 7b**, no current response was observed for any of the species, except for the analyte. Furthermore, the sensitivity of $0.36 \pm 0.01 \mu\text{A ppm}^{-1}$ in the amperometric study with 200 ppm of free Cl in **Figure 7c** confirmed that CB was among the ideal materials with superb selectivity and sensitivity. **Figure 7d** illustrates the fabrication process wherein the thermoplastic polyurethane-based 3D-printed electrodes underwent mechanical abrasion treatment, followed by CB drop-casting.^[159] Consequently, a homogeneous CB film with a large electroactive area was fabricated. The CV response of the CB electrode, depicted in **Figure 7e**, confirmed an

Table 3. Performance of electrochemical-free Cl sensors depending on materials.

Electrode materials	Functionalization	Sensing techniques	Sensitivity	Range	LOD	Ref.
CPE	Ferrocene	Potentiometry	52.90 mV log([OCl ⁻]) ⁻¹	1–15 ppm	1 ppm	[19]
Au	–	amperometry	0.327 $\mu\text{A ppm}^{-1}$	0–6 ppm	0.06 ppm	[132]
Pt	–	amperometry	80 nA ppm ⁻¹	–	0.07 ppm	[50]
MWCNT – epoxy composite	CuO NPs	amperometry	0.4462 $\mu\text{A ppm}^{-1}$	0.0006–0.0009 ppm	0.0006 ppm	[75]
SPE	PB	Amperometry, FIA	16.2 $\mu\text{A ppm}^{-1} \text{ cm}^{-2}$	0–3 ppm	0.008 ppm	[92]
GLC	PCAT	chemiresistive	–	0.05–1.75 ppm	0.05 ppm	[113]
graphene	PEDOT	chemiresistive	–	0.1–500 ppm	0.13 ppm	[115]
GLC	PCAT	chemiresistive	–	0.01–1.4 ppm	0.001 ppm	[117]
Pt	–	LSV	–	100–12 000 μM	100 μM	[134]
Au	–	amperometry	–	–	0.08 ppm	[137]
GUIAR	–	CV, CA	CV: 215.8 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$ CA: 55.24 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	CV: 0–5000 μM CA: 200–2200 μM	CV: 1.0 μM CA: 0.5 μM	[148]
Pencil graphite	–	amperometry	0.05 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	–	46	[149]
MWCNT – epoxy composite	–	amperometry	0.05 $\mu\text{A ppm}^{-1} \text{ cm}^{-2}$	0.02–4 ppm	0.02 ppm	[155]
SPE	CB	amperometry	0.32 $\mu\text{A ppm}^{-1} \text{ cm}^{-2}$	0.05–200 ppm	0.01 ppm	[158]
TPU filament	CB	CA	0.128 $\mu\text{A ppm}^{-1}$	0.2–20 ppm	0.04 ppm	[159]
BDD	–	CV	0.744 $\mu\text{A ppm}^{-1} \text{ cm}^{-2}$	0.1–2.0 ppm	0.0083 ppm	[165]
BDD	–	CV	9.108 $\mu\text{A ppm}^{-1} \text{ cm}^{-2}$	5–200 ppm	0.056 ppm	[167]
GCE	Poly MnTAPP-nano Au film	amperometry	–	24.7 μM to 0.107 M	24.7 μM	[178]
GCE	PEDOT-Au NPs composite	amperometry	0.2088 $\mu\text{A ppm}^{-1} \text{ cm}^{-2}$	0.001–0.932 μM	0.001 μM	[179]
Graphite	CuO NPs	CV, SQWV	–	0.01–0.09 μM	0.01 μM	[185]
Indium tin oxide (ITO)	Crumpled Graphene Oxide (CGO) decorated SnO ₂ nanocolumns	LSV, amperometry	2.69 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	0.1–10.08 ppm	0.1 ppm	[186]
GCE	Ferrocene-enhanced polyvinyl chloride (PVC)	Potentiometry	67.6 mV log([OCl ⁻]) ⁻¹	1–20 ppm	1 ppm	[188]
GCE	PB	Amperometry	12 $\mu\text{A ppm}^{-1} \text{ cm}^{-2}$	0.009–10 ppm	0.009 ppm	[191]
ITO	rGO-MWCNT-PB nanocomposite	Amperometry	0.1409 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	50–600 μM	2.1 μM	[192]
Fluorine doped tin oxide (FTO)	PB	Amperometry	0.809 $\mu\text{A cm}^{-2} \text{ ppm}^{-1}$	1.7–99.2 μM	1.7 μM	[193]
SPE	PB	amperometry	7.6 $\mu\text{A ppm}^{-1} \text{ cm}^{-2}$	0.06–6.28 ppm	0.06 ppm	[194]
SPE	PB (ink)	amperometry	0.0426 $\mu\text{A ppm}^{-1}$ (low concentration) 0.1318 $\mu\text{A ppm}^{-1}$ (high)	0.5–500 ppm	0.2	[195]
SPE	Polymelamine	amperometry	0.058 $\mu\text{A } \mu\text{M}^{-1}$	10 μM to 7 mM	5.5 μM	[196]
graphite	Ammonium carbamate	CA	0.303 $\mu\text{A ppm}^{-1} \text{ cm}^{-2}$	0–6 ppm	–	[197]
GCE	Polydopamine(PDA)-rGO composite	amperometry	0.0071 $\mu\text{A } \mu\text{M}^{-1}$	9.9–215.2 μM	0.044 μM	[198]
PPMM	PDA, PEI, Ag	LSV	2.13 mC/(ppm cm ²)	0.1–20 ppm	0.07 ppm	[199]
SPE	4-APBA	Voltammetry, FIA	0.4082 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$	1–10 000 μM	0.23 μM	[200]
SPE	Asparagine modified GO	amperometry	0.43 $\mu\text{A cm}^{-2} \text{ ppm}^{-1}$	0–8 ppm	0.2 ppm	[202]
SWCNTs	PCAT	chemiresistive	–	0.06–60 ppm	0.06 ppm	[205]
Plastic Formed Carbon (PFC)	N,N-Diethylaniline (DEA)	Voltammetry, amperometry	0.0704 $\mu\text{A } \mu\text{M}^{-1}$	2.2 μM –2.2 mM	0.1 μM	[206]
GCE	Poly(cafeic acid) (p-CFA) decorated rGO	Amperometry	0.0361 $\mu\text{A } \mu\text{M}^{-1}$	20–20 000 μM	0.03 μM	[209]
CPE	Co-MOF modified GO	Amperometry	–	0.1–700 ppm	0.01 ppm	[217]
BDD	Laser micromachining	LSV	2.25 $\mu\text{A ppm}^{-1} \text{ cm}^{-2}$	3–96.4 ppm	3 ppm	[218]

