Modern designs of electrochemical sensor platforms for environmental analyses: Principles, nanofabrication opportunities, and challenges

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ABSTRACT

In recent decades, much attention has been paid to using nanomaterials in the development of highly-sensitive sensors for environmental monitoring. This review describes how nanomaterials are being used to develop electrochemical sensing platforms for environmental analysis (air pollution, water quality, soil nutrients, and soil pathogens). In particular, we discuss the use of nanofabrication techniques (e.g., monolayer self-assembly, drop-casting, molecular imprinting, electrodeposition, in situ polymerization, hydrogenation, and 3D printing) in the fabrication of high-sensitive electrodes is addressed. The potential use of carbon, organic, inorganic, and hybrid nanomaterials in electrochemical sensing platforms and to enable automation, real-time detection, and multi-plexed test development are also addressed. Recent applications of mobile, disposable, wearable, implantable, and self-powered electrochemical sensors for monitoring ions, particles, compounds, nutrients, microorganisms, and contaminants in real environmental samples are covered. Finally, the opportunities and challenges in nanofabrication high-performance electrochemical sensors and optimizing their performance in testing real samples are highlighted.

1. Introduction

Environmental monitoring describes the quantitative or qualitative measurement of the presence or effect of particles, compounds, nutrients, and pollutants in a given environment. Environmental monitoring is crucial for putting in place and monitoring safety measures to maintain environmental and food quality. It has been estimated that air, water, and soil pollution causes 9 million premature deaths yearly. This represents one in six deaths and costs trillions of dollars [1]. Environmental monitoring can detect toxic pollutants and pathogens released in the air, soil, or water. The global environmental monitoring market was estimated at $14.5 billion in 2021 and should increase to $17.9 billion in 2026, (i.e. a compound annual growth rate of 4.5%). However, continuous environmental monitoring requires sophisticated and automated analytical approaches that allow sample preconditioning and system standardization [2]. Efforts in developing, and automating analytical instruments are needed to improve the accuracy and cost-effectiveness of monitoring programs.

Many laboratory instruments (e.g. UV-Vis spectroscopy, liquid chromatography-mass spectrometry, fluorescence spectrophotometry, capillary electrophoresis, gas/liquid chromatography-mass spectrometry) can be employed to analyze real environmental samples with acceptable dynamic concentration ranges and limit of detection (LOD; micromolar to nanomolar). However, they are expensive and require

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complex sample preparation, long processing time, and high power. Therefore, to decrease power consumption and improve sustainability, environmental monitoring techniques increasingly rely on electrochemical sensors, an interesting class of electronic devices that can overcome almost all the drawbacks of conventional analytical devices [3]. They allow real-time quantitative and qualitative analyses of complex samples with excellent sensitivity (micromolar to picomolar), low LOD (nanomolar to femtomolar), high selectivity relative to interfering species, a short response time (few minutes), and a long lifetime. Electrochemical sensors are widely used for environmental sample monitoring because they offer low implementation costs, multiplexing, miniaturization, easy handling and storage, easy automation, and real-time field monitoring [4].

Electrochemical sensors started to be used in the 1950 s for monitoring industrial oxygen. Currently, many electrochemical sensors are available (e.g. impedimetric, amperometric, potentiometric, photoelectrochemical, and electrochemiluminescence sensors) to improve detection sensitivity, selectivity, LOD, and response time, and for multiplexing. Mobile, disposable, wearable, user-friendly electrochemical sensors offer the possibility of checking in real time the quality of air (e. g. toxic gasses, particulate matter, volatile organic compounds, and microbes), water (e.g. electrical conductivity, turbidity, dissolved oxygen, pH, microbes, inorganic and organic pollutants), and soil (nutrients such us fertilizers, nitrogen, potassium, phosphorus, molybdenum, iron, zinc, copper, boron, manganese, chlorine, and contaminants such as pesticides, herbicides, microbes, and pathogens) [5]. Wearable and implantable electrochemical sensors are useful also for environmental monitoring (radiation, toxic gasses, pathogens) in military and healthcare settings. As environmental samples are complex and analyte concentrations are often low, the sensitivity and detection limits of electrochemical sensors need to be further improved. Due to their excellent electrical, optical, thermal, and catalytic properties and high mechanical strength, nanomaterials offer great opportunities for designing user-friendly, mobile, disposable, wearable, implantable, and energy-autonomous sensing devices for environmental and also for biomedical and food monitoring.

Electrochemical sensors can potentially address the need of low-cost, ultrasensitive, multiplexed analysis, and real-time monitoring of environmental samples. This review gives an update on the nanofabrication techniques used in developing electrochemical sensor platforms for environmental monitoring. First, nanofabrication methods to produce ultrasensitive electrochemical sensors are discussed, particularly monolayer self-assembly, drop-casting, molecular imprinting, electrodeposition, polymerization, gelation, and 3D printing. Then, the potential use of various nanomaterial types (carbon, metal, polymer, and hybrid) to develop electrochemical sensing platforms is presented. Recent developments in electrochemical sensors (mobile, disposable, wearable, implantable, and self-powered) also are described to overcome the shortcomings of conventional sensor design. Issues related to electrochemical sensor performance, including sensitivity, selectivity in complex environmental matrices, automation, real-time detection, and multiplexing, are highlighted. The last section summarizes the current advances, future prospects, limitations, and challenges in their production.