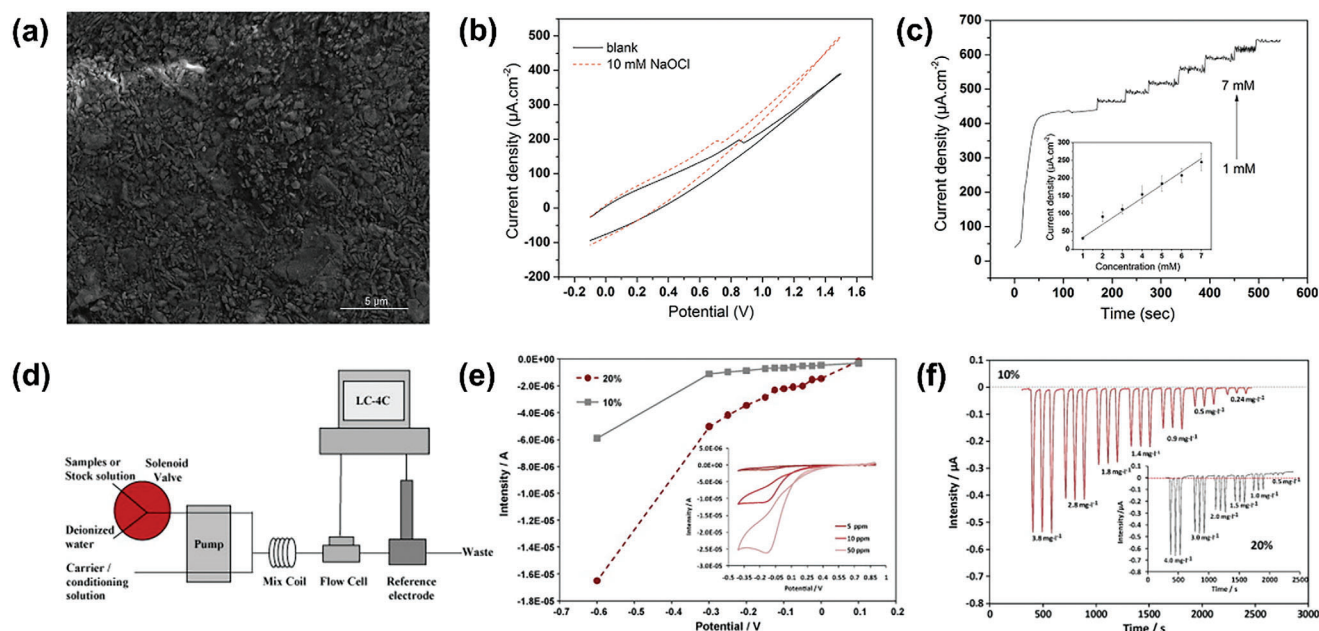
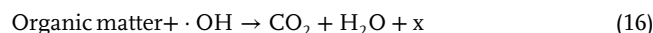


Figure 6. a) SEM image of a pencil-drawn paper electrode (PDPE) after drawing ten lines. Reproduced under the term of CC-BY license.^[149] Copyright 2021, the Authors, published by Public Library of Science. b) CV response of PDPE in the presence of 10 mM NaOCl in 0.1 M PBS, scan rate 0.05 Vs⁻¹. Reproduced under the term of CC-BY license.^[149] Copyright 2021, the Authors, published by Public Library of Science. c) Amperometric response with successive addition of 1 mM free Cl in 0.1 M PBS at an applied potential of 1.5 V on PDPE. Reproduced under the term of CC-BY license.^[149] Copyright 2021, the Authors, published by Public Library of Science. d) Schematic of an improved FIA system used for Cl determination. Reproduced with permission.^[155] Copyright 2010, Elsevier. e) Free Cl hydrodynamic curve recorded with different composite electrodes in the 2 mg L⁻¹ of free Cl concentration. The inset shows voltammogram plots for different amounts of free Cl in PBS at pH 5.5. Scan rate: 100 mV s⁻¹. Reproduced with permission.^[155] Copyright 2010, Elsevier. f) Amperometric signal of sensor with the improved-FIA system in a range between 0 and 4 mg L⁻¹. Reproduced with permission.^[155] Copyright 2010, Elsevier.

improvement in the cathodic current, leading to enhanced sensitivity to free Cl. The sensor demonstrated a linear correlation in the range of 0.2–20 ppm of free Cl with an LOD of 0.01 ppm in CV measurements conducted for tap water (Figure 7f,g).

Diamond, a carbon allotrope, is an electrical insulator with a bandgap of 5.47 eV and a resistivity range of 100 GΩ·m to 1 EΩ·m, despite its excellent mechanical stability and thermal conductivity.^[160] However, boron doping transforms diamonds into boron-doped diamond (BDD), which exhibit p-type semiconducting properties at doping levels above 10¹⁹ B atoms cm⁻³ and metallic properties at levels exceeding 10²⁰ B atoms cm⁻³.^[161] The properties of BDD can be precisely controlled by the surface termination and orientation, rendering it a superior electrode material.^[162] BDD electrodes offer a wide potential window, low noise and background currents, mechanical and chemical stabilities, and biocompatibility, which render them highly suitable for cathodic and anodic reactions.^[163,164] Figure 8a presents the CVs of microwave plasma-assisted chemical vapor deposited BDD electrodes in 0.1 M NaClO₄.^[165] The linear calibration curve and the distinct oxidation peak in the inset demonstrate that the BDD electrodes achieved free Cl detection with a sensitivity of 0.744 μA cm⁻²mg⁻¹L. However, the pH dependency of the redox reaction owing to the difference in electrochemical activity between HOCl and OCl⁻ results in fluctuations in the oxidation potential and peak current within the pH range of 5–8. (Figure 8b,c) The follow-up work confirmed that pH is a critical parameter that significantly affects the performance evaluation

of free Cl sensors.^[166] The excellent stability of BDD facilitates the batch production of silicon-substrate-based electrochemically free Cl sensor chips employing microelectromechanical system technology^[167] (Figure 8d). Moreover, the BDD electrode exhibits self-cleaning properties by generating hydroxyl radicals (•OH) through the anodic oxidation of water molecules, which degrade the organic pollutants responsible for fouling. The decomposition process is described in Equations (15) and (16).



The proposed antifouling characteristics of the BDD electrodes facilitate the sensor in monitoring free Cl in seawater containing high levels of organic contaminants with exceptional durability.

3.3. Functionalization

Bare electrodes, which form the basis of an electrochemical sensor, do not exhibit sufficient sensitivity for the detection of free Cl. To achieve performance levels comparable to those of commercially viable alternatives to DPD, it is necessary to enhance the sensor's response to trace amounts of free Cl. This improvement can be accomplished by functionalizing the WEs via surface treatment with additional materials.^[168–170] Functionalization is