2. Importance of environmental monitoring

Air pollutants are a major issue, especially in industrial cities, because of their negative effects on human health and the global economy. Air pollutants (gaseous emissions and particulate matter) are extremely dangerous. According to the Lancet Commission on Pollution and Health, air pollution is the leading cause of premature death. The World Health Organization (WHO) estimates that each year, indoor air pollution (smoke from dirty cookstoves and fuels) and outdoor air pollution kill ~3.2 million and 4.2 million people, respectively. The global cost of air pollution-related health damage is $8.1 trillion, or

6.1% of the global gross domestic product. The environmental monitoring market worldwide was estimated at $19.89 billion in 2020 and should increase to $43.48 billion by 2030, with an average growth rate of 8.2% between 2021 and 2030 [6].

Air pollutants are divided into two groups: i) primary gasses produced naturally or by human activities (e.g. CO, NO_2, NH_3, SO_2, NO), and ii) gasses produced by the interaction of pollutants from the first group (e.g. O_3, SO_3, NH_4, and particulate matter) [1]. In urban areas, hazardous particulate matter and gas emissions cause respiratory, cardiovascular, and allergic diseases as well as intracerebral hemorrhages and cancer. Excessive humidity can increase the rate of hazardous or toxic chemical compounds in the air, such as smog. Air-borne bacteria and viruses cause skin, eye, and respiratory infections. Various types of analytical tools are available for monitoring airborne particulate matter and gas emissions, but they are time-consuming, expensive, and rarely used in real-time [7]. Therefore, the scientific community has put much effort into developing electrochemical sensors for monitoring air pollution. However, some technical challenges remain, for example, the development of highly sensitive sensors for outdoor gaseous pollutants present at low concentrations.

Similarly, the quality of water also is crucial for the planet's health and sustainability. Major water contaminants include bacteria, viruses, parasites, heavy metals, dyes, insecticides, disinfectants, water hardeners, fertilizers, pesticides, pharmaceutical by-products, fecal matter, and radioactive materials. According to WHO, ~2 billion people drink water contaminated by fecal matter. After air pollution, water pollution is the second leading cause of death. Specifically, infections (e.g. diarrhea, cholera, dysentery, typhoid, poliomyelitis) caused by consumption of polluted water lead to the death of 1.8 million people each year. Each year, worldwide, $260 billion are lost due to lack of clean water and sanitation. The market for water quality monitoring systems was $3815.9 million in 2017 and should increase to $6692.3 million in 2025 (i.e. a compound annual growth rate of 7.3%).

As these hazardous substances do not always change the color of water, they are often invisible contaminants. Therefore, portable electrochemical sensors are an interesting option for the real-time identification of minerals/contaminants at low concentrations in water. The main challenge is to develop portable electrochemical sensors that are inexpensive and user-friendly, consume little power, and do not require sample preparation, expensive laboratory techniques, and trained personnel.

Soil is a natural world component. The global soil monitoring market was $345.6 million in 2019 and should increase to $872.3 million in 2027 (i.e. a compound annual growth rate of 13.0%). A significant portion of antibiotics used in agriculture is released into the environment after being excreted by the animals to which they were administered, favoring the development of antimicrobial drug-resistant bacteria that compromise the effectiveness of antibiotics. Each year, approximately 700,000 deaths are due to antimicrobial drug-resistant bacteria. Soil sample analysis focuses on three aspects: (1) organic content, (2) particle size distribution of mineral soil fractions, and (3) mineralogical analyses. N, K, and P, followed by Mo, Fe, Zn, Cu, B, Mn, and Cl, are the main minerals in the soil, and they all are required for plant growth and high yields. Pesticides are the most common soil contaminants that affect soil quality. Industrial waste contains toxic chemicals (e.g. Hg, Pd, Cd, CN, acids, and alkalis) that directly or indirectly enter the soil and affect soil quality. Soil acidity and moisture influence how quickly plants can absorb nutrients from the soil [8]. Portable electrochemical sensors combined with an analyte-selective membrane can monitor soil analytes (nutrients and contaminants) in real-time, unlike chromatographic and spectroscopic techniques that need a complex optical set-up. Portable electrochemical sensors require only a small electronic circuit to read the sensor output and a battery for on-site measurements.

3. Electrochemical sensor platforms

The typical electrochemical sensor set-up includes a working, a reference, and a counter electrode that are insulated by a thin electrolyte layer [9]. Digital signals are generated by potentiometry, conductometry, amperometry, voltammetry, or impedimetry and can then be further analyzed (Fig. 1). Potentiometry can be used to measure the analyte concentration by quantifying the difference in potential between two electrodes without current flow. The analytical signal is given by the open-circuit voltage between the working and reference electrode that varies in function of the analyte concentration. When using impedimetry, the output is an electrical impedance signal (i.e. charge transfer resistance) that is proportional to the analyte activity. Swept voltammetry or pulsed voltammetry quantifies the analyte concentration by monitoring the sample redox response while varying the potential window. In voltammetry, a potentiostat is placed between the working and counter electrodes to perform a potential sweep (linear and cyclic sweeping voltammetry) or a pulsed potential (square wave voltammetry) relative to the reference electrode. The current produced is the analytical signal. Amperometry, also called chronoamperometry, is a time-dependent technique in which the current response time variation is studied under potentiostatic control. Conductimetry is based on a method used in enzyme catalysis to determine the enzyme activity and substance concentration. Selectivity is ensured by the enzymes that catalyze specific reactions.

Designing electrochemical sensing platforms for the multiplex analysis of the different components present in environmental samples is a key issue. Electrodes with nano-surface features might allow detecting with higher selectivity and sensitivity target compounds in such samples. In electrochemical sensors, noble metals are generally used in the working electrode because they are chemically stable in the presence of different electrolytes. Moreover, their surface chemistry can be easily matched to the bond and has a high binding affinity for many different analytes [10]. Carbon electrodes (e.g. glassy carbon and graphite electrodes) are an expensive electrode material and are difficult to pretreat to obtain a reproducible behavior. Indeed, modification of the electrode surface by immobilization of recognition elements is used to enhance the selectivity and sensitivity of the binding to the target analyte. Glassy carbon electrodes (GCE) display very slow electron transfer kinetics in most redox chemistry processes of many analytes and also interferences, especially if they are clean and have low oxygen functionality. Moreover, most species are not adsorbed on GCEs. Electrochemical pretreatment of carbon electrodes (e.g. in acid) generally makes them more suitable for electron transfer by introducing more oxygen functionalities on the surface, but only when the potential excursions are above $+ 1.2$ V to Ag/AgCl [11].

Analytically selective membranes are an essential component of electrochemical sensing platforms. Indeed, the electronic current through the transistor, known as drain current, can be controlled by changing the surface potential of these membranes. They serve as simple mechanical supports, can be part of the transduction mechanism, or are used to filter or concentrate analytes in real samples. The choice of membrane material is influenced by its manufacturability, capacity to avoid electrolyte leakage, permeability to the target analyte, thickness, durability over a wide temperature range, and environmental stability. Polymeric membranes are more frequently used for sensing applications
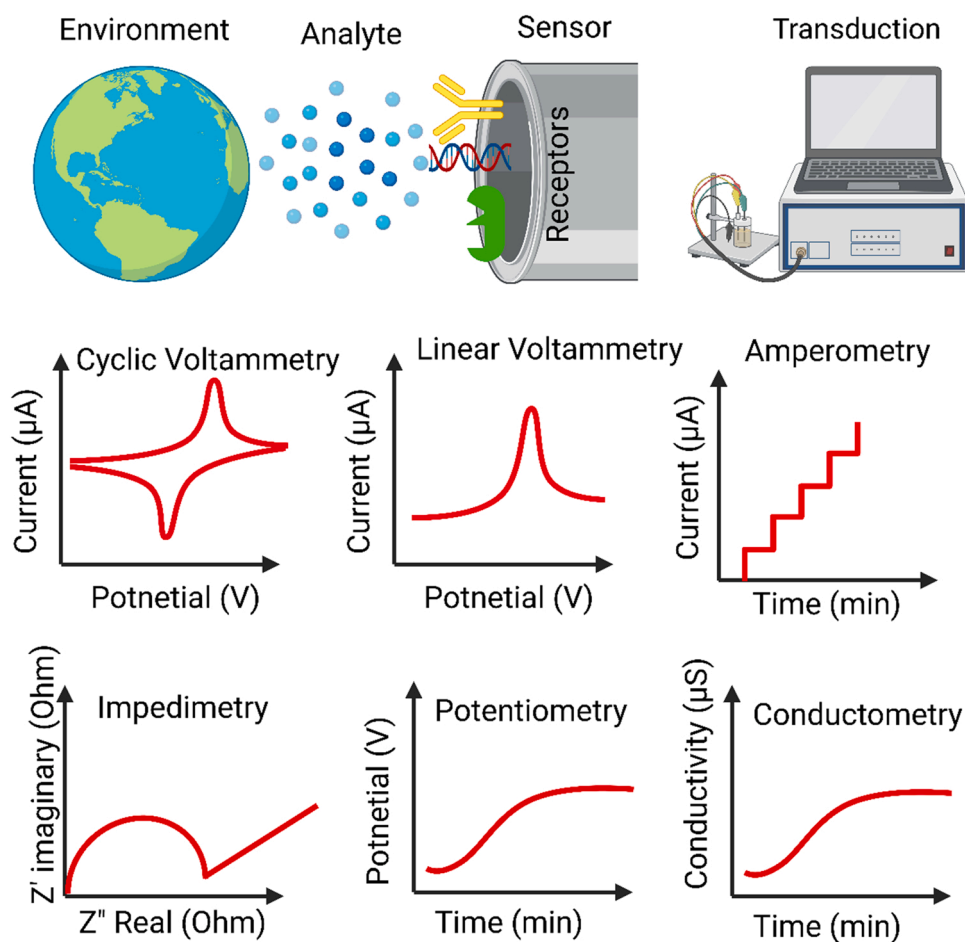

Fig. 1. Schematic diagram of electrochemical signal transduction used in electrochemical sensors: voltammetry, amperometry, impedimetry, potentiometry, and conductometry. The image was created using Biorender.

than glass or inorganic membranes. Electrospun nanofiber materials with unique properties are particularly interesting as membrane materials [12]. Potentiometric sensors made of molecularly imprinted polymers (MIP; i.e., the receptors) have been developed to monitor environmental analytes. However, unlike conventional recognition elements (e.g. polyvinyl chloride and Teflon) that easily dissolve in the plasticized polymer membranes, MIPs are usually rigid and highly cross-linked, and they are not easily dissolved, but disperse in the plasticized polymer matrices. MIP insolubility is an undesired feature for the development of selective analyte membranes [13].