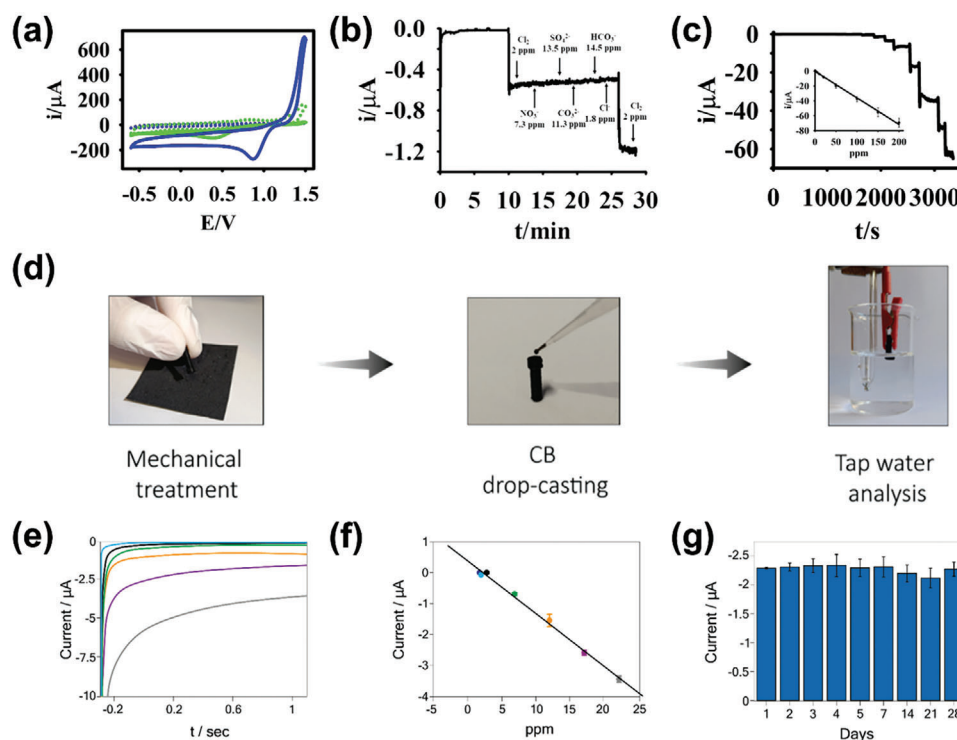


Figure 7. a) CVs from bare GC (green curve) and GC modified with CB (CB-GC curve) (blue) in nitric acid 0. M in the presence and absence of 2000 ppm free Cl. Reproduced with permission.^[159] Copyright 2018, Elsevier. b) Interference study in CB-GC with the addition of interfering species. Reproduced with permission.^[159] Copyright 2018, Elsevier. c) Amperometric study using CB-SPE to evaluate the response of the sensor toward free Cl up to 200 ppm. Inset: the calibration curve, $n = 3$. Reproduced with permission.^[159] Copyright 2018, Elsevier. d) Schematic of a fabrication process of the 3D printed WEs. Reproduced with permission.^[159] Copyright 2024, Elsevier. e) CA conducted at -0.1 V vs Ag/AgCl in tap water across a range of free Cl concentrations from 0.2 to 20 ppm. Reproduced with permission.^[159] Copyright 2024, Elsevier. f) Corresponding calibration curve obtained by plotting current values versus free Cl concentration. Reproduced with permission.^[159] Copyright 2024, Elsevier. g) Stability test of the sensor by measuring 15 ppm of free Cl over a period of 28 days. Reproduced with permission.^[159] Copyright 2024, Elsevier.

a proven approach for enhancing the material performance through physical, chemical, and electrochemical methods. It imparts new properties that facilitate various applications.^[171–173] Enhancing the sensitivity, selectivity, and stability through functionalization is particularly crucial for free Cl sensing in seawater, which contains various chemical and biological impurities.

Inorganic functionalization using metal and metal-oxide nanostructures is a prominent method for enhancing the performance of electroanalytical devices. Metal/metal oxide-modified electrodes improve the sensitivity and stability of sensors through direct electrochemical reactions with the analyte and by enhancing the active surface area and electrocatalytic activity.^[170,174–177] **Figure 9a** shows an SEM image of a poly(manganese tetra(o-amino phenyl) porphyrin) (MnTAPP)-nano Au film electrodeposited on a glassy carbon electrode (GCE).^[178] The poly MnTAPP-nano Au film was prepared via repetitive potential scanning in an H_2SO_4 solution containing 0.1 mM MnTAPP and 1 mM KAuCl_4 . The shifts in the Au^{3+} reduction peak and its overlap with the reduction peak of poly MnTAPP in the CVs confirmed the successful deposition of Au NPs on the poly MnTAPP surface. Au NPs with sizes ranging from 170 to 350 nm were uniformly distributed across the poly-MnTAPP layer. This uniform distribution was also observed in the atomic force microscope (AFM) image of the poly MnTAPP-nano-Au film on ITO (Figure 9b). The average roughness (AR) was

measured using tapping mode AFM analysis. It indicated that the increased AR of the poly MnTAPP-nano-Au-modified ITO (26.9 nm) compared to that of bare ITO (2.19 nm) and poly MnTAPP-modified ITO (3.82 nm) contributed to the expansion of the electroactive surface area of the electrode. The CV responses of the electrodes are depicted in Figure 9c, illustrating the enhanced signals of the poly MnTAPP-nano-Au-film-modified GCE compared to those of the other electrodes. The electrode could detect free Cl in the range of 2.47×10^{-5} – $1.07 \times 10^{-2}\text{ M}$ at a pH of 10.4. Another functionalization approach involves using AuNPs/poly(3,4-ethylenedioxythiophene) (PEDOT) nanocomposites.^[179] AuNPs/PEDOT was co-deposited on the GCE, with the surface morphology shown in Figure 9d,e. Consequently, XRD analysis, SEM, and AFM images confirmed the presence of Au and the uniform distribution of the AuNPs/PEDOT nanocomposite on the electrode. Although the electron transfer resistance (R_{et}) of the AuNPs/PEDOT-functionalized electrode, as shown by the EIS results, was higher than that of the PEDOT/GCE, it was lower than those of the AuNPs/GCE and bare GCE. Thus, PEDOT effectively enhances the electron transfer rate. Consequently, the AuNPs/PEDOT/GCE exhibited a lower overpotential and higher current response, as shown in Figure 9f. Kodera et al. reported the microwave-assisted synthesis of graphene-Ni composites and the fabrication of porous microelectrodes (PME).^[180] The PME