Electrochemical redox reactions are associated with a change in electrolyte resistance, adsorption of redox probes, charge transfer at the electrode surface, and mass transfer to the electrode surface. In the circuit that describes these processes, the working electrode serves as an interface where analyte and probe are immobilized and acts as a transduction element to trigger electrical fluctuations. The counter electrode forms a continuum with the electrolyte solution and maintains the circuit. The electrolyte in the sensor allows the dissolution of reactants and products for efficient electrical chemical contact between the working, counter, and reference electrodes. Conductometric sensors (i.e. devices with two electrodes) measure the electrolyte conductivity that changes after exposure of the cell to the environment to be tested. Upon analyte detection, the electrochemical sensor cell generates a small current that is proportional to the catalyst concentration [14]. Aqueous electrolytes (sodium hydroxide, sulfuric acid, and potassium chloride), non-aqueous electrolytes (propylene carbonate-lithium perchlorate), and solid electrolytes (polymeric Nafion and yttrium-stabilized zirconia, alumina, and NASICON for high-temperature sensors) have been described in the literature [15]. However, the most common electrolyte is usually an aqueous solution of strong inorganic acids.

4. Nanofabrication and modification of sensor platforms

Nanofabrication techniques allow the production of sensors with sub-micrometer features and extremely high sensitivity compared with conventional sensors. The electrode surface can be decorated with nanomaterials to improve electrochemical detection (sensitivity, selectivity, and repeatability). However, it is crucial to overcome the challenges of nanomaterial fabrication for the scalable, cost-effective, and timely production of electrochemical sensors with widespread applications. To date, electrochemical sensors have been fabricated using many new nanomaterials, such as graphene, carbon dots, 2D transition metal dichalcogenides, and phosphorene [16]. In this section, nanofabrication techniques, such as drop-casting, electrodeposition, self-assembly of monolayers, inkjet printing, and 3D printing, are discussed in detail.

4.1. Self-assembling of capture monolayers

Self-assembled monolayers (SAM) are molecular arrays of organic molecules deposited on the electrode surface, generally by chemisorption of "polar head groups" in the vapor or liquid phase. The "head groups" arrange together on the electrode surface, while the tail groups arrange away from the substrate. Areas of densely packed molecules grow until the substrate surface is covered by a single monolayer. Initially, the adsorbed molecules form a disordered layer; then, in minutes to hours, they form semi-crystalline 3D structures on the electrode surface. The most commonly used molecules are carboxylic acids, followed by longer compounds (up to ten carbons) and cysteine and its derivatives (e.g. penicillamine) [17]. SAM sensitivity and stability can be improved by crosslinking to generate monomolecular polymer films, and by thickening via bridging with polymers. Indeed, SAMs with a thickness of 10–20 nm are more stable and can be used in electrochemical sensors [17].

Gold electrodes also are widely used to fabricate SAMs for various electrochemical sensing applications. SAM stability, uniform surface

structure, and relatively easy variation of the effective thickness are attractive features for biosensor development. Antibody immobilization on gold electrodes can be enhanced by activating thiol COOH groups with 1-ethyl-3-(3 dimethylaminopropyl)carbodiimide (EDC) and N-hydroxy succinimide (NHS) (Fig. 2a) [18]. Alsefri et al. [18] described an electrochemical sensor for PCB monitoring using SAMs
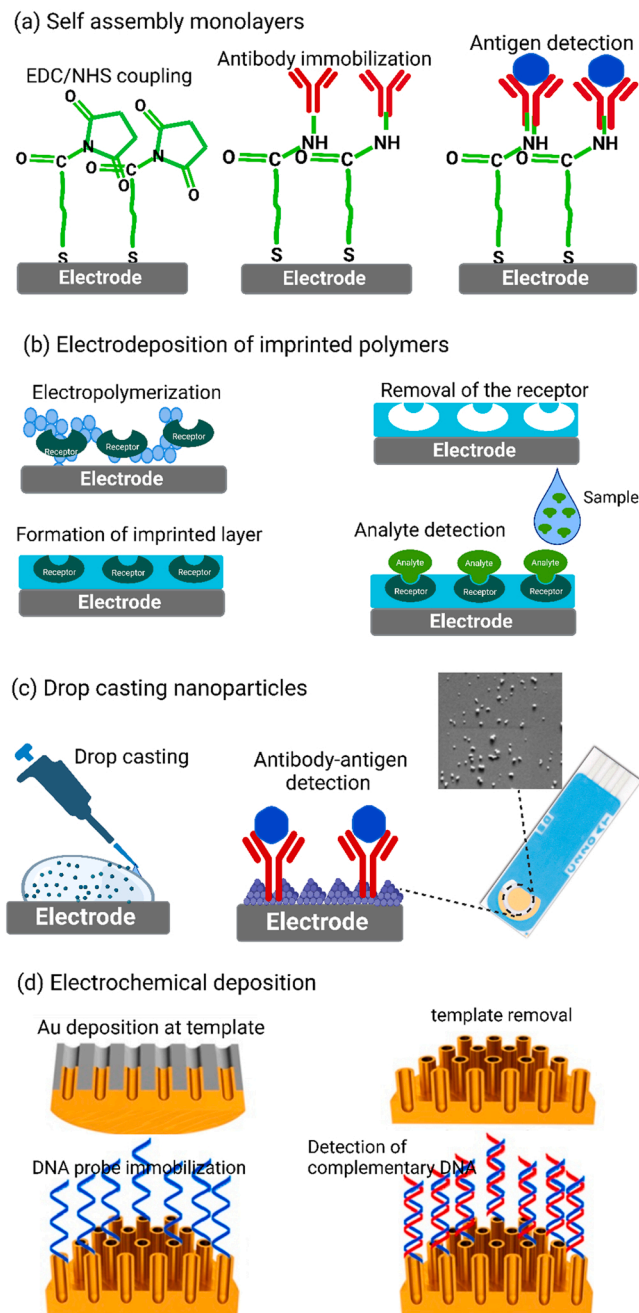