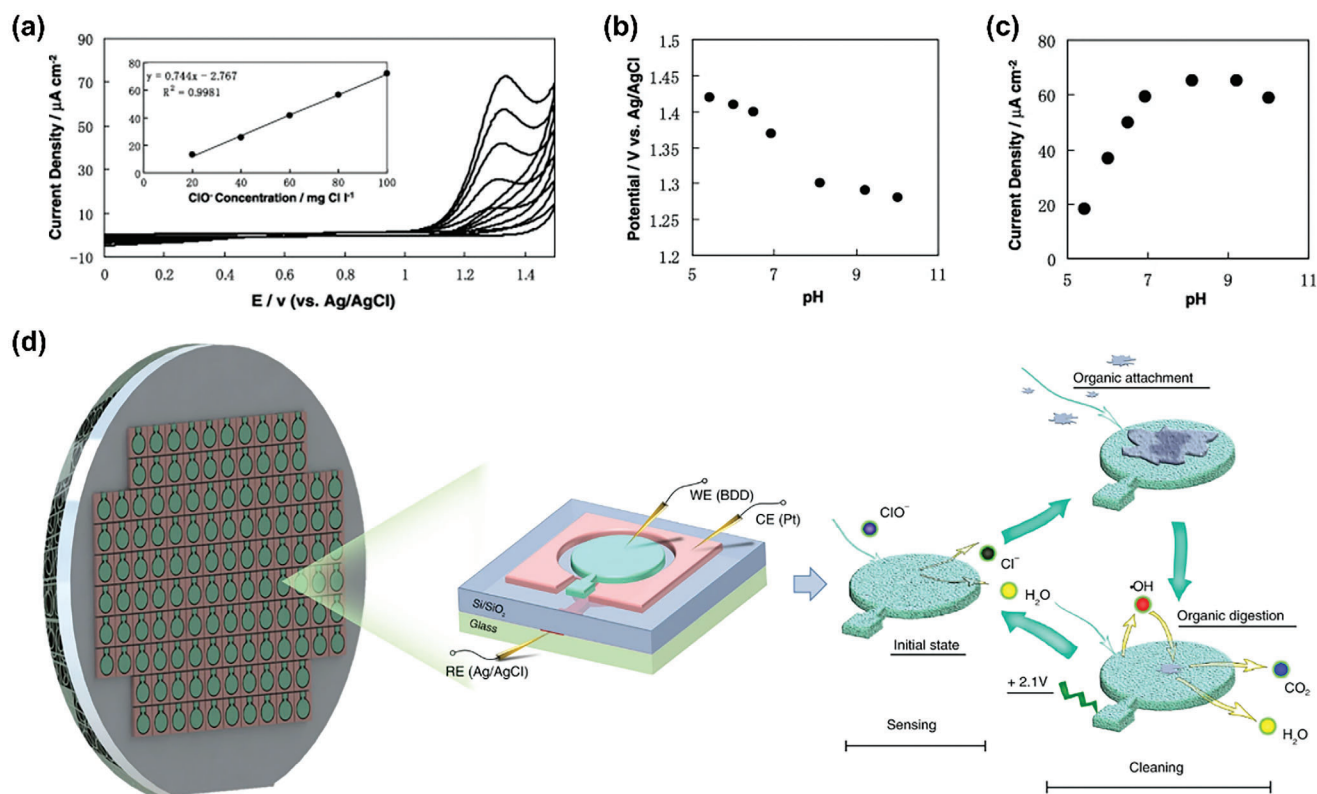


Figure 8. a) CVs of a 0.1 M NaClO₄ solution in the presence of free Cl concentration ranging from 2–100 mg Cl L^{−1}. Reproduced with permission.^[165] Copyright 2008, Elsevier. b) The pH dependence of oxidation potential in the CVs of 50 mg Cl L^{−1} in 0.1 M PBS. Reproduced with permission.^[165] Copyright 2008, Elsevier. c) The pH dependence of peak current in the CVs of 50 mg Cl L^{−1} in 0.1 M PBS. Reproduced with permission.^[165] Copyright 2008, Elsevier. d) Schematic of batch microfabrication, sensing, fouling, and self-cleaning process of silicon-based electrochemical sensor. Reproduced under the term of CC-BY license.^[167] Copyright 2022, the Authors, published by Springer Nature.

exhibits a reduction current at a more positive potential (+0.3 V). The linear relationship between the reduction current and free Cl concentration indicates that Ni nanomaterials can be used for electrode functionalization in free Cl detection.

Copper oxide (CuO) is a p-type semiconductor that can be synthesized into various nanostructures. It holds significant potential for applications in various devices, including electrochemical sensors.^[181–183] The incorporation of CuO NPs into carbon-based materials enhances sensor performance by improving the charge transfer between the supporting matrices and analytes.^[184] Figure 10a illustrates the synthesis of the CuO NP-modified (MWCNT/epoxy) nanocomposite electrode.^[75] Ellipsoidal CuO NPs were formed via intermatrix synthesis (IMS), mixed with MWCNTs in an epoxy resin, and subsequently synthesized into the electrode. The modified sensor demonstrated improvements in electrocatalytic activity, an increased electroactive surface area, and a more efficient electron transfer process. These collectively facilitated an enhanced sensitivity of 0.45 μA ppm^{−1} and a lower LOD of 0.6 ppb for free Cl. In addition, CuO NPs have been used to modify graphite sheets on paper substrates using inkjet printing.^[185] In CV measurements, oxidation and reduction peaks at +0.20 and −0.71 V confirmed the successful deposition of CuO NPs on the graphite sheet. The electrode was evaluated using square-wave voltammetry (SQWV) and exhibited a linear increase in oxidation current with NaOCl con-

centrations ranging from 10 to 90 mM. Furthermore, an LOD of 13.15 nM was realized. Figure 10b depicts the fabrication process of crumpled GO-decorated SnO₂ nanocolumn (CGO-SnO₂) composites.^[186] The SnO₂ nanocolumns, fabricated via aerosol chemical vapor deposition, were functionalized with GO sheets via electrospray deposition, thereby forming crumpled GO structures. The composites contained minor carbon impurities and exhibited a crystalline structure consistent with that of cassiterite, with preferential growth along the (211) plane, which is known for its enhanced catalytic activity. The performance of the CGO-SnO₂-modified electrodes was investigated in a pH 7.4 PBS solution using CV. The reduction peak at −0.44 V and a current increment of 60.80 μA demonstrated the remarkable electrocatalytic performance of the composites. Further, the sensor exhibited a sensitivity of 5.86 μA μM^{−1} cm^{−2} for tap water.

Iron compounds are widely used for electrochemical applications. Ferrocene (Fc) exhibits stable and reversible redox behavior, ease of functionalization, and enhanced electrocatalytic activity.^[187] Consequently, Fc has been reported for use in detecting free Cl owing to its ion-selective properties.^[19,188] Figure 11a shows the potential response of an Fc-modified GC electrode with a zephiran chloride (ZephCl)-containing polyvinyl chloride (PVC) coating-based potentiometric sensor.^[188] Fc functions as both a phase-transfer catalyst and an ion-to-electron transducer. OCl[−] oxidizes Fc in the solution, prompting the diffusion of