Fig. 2. Fabrication and modification of electrode surface for electrochemical detection of environmental analytes: (a) chemisorption of a self-assembled monolayer of 11-mercaptoundecanoic acid (thiols) followed by activation of the terminal -COOH groups with EDC/NHS and immobilization of the capture antibody, (b) electrochemical deposition of molecularly imprinted polymers (capture layer) in the presence of a analyte, followed by analyte (template) removal, (c) drop casting of nanoparticles onto the electrode surface to enhance electrochemical absorption, (d) fabrication of a nanotube array electrode by electrochemical deposition of an Au layer followed by template removal and chemisorption of the DNA sample (capture layer). The image was created with biorender.

(11-MUA/EDC/NHS) to immobilize anti-PCB antibodies on a gold electrode. This sensor LOD and linear range were 0.09 ng/mL^{-1} and 0.101–220 ng/mL^{-1}, respectively. Similarly, Messaoud and coworkers [19] fabricated a cheap, transportable, label-free electrochemical sensor in which anti-*Aeromonas salmonicida* antibodies were covalently attached to the electrode gold surface via SAMs. The sensor linear working range and LOD were 1–10^7 CFU mL^{-1} and 1 CFU mL^{-1}, respectively.

4.2. Molecularly imprinted recognition elements

Compared with conventional recognition elements, MIPs are easy and cheap to produce and display high selectivity. Their recognition sites mimic the binding sites of biological molecules, such as antibodies and enzymes. As recognition by MIPs is mechanically and chemically stable, even at high pH and temperature, they are ideal for environmental applications. MIPs are mainly synthesized using templates (analytes) generated by the formation of complementary recognition cavities. Multi-step swelling, suspension, and precipitation polymerization methods are used to prepare MIPs [20]. MIP selectivity for and binding to target analytes can be optimized by selecting the appropriate monomers, crosslinkers, initiators, and reaction conditions. Complementary microcavities for specific targets (e.g. "lock and key") are built to obtain side-effect recognition functions. Fig. 2b shows the general steps for nanofabrication and characterization of a MIP-based electrochemical sensor. After the removal of the template molecules, the target-specific cavities in the polymer can bind to the target analyte. After MIP incubation with a target-containing sample, the target molecules bind selectively to the cavities.

Metal ions, drugs, hormones, pollutants, phytochemicals, biomarkers, peptides, proteins, viruses, bacteria and yeast cells have been detected using electrochemical sensors with MIPs. Boeluekbaşı et al. [20] produced an electrochemical sensor using MIP/MoS$_2$ @MWCNTs to measure paraoxon (an organophosphorus pesticide widely used in agriculture) with a LOD of 2.0×10^{-12} M. Kou et al. [21] developed a MIP-based potentiometric sensor to detect neutral bisphenol A (LOD of 0.02 µM). Wang et al. [22] developed a very sensitive electrochemical SiO$_2$ @MIP sensor based on multi-walled carbon nanotubes (MWCNTs) and gold nanoparticles to detect dibutyl phthalate is widely used to increase plastic flexibility, but also is an environmental pollutant. This sensor has a LOD of 5×10^{-9} g.L^{-1} and quantifies dibutyl phthalate at concentrations ranging from 10^{-7} g·L^{-1} to 10^{-2} g·L^{-1}. Several studies showed that MIP-based electrochemical sensors can be used to identify pesticides, such as hydrazine, trichlorfon, cypermethrin, and glyphosate [23].

4.3. Drop casting of nanoparticles

The working electrode surface can be modified with nanoparticles and analyte-selective membranes using the drop-casting technique. However, this method for membrane modification gives films that are not uniformly thick, and that may crack after solvent evaporation. In this method (Fig. 2c), a droplet of liquid containing a suspension of the desired nanoparticles is first applied to the electrode surface, ideally only of the conducting electrode, without spilling into the insulating environment [24]. Droplet casting is inexpensive and easy. Unfortunately, electrochemical sensing platforms require the fabrication of uniformly modified surfaces, and coffee rings and associated effects are significant limitations to the reproducibility of surfaces modified by drop casting. Most studies on materials (nanoparticles or polymers) drop-casted on electrode surfaces assume that the base material does not influence the electrochemical response. However, as the drop-casted coating is porous, the analyte may diffuse to the base material through electroactive pores. Therefore, studies, where drop-casting is used to coat the electrode surface, should take into account also the base electrode contribution to the total current or potential [24].

Ruecha and co-workers [25] fabricated by drop casting and electrospray a graphene/polyaniline-modified electrode to be used as an electrochemical sensor to concomitantly identify Zn^{2+}, Cd^{2+} and Pb^{2+}. Compared with the unmodified electrode, electrochemical conductivity and peak anodic current were increased in the modified electrode that displayed a linear operating range from 1 µg L^{-1} to 300 µg L^{-1} (LOD of 1.0 µg L^{-1} for Zn^{2+} and 0.1 µg L^{-1} for Cd^{2+} and Pb^{2+}). This modified electrode could selectively identify target analytes against metal ions (e. g. Mn^{2+}, Cu^{2+}, Fe^{3+}, Fe^{2+}, Co^{3+}, and Ni^{2+}). Hatamie and coworkers [26] drop-casted graphite carbon nitride nanosheets onto GCEs for the fast and sensitive identification of Pd^{2+} by voltammetry. Drop-casting of nanosheets (45 m^2/g) increased the GCE microscopic surface area by a factor of 20 compared with the non-modified GCE rod electrode and consequently led to higher peak current intensity in voltammetric studies. The LOD for lead ions was 3 ppb.