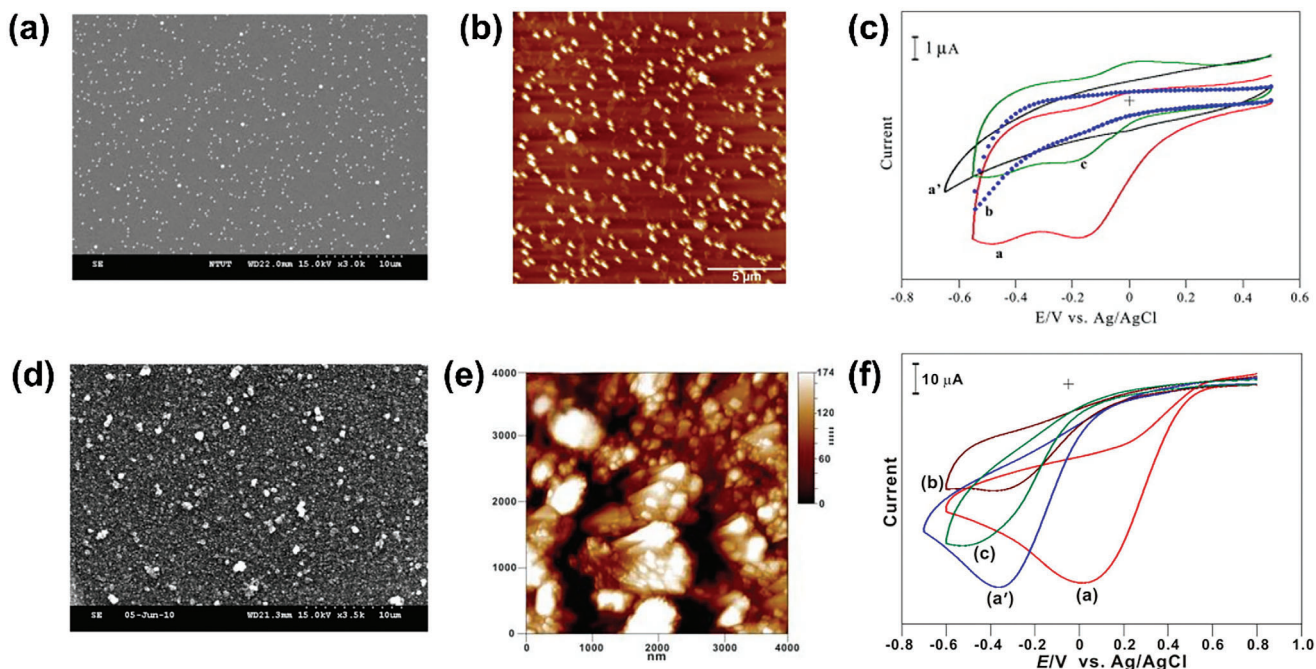


Figure 9. a) SEM image of the poly MnTAPP-nano Au film at a view angle of 90° . Reproduced with permission.^[178] Copyright 2011, Elsevier. b) AFM image from the poly MnTAPP-nano Au film on ITO. Reproduced with permission.^[178] Copyright 2011, Elsevier. c) CV measurements for NaOCl detection (0.01 M) at (a') bare, (a) poly MnTAPP-nano Au, (b) poly MnTAPP modified GCE and (c) CV response of poly MnTAPP-nano Au film modified GCE in pH 10.4 NaOH (absence of NaOCl). Reproduced with permission.^[178] Copyright 2011, Elsevier. d) SEM image of AuNPs/PEDOT modified GCE. Reproduced with permission.^[179] Copyright 2011, Elsevier. e) AFM image of AuNPs/PEDOT modified GCE. Reproduced with permission.^[179] Copyright 2011, Elsevier. f) CVs of (a) AuNPs/PEDOT/GCE, (b) PEDOT/GCE, (c) AuNPs/GCE, and (a') bare GCE examined in 0.1 M PBS (pH 7) containing 10^{-4} M NaClO, scan rate = 0.1 s^{-1} . All tests were conducted in the absence of oxygen by sealing the electrochemical cells. Reproduced with permission.^[179] Copyright 2011, Elsevier.

anions such as OCl^- and Cl^- into the PVC coating of the electrode to maintain charge neutrality. Owing to the induction effect, Zeph^+ interacts more strongly with the larger anion OCl^- than with Cl^- . Consequently, the presence of Fc facilitates the diffusion of more analytes into the PVC coating, resulting in increased sensor sensitivity and reduced charge-transfer resis-

tance, which reduces the response time. Figure 11b illustrates the potential response to dissolved oxygen and coexisting ions. As evident, no potential was measured for interfering ions other than free Cl. Thus, the catalytic reaction facilitated by Fc exhibited high selectivity. In the long-term stability assessment shown in Figure 11c, the electrode maintained a stable potential

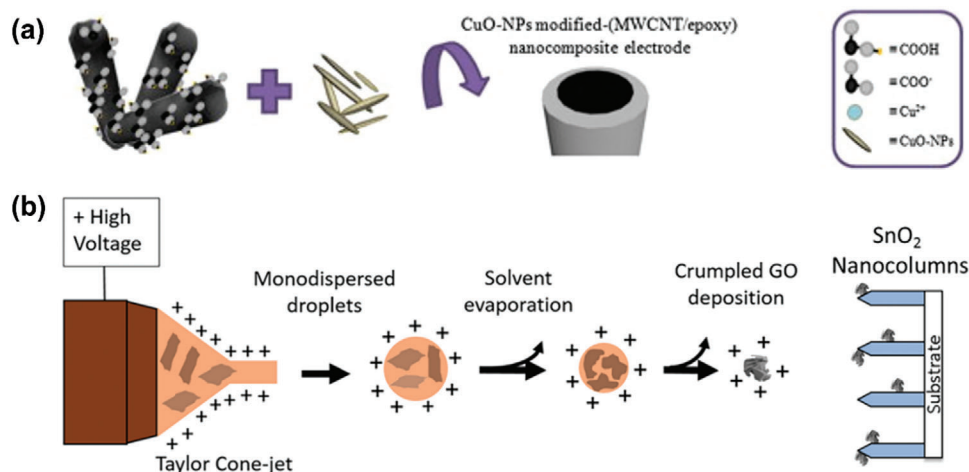


Figure 10. a) Schematic of the synthesis process of CuO-NPs incorporated MWCNT/epoxy nanocomposite electrodes. Reproduced with permission.^[75] Copyright 2015, Elsevier. b) Schematic of deposition procedure for the crumpled graphene oxide decorated SnO_2 nanocolumns. Reproduced under the term of CC-BY license.^[186] Copyright 2017, the Authors, published by Springer Nature.

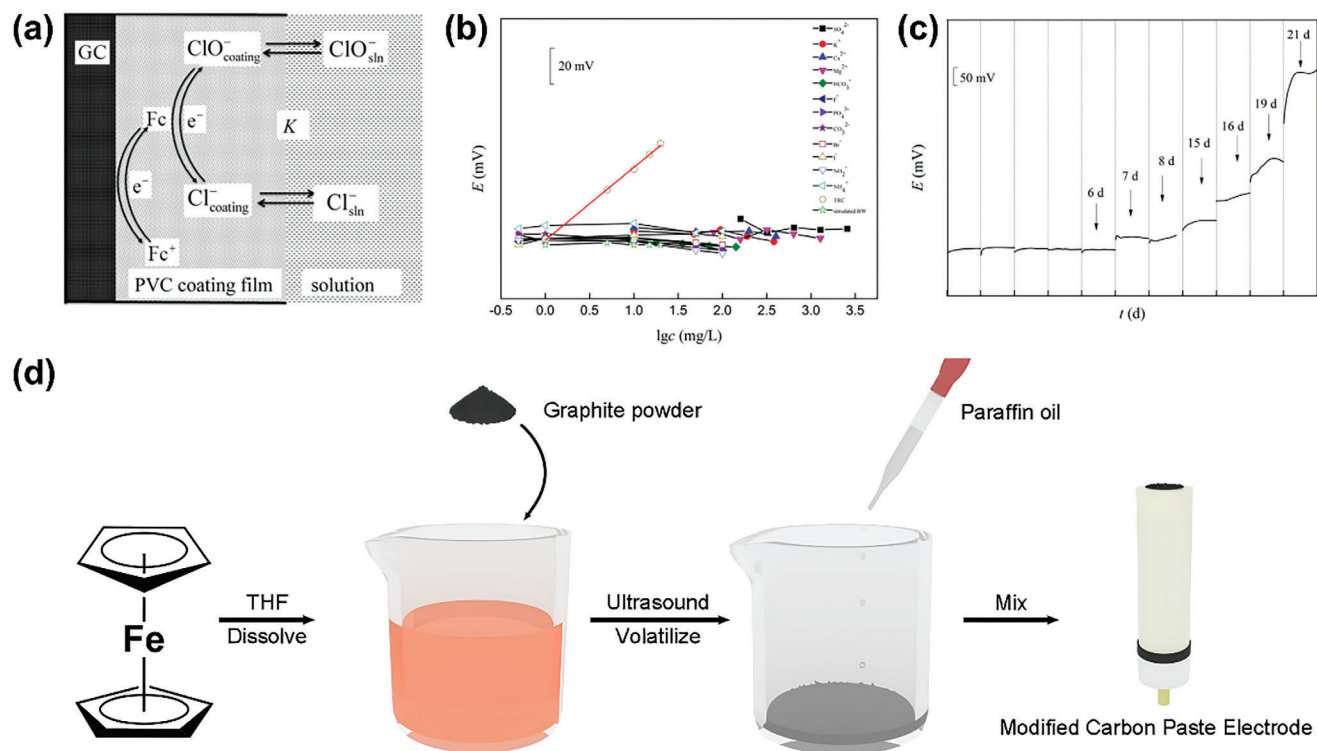


Figure 11. a) Schematic of the potential response of Fc-PVC-ZephCl-GC electrode to free Cl. Reproduced with permission.^[188] Copyright 2016, Elsevier. b) Current response of the Fc-PVC-ZephCl-GC electrode in a solution of free Cl with co-existing ions. Reproduced with permission.^[188] Copyright 2016 Elsevier. c) Stability test of Fc-PVC-ZephCl-GC electrode. Reproduced with permission.^[188] Copyright 2016, Elsevier. d) Schematic of the fabrication process of Fc modified carbon paste electrode. Reproduced under the term of CC-BY license.^[19] Copyright 2021, the Authors, published by Springer Nature.

for six days; however, after seven days, the potential deviation began to increase. Further, after two weeks, the electrode ceased to function properly. This deterioration was attributed to the dissolution of Fc⁺ and Zeph⁺ from the PVC coating into the solution. Figure 11d presents a schematic of the fabrication of a carbon-paste electrode using Fc-modified graphite.^[19] The Fc/Fc⁺ redox couple increased the current density of the reaction between free Cl and Cl⁻, thereby shortening the response time of the electrode. Consequently, the electrode can achieve electrochemical equilibrium more quickly while maintaining a stable potential. In addition, Fc protects the electrode surface from oxidation and contamination, thereby facilitating the stable and long-term monitoring of free Cl. The Fc-modified CPE demonstrated high sensitivity with a Nernstian slope of 52.90 mV/decade, excellent selectivity against various interfering ions, robust stability with less than $\pm 1.7\%$ deviation over 16 days, and preservation of functionality after five months of storage.

PB is well known for its strong electrocatalytic activity, stability, and biocompatibility. These render it an ideal candidate for biosensors and environmental monitoring applications.^[189,190] Because of its catalytic activity in redox reactions involving various analytes, PB has been employed in the development of electrochemical sensors for free Cl detection. Salazar et al. electrodeposited PB onto a GCE by mixing it with the cationic surfactant benzethonium chloride (BZTC).^[191] Raman spectra confirmed the precise electrodeposition of PB on the films. The use of a

surfactant improved the deposition efficiency and electrochemical properties of the PB film, thereby resulting in a sensor with a sensitivity of $12.3 \mu\text{A ppm}^{-1} \text{cm}^{-2}$, a linear detection range of 9–10 ppm, and reproducibility of 4.2%. In a subsequent study on electrodeposition using PB and BZTC, a PB-modified SPE-based sensor exhibited improved sensitivity of $16.2 \mu\text{A ppm}^{-1} \text{cm}^{-2}$, a LOD of 8.25 ppb, and a relative standard deviation of 6.2%.^[92] In addition, in amperometric FIA, the sensor exhibited no current response to interfering substances such as nitrate, nitrite, and sulfate ions. Silva et al. synthesized ternary nanocomposites of reduced graphene oxide (RGO), MWCNTs, and PB for the detection of strong oxidants, such as hydrogen peroxide and free Cl.^[192] Using an interfacial method, PB NPs with a controlled morphology and particle size were uniformly distributed within the carbon matrix without aggregation. This significantly increased the surface area of the electrode. The functionalized film exhibited enhanced stability in neutral and basic solutions, attributable to the π - π interactions between MWCNT and RGO acting as donors and PB functioning as an acceptor, facilitating ionic interactions. The sensor maintained high stability and facilitated repeated measurements across a wide pH range. The application of PB, through the optimization of the electrodeposition process, enhances the sensitivity, stability, and reproducibility of the electrode, enabling accurate measurements in diverse real-world water matrices, such as graywater.^[193] Research on an in-situ deposition process using conductive ink

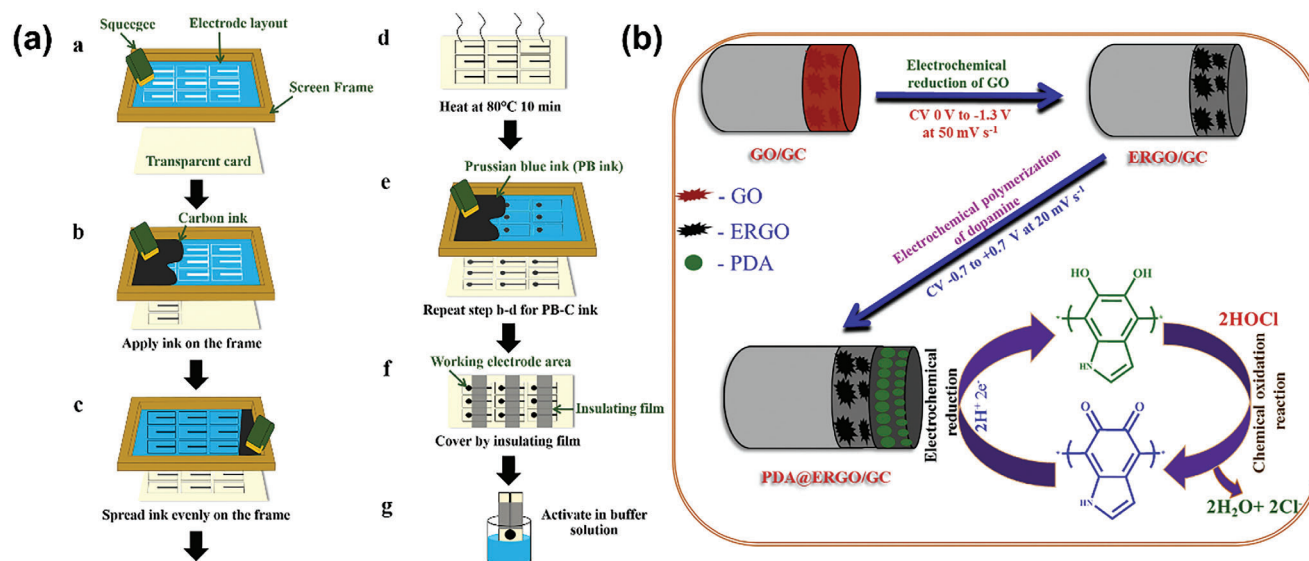
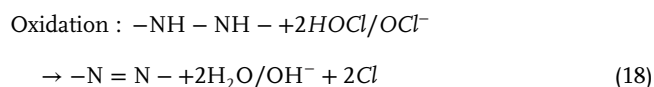
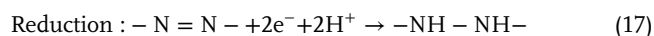


Figure 12. a) Schematic of the fabrication process of PB-modified SPE. Reproduced with permission.^[195] Copyright 2021, Elsevier. b) Schematic of the fabrication and free Cl determination process of polydopamine-modified electrochemically reduced GO/GCE. Reproduced with permission.^[198] Copyright 2017, Elsevier.

has also been proposed, offering a cost-effective alternative to electrodeposition.^[194] The schematic in **Figure 12a** illustrates the screen-printing process of the ink onto a flexible substrate, where carbon and PB-graphite inks are sequentially screen-printed, followed by drying, insulation, and activation to create a functional electrochemical sensor.^[195] The uniformly distributed PB-graphite layer, deposited with a consistent thickness on the flexible substrate, demonstrated high sensitivity and stability in the detection of free Cl, achieving a low LOD of 0.2 mg L⁻¹ in a lab-made flow cell. The electrode exhibited a consistent performance over extended use, confirming its reliability for continuous water quality monitoring applications.