4.4. Electrochemical deposition of nanoparticles and thin films

Electrochemical deposition is one of the most widely used methods for depositing nanoparticle films on conductive substrates. Indeed, the morphology (even without a template) and the size of the fabricated nanostructured films can be modulated by adjusting the experimental synthesis settings, particularly the current density, applied potential, and synthesis time. The main electrodeposition parameters are influenced by the (1) current density, (2) temperature, (3) pH of the solution, (4) type of working electrode, (5) electrolyte, (6) bath composition, and (7) additives or impurities present in the solution. Such modified electrodes have been investigated to understand the charge transfer and charge transport mechanisms in thin films.

Currently, electrochemical deposition is performed using different methods, for instance, cyclic voltammetry, potential jump, and double pulse deposition. The particle size can be precisely controlled by adjusting the current density, the applied potential, and the electrolysis time. Many different 3D networks can be produced by electrochemical synthesis with a template. For example, a biosensor was fabricated by electrochemically depositing a gold nanotube array with 200 nm pores inside the membrane using a gold plating solution at 1.0 V (vs. Ag/AgCl) (Fig. 2d) [27]. This biosensor can detect *Mycobacterium tuberculosis* DNA using the methylene blue redox probe, with a LOD of 0.05 ng µL^{-1}. Importantly, these nanotube arrays were less susceptible to deformation or clustering than those prepared by physical or chemical vapor deposition [27].

Moreover, an amperometric sensor was fabricated by 3D printing the Ag working electrode with electrodeposited Cu nanoclusters for nitrate detection in water (sensitivity of 19.578 µA/mM, LOD of 0.207 nM, and linear concentration range from 0.05 mM to 5 mM) [28]. The device was hardly affected by interfering species (Fe^{2+}, Fe^{3+}, Mn^{2+}, Na$^+$, Cu^{2+}, NO$_2^-$, Cl$^-$, SO$_4^{2-}$, HCO$_3^-$, CH$_3$COO$^-$). Another study showed that layer-by-layer multilayer films, which were electrochemically synthesized using MWCNTs and metal-organic frameworks (MOFs), enhanced the simultaneous determination of Cd^{2+} and Pd^{2+} by electrochemical sensors [29]. GCEs modified with this three-layer film (MWCNTs-COOH/UiO-66-NH$_2$/MWCNTs-COOH) increased the sensitivity for Cd^{2+} (0.090 ppb) and Pb^{2+} (0.071 ppb) and showed better linear relativity.

4.5. Depositing hydrogel layers

Hydrogels are often used to fabricate ultrasensitive electrochemical sensors with high stability and flexibility and very good electrical conductivity. Hydrogels offer a highly porous matrix for analyte extraction and rapid electron transport and are very sensitive to external stimuli. Their excellent biocompatibility facilitates the encapsulation and crosslinking of biomolecules (e.g. nucleic acids and proteins) in polymer matrices, thus preserving their bioactivity for practical applications. Moreover, functional additives (nanoparticles, conductive polymers)

can significantly alter the stiffness and gelling temperature of hydrogels used in electrochemical sensors. Polymer gelators and nanoparticles form nanohybrid hydrogels by interacting in different ways (Van der Waals forces, π-π-stacking, hydrogen bonding, and dipolar and electrostatic interactions) [30]. For instance, functionalized metal nanoparticles interact through Van der Waals forces, whereas carbon nanoparticles interact through π-π stacking. Upon exposure to external stimuli, conformational changes (phase transition) are observed in the hydrogels, leading to the production of signals that can be recorded by transduction systems. The signal intensity is influenced by the hydrogel composition, shape, and crosslinking density [31].