Effective applications of various amine-containing materials have been reported, primarily through electrochemical reactions with carbon-based substrates for surface functionalization.^[196–202] Amine functional groups can be successfully grafted onto electrodes based on graphene, CNTs, or SPCE to ensure stable functionalization.^[203,204] Consequently, functionalization using amines is a low-cost and effective strategy for enhancing stability under harsh conditions and improving sensitivity to free Cl. Senthilkumar et al. developed a free Cl sensor based on SPE modified with polymelamine.^[196] The electrode exhibited an enhanced cathodic peak current in the presence of free Cl. This was attributed to the electrochemical reduction of the hydrazo functionality of polymelamine, which was subsequently reoxidized by free Cl. The redox cycle of the polymelamine functional groups in the presence of free Cl is described by Equation (17):



Thus, these functional groups serve as catalysts for the efficient progression of redox reactions with free Cl. The FIA responses of the functionalized electrodes exhibited a linear calibration curve over the range of 10 μM to 7 mM of free Cl. The polymelamine-SPCE sensor demonstrated a low LOD of 5.5 μM, improved stability with a relative standard deviation of 1.7% after 30 continuous injections, and high selectivity for free Cl in complex environmental samples. Pan et al. modified graphite electrodes with ammonium carbamate. The delocalized π bonds in graphite facilitated the redox of free Cl on the electrode surface through electrochemical amination.^[197] Figure 12b shows a schematic of the functionalization of a GC electrode using electrochemically reduced GO and polydopamine.^[198] GO, which was formed on the GC surface through drop-casting, was subjected to potential cycling with dopamine. During the fabrication process, GO was reduced by removing oxygen groups, restoring sp²-hybridized carbon bonds, and converting GO into graphene. Meanwhile, dopamine was oxidized to dopamine quinone, facilitating the electropolymerization of polydopamine. Polydopamine exists on the RGO surface as agglomerations with a sphere-like morphology owing to various defects. The PDA-RGO/GC sensor, with its high current response and fast electron transfer kinetics, is highly effective in the electrocatalytic reduction of free Cl. It can detect free Cl within a concentration range of 9.9–215.2 μM, with a LOD of 44 nM. Moreover, testing in real samples, such as swimming pool water, demonstrated high recovery rates, which further confirmed the stable functionalization effect provided by the introduction of amine groups. Chiang et al. developed a porous Ag electrode by forming Ag NPs on a polydopamine and polyethyleneimine (PEI) co-deposited flexible polypropylene micromembrane (PPMM).^[199] Dopamine was polymerized into polydopamine on the PPMM surface in the presence of oxygen, and the phenol groups of polydopamine bound to the PP fibers, resulting in an agglomerated morphology. The amino groups in PEI formed a uniform PDA/PEI coating on the PP fibers

through strong covalent bonding with the C=C bonds in polydopamine. Ag was introduced into the film via electroless deposition, where the catechol groups in polydopamine reduced the Ag⁺ ions to Ag NPs. Consequently, the conductive Ag membrane uniformly coated with modifiers exhibited enhanced mechanical strength. Polydopamine-PEI-Ag-modified flexible sensor performed exceptionally well in the detection of free Cl, offering an LOD of 0.07 ppm, a wide linear detection range of 0.1–20 ppm, and a sensitivity of 2.13 mC/(ppm cm²). This enabled the sensor to accurately detect even minor changes in Cl levels with a linear response observed across a broad range. The sensor maintained its mechanical strength and electrical stability even after more than 10 000 bending cycles. This renders it reliable for flexible and repeated use. These enhanced characteristics demonstrate the effectiveness of functionalization as a tool for Cl detection in various environments. Thiruppathi et al. reported a functionalized SPCE-based sensor for the detection of OCl[−], glucose, and fructose based on the electrochemical dimerization of amine-containing 4-aminophenylboronic acid (4-APBA).^[200] Fluoride-free dimerization of 4-APBA occurs through the oxidation of the amine group, and the azo functionality of the dimer selectively detects free Cl. The dimer-modified SPCE sensor exhibited a linear range of 1 μM to 10 mM for OCl[−] detection, with a LOD of 0.23 μM. Additionally, aminopyrene has been reported to stably bind to graphene surfaces, allowing for modification with improved selectivity for free Cl due to the amine groups.^[201] Similar chemical functionalization using asparagine which contains amine groups has also been reported.^[202] In this process, sodium hydroxide was added to neutralize the carboxylic acid groups of GO, preventing the formation of amide bonds. The asparagine-functionalized GO-based amperometric sensor demonstrated a sensitivity of 0.30 μA ppm^{−1}, low hysteresis, a rapid response time of 50 s, and selectivity in the presence of common interfering ions, making it highly effective for real-time free Cl detection in water. The biodegradable properties of asparagine and the solution-based fabrication process make it a promising tool for widespread water quality monitoring applications. However, the current response is affected by the temperature dependency of the free Cl diffusion rate. Therefore, when applied in BWMS, the sensor needs to be paired with a temperature sensor in a tandem structure for compensation.

Research on chemiresistive sensors utilizing PCAT with aniline has been ongoing. For example, Hsu et al. adsorbed PCAT onto the surface of SWCNTs.^[205] The oxidation of PCAT by free Cl converts SWCNTs into a p-doped state, reducing resistance. The p-doped PCAT-SWCNTs can be electrochemically reversed to an un-doped state by applying a voltage of −0.8 V, leading to increased resistivity. The chemiresistive sensor measured free Cl within a detection range of 0.06–60 mg L^{−1}, although concerns were raised about low sensitivity due to the potential oxidation by other oxidants. Patel et al. developed a flexible chemiresistive sensor using PCAT-modified GLC and gold leaf contact electrodes.^[113] The sensor demonstrated a significant increase in resistivity and a decrease in current response when exposed to free Cl at concentrations of 0.05–1.75 ppm due to the oxidation of PCAT, attributed to the p-type doping effect on the GLC. The reduction of PCAT can be achieved by rinsing the sensor in ascorbic acid, although this process requires additional cleaning with deionized water. Laserna et al. further improved this

PCAT-modified GLC-based chemiresistive sensor to enable continuous monitoring of free Cl without the need for chemical or electrochemical resetting.^[117] The sensor response was evaluated by increasing the amount of free Cl, with the raw data fitting a Langmuir isotherm model, suggesting that the sensor operates primarily through a surface adsorption process and reaches saturation as the free Cl concentration increases. Analysis of the correlation between response and saturation concentration according to the thickness of the GLC film revealed that as thickness increases, charge transfer and electrostatic gating effects decrease, leading to a reduction in response but an increase in saturation concentration. The chemiresistive sensor exhibited high sensitivity with a LOD of 1 ppb, a dynamic range of 0.01–1.4 ppm, and a decreased current response at low free Cl concentrations, indicating that external resetting is not necessary. Morita et al. reported an electrode with electrocatalytic activity that shifts the reduction potential of free Cl to a more positive value by grafting diethylaniline (DEA), generated from DPD, onto a carbon electrode.^[206] Yen et al. reported the use of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) in a chemiresistive sensor.^[115] When PEDOT:PSS is used to modify a paper substrate in the form of nanocomposites with graphene, it effectively fills the small gaps in the cellulose fibers, forming a uniformly coated conductive surface. Due to the conductive properties of PEDOT:PSS, the thiophene in PEDOT reacts with free Cl and oxidizes, reducing the sensor's conductivity. As a result, the chemiresistive sensor exhibits a linear response to free Cl concentrations ranging from 0.1 to 500 ppm, with a LOD of 0.07 ppm for PEDOT:PSS sensors and 0.13 ppm for PEDOT:PSS/graphene nanocomposite sensors. The sensor shows high selectivity against interfering ions and enables real-time data transmission to mobile devices, offering a cost-effective and portable solution for on-site water quality monitoring.