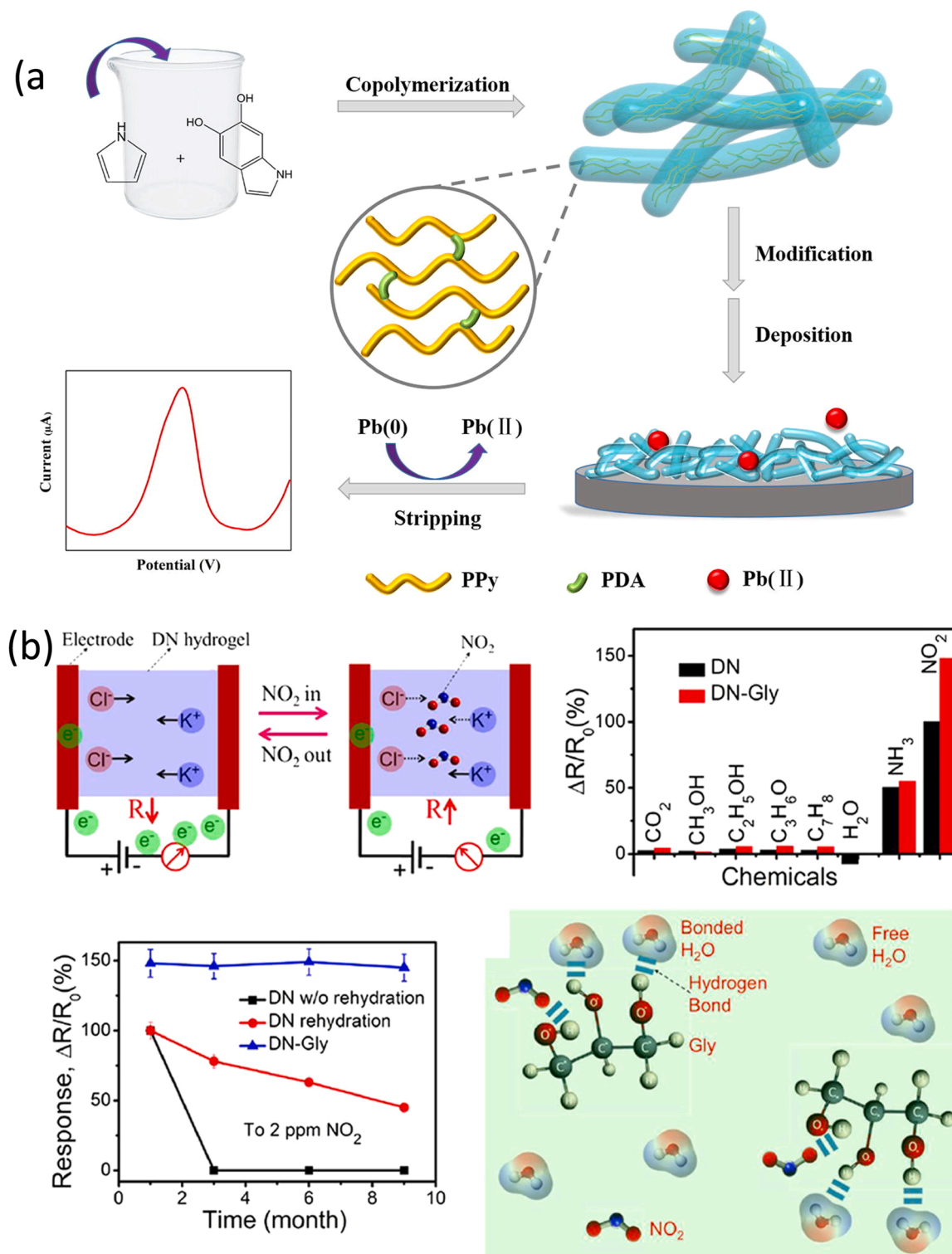Hydrogels for sensing applications can be prepared using synthetic

Fig. 3. Hydrogel-based electrochemical sensor: (a) screen-printed carbon electrode coated with a hydrogel layer of polypyrrole(PPy)/polydopamine(PDA) for the detection of Pb^{2+} ions in water © Elsevier [30], (b) glycerol-modified ionically conductive hydrogel (DN -Gly) for NO_2 detection in the gas phase. Inset: quantitative responses to 2 ppm NO_2 as a function of operating time by DN sensors without (black) and with (red) rehydration and by the DN -Gly sensor without rehydration (blue) © American Chemical Society, [31].

polymers, such as poly(N-isopropylacrylamide) or poly(vinyl-pyrrolidone), and also some biopolymers derived from polysaccharides and polypeptides (e.g. chitosan, pectin, agarose, cellulose, collagen) [32]. Biocompatible polymer hydrogels and innovative electrode printing technologies allow the development of advanced, flexible, and wearable next-generation bioelectronics with superior sensing capacities [33]. Hydrogels have been integrated in electrochemical sensors to detect a wide range of molecules, from biomolecules to environmental pollutants. For instance, a hydrogel-modified screen-printed electrochemical sensor [30] allows for efficiently monitoring Pb^{2+} presence in wastewater (LOD of 0.15 μg L^{-1} and sensitivity of 0.17 μg L-1 $μA^{-1}$) (Fig. 3a). The screen-printed working electrode was coated with a hydrogel prepared from a polypyrrole-doped dopamine polymer [30].

Hydrogels that contain an electrolyte are used as a substitute of liquid electrolytes to improve the sensor resistance to electrolyte leakage and viscosity and reduce its evaporation rate. Wu and coworkers [31] used ionically conductive hydrogels based on poly-acrylamide/carrageenan double networks to produce sensors that detect NH_3 and NO_2 with a sensitivity of 78.5 ppm^{-1} and a lower theoretical LOD for NO_2 (1.2 ppb). Quantitative responses of the ionic conductive hydrogel as a modifier, compared with sensors without glycerol (DN), to

100 ppm CO_2, 2 ppm NO_2, 50 ppm NH_3, 72% relative humidity, toluene, methanol, and acetone vapors. The DN-Gly sensor can retain water via the formation of hydrogen bonds between Gly and water molecules. Such hydrogels can bear up to 1200% of mechanical stress, long-range ding, and twisting and the sensors maintain their sensitivity for up to 9 months (Fig. 3b). Their excellent sensitivity might be due to the well-designed polymer chains and the solvent with the large oxygen-containing functional groups. The increased sensitivity to NO_2 in the presence of glycerol was explained by hydrogen bonds between NO_2 and glycerol molecules [31].

4.6. 3D printing and inkjet printing technologies

Screen-printed electrochemical sensors combine advanced electrochemical systems with screen-printing technology and are a potentially powerful analytical tool for monitoring water pollution. This combination offers simple, low-cost, one-use, transportable instruments for pollution monitoring in the field that can be fabricated at the industrial scale [34]. The carbon ink, which has the most important role according to the manufacturer, is made of graphite powder, polymeric binders, and other functional additives to improve the sensor performance. Carbon
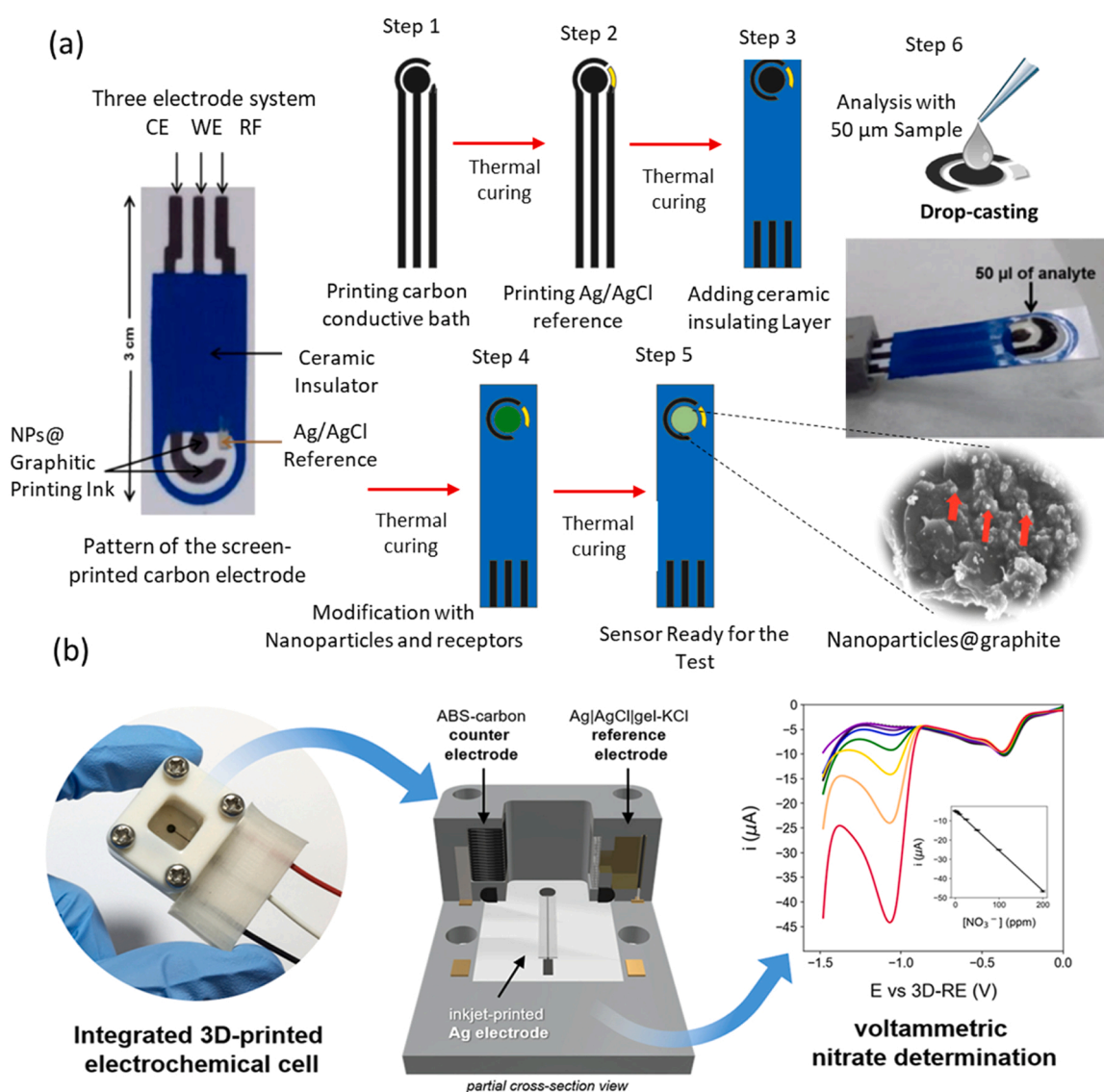

Fig. 4. Electrochemical sensors based on electrically conductive printed inks as electrode materials: (a) screen-printed electrodes coated with carbon paste ink decorated with Ag- NP, (b) 3D-printed electrochemical cell based on inkjet-printed Ag electrode for detecting nitrate ions. © Elsevier [36].

nanomaterials may be combined with metallic nanoparticles to obtain hybrid systems with synergistic electrocatalytic activity [35]. The electrochemical response of carbon nanomaterials can be improved by metal and non-metal doping. This carbon electrode type is widely used in biosensors, environmental monitoring, food analysis, and immuno-assays. Fig. 4a describes the drop-casting of metal nanoparticles onto screen-printed carbon electrodes to improve the sensor performance. The electrode pattern, fabricated with the same technology used for most glucose sensors, includes carbon-based working and counter electrodes, and an Ag/AgCl reference electrode.

Recently, 3D printing and inkjet printing were used to make several miniaturized electrochemical sensors to monitor water quality directly at aquaculture sites at a low cost. For instance, a reusable electrochemical cell [36] was 3D printed using an acrylonitrile-butadiene-styrene (ABS) filament (Fig. 4b). It included a 3D printed ABS-carbon counter electrode and an Ag/AgCl/Gel-KCl reference electrode