Alcohols can also be grafted onto the surface of carbon-based materials, making them useful for further functionalization.^[207,208] Kesavan et al. coated poly(cafeic acid) (p-CFA) with catechol groups onto electrochemically reduced GO.^[209] The catechol groups within the p-CFA matrix undergo reversible oxidation to o-quinone and subsequent reduction back to catechol. This 2-electron/2-proton redox process significantly enhances electron transfer at the electrode surface, which is crucial for efficient interaction with free Cl. The redox cycling amplifies the electrochemical signal, improving the sensitivity of the amperometric sensor. The p-CFA@ERGO/GC sensor exhibited a wide detection range for free Cl from 20 μM to 20 mM, with a high sensitivity of 0.0361 μA μM^{−1}, a LOD of 0.03 μM, and excellent recovery rates between 98.5% and 99.9% when applied to real water samples.

Metal-organic frameworks (MOFs) are porous materials constructed by links between inorganic metal ions or clusters and organic ligands. The unique structures have garnered significant attention due to the high surface area, high porosity, tunable pore size, flexible structure, and stability.^[210] Based on the varied functionalities, MOFs have been widely applied in various fields including catalysis and energy storage.^[211–213] Recently, the potential application of MOFs in electrochemical sensing has been extensively explored, as the presence of metal centers within MOFs can facilitate electron transfer processes, making them highly effective in detecting various analytes.^[214–216] Jafari et al. reported

the modification of carbon paste electrodes using cobalt-based MOF (Co-MOF) and functionalized GO (FGO) composites.^[217] GO is functionalized using nitrogen-containing materials such as imidazole, then forms a coordination bond with the cobalt ion of the Co-MOF in the composites. The modified electrode exhibited a high current response and a small potential difference between the oxidation and reduction peaks in CV measurements, which can be attributed to the enhanced electron transfer rate and increased surface area. The modified electrode exhibited a significantly high current response and a small potential difference between the oxidation and reduction peaks. The improved electrochemical properties are attributed to the enhanced electron transfer rate and the surface area of the functionalized electrode. In addition, the electrode modified with FGO alone did not show a distinct response to free Cl other than an increase in background current, indicating that the Co-MOF contributes most to the enhanced detection of free Cl. The increased surface area and adsorption properties of the Co-MOF promote the redox reaction of free Cl, amplifying the current response. The electrode provides a rapid and linear current response over a broad concentration range, making it suitable for precise monitoring of free Cl in diverse applications. The Co-MOF-FGO/CP showed a wide detection range of 0.1–700 ppm for free Cl, with a correlation coefficient (R^2) of 0.995 indicating high accuracy across various concentrations, and a LOD of 10 ppb. Due to the tunable properties of MOFs achieved through the alteration of metal ions, modification of organic ligands, control of synthesis conditions, and post-synthetic modifications, MOFs have been focused as significant attention as promising candidates for future functionalization methods.

The performance of electrochemical sensors can be improved also by modifying the synthesis methods of electrode materials or physically processing the electrodes.^[148,218] For instance, utilizing a carbon material known as GUITAR, synthesized through the University of Idaho Thermolyzed Asphalt Reaction, the sensor exhibits high corrosion resistance and fast heterogeneous electron transfer, enabling continuous monitoring of free Cl.^[118] Lucio et al. reported a voltammetric pH and free Cl sensor based on laser-patterned BDD electrodes.^[218] Laser patterning creates sp^2 carbon regions containing quinone on the surface of the BDD electrode, allowing for the simultaneous monitoring of pH and free Cl.

4. Conclusion

Electrochemical sensors are promising alternatives to conventional DPD-based colorimetric methods in the field of TRC sensing applications for BWMS, owing to their fast response, long-term stability, safety, low price, and low footprint. This study reviewed the fundamental principles and mechanisms of various electrochemical methods commonly used for free-Cl sensors. Certain key characteristics of prominent electrode materials were classified, and the properties of free Cl sensors composed of these electrode materials were compared. In addition, we highlighted the recent advancements in functionalization techniques for enhancing the sensing performance of electrochemical sensors. Nevertheless, there are still certain limitations that must be overcome before its utilization in BWMS for TRC monitoring.

Although the poor performance of electrochemical sensors using bare electrodes, such as noble metals and carbon-based materials, can be improved by introducing various functionalization processes to achieve superior properties of high reactivity and selectivity to free Cl, there is still room for further development compared to DPD-based colorimetric measurements. The low response of the electrochemical sensor results in reduced sensitivity to changes in free Cl concentrations compared with conventional detection methods. To improve the sensitivity, LOD, and response time, functionalization based on more effective materials or processes must be discussed. Enhancing the stability of the electrodes to withstand severe working environments is also a key issue for the commercialization of electrochemical sensors. Yin developed a BDD electrode with outstanding durability, retaining 83.9% of its initial response value in tap water after 30 days of online monitoring, owing to its self-cleaning properties.^[167] The search for novel electrode materials exhibiting antifouling properties could be a suitable approach for overcoming the limitations of fabricated electrodes for online free Cl monitoring in ballast water. Nonetheless, most functionalized electrode materials are vulnerable to environmental factors such as seawater. Biofouling is a major challenge faced by electrochemical sensors that are integrated into BWMS. Marine microorganisms attach to the surface of the sensor and cause fouling, consequently increasing maintenance costs and reducing data accuracy. Several antifouling strategies have been adopted to overcome these limitations. Current antifouling strategies include coatings with materials such as silicon, biocides, and self-polishing copolymers. Mechanical cleaning using wipers and ultrasonication is a relatively simple and effective method for cleaning surfaces during continuous operation of electrochemical sensors. Despite various methods, including the aforementioned strategies, UV irradiation, the use of photocatalytic materials, and biomimetic approaches, there is still a need for the development of unique materials and technologies that can provide long-term protection without reducing sensor performance, coupled with continued research into sustainable and effective antifouling strategies.^[219]

Another issue to address is maintaining consistency in the sensitivity and selectivity of electrochemical sensors under seawater conditions, where the sensing performance is affected by various factors such as pH, temperature, salinity, and even the flow rate. Although many studies have been published on the development of free Cl sensors for water quality measurements, electrochemical sensors, particularly those applied for the online monitoring of ballast water, have seldom been investigated. Zhang conducted a selectivity test on a modified CPE by checking the potential difference with increasing concentrations of possible interfering ions or salts in ballast water.^[19] Therefore, more research on selectivity and sensitivity tests should be conducted under a variety of seawater conditions such that the developed sensor can be further adopted in practical applications.

Achieving high sensitivity and selectivity with long-term stability for online-monitoring electrochemical sensors in BWMS is a difficult task, but electrochemical methods have considerable potential to replace conventional DPD-based colorimetric measurements. The key to overcome these limitations is the development of novel electrode materials. Furthermore, a suitable measurement setup and sensor structure design should be considered when integrating sensors with BWMS for practical applications.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

P.J.P., W.J.J., and D.J.L. contributed equally to this work. T.J.P. and S.Y.K. were instrumental in the completion of the final manuscript and provided overall supervision for the project.

Keywords

ballast water, electrochemical sensor, electrode, free chlorine

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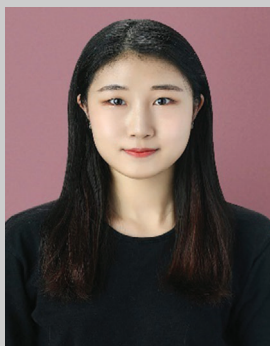
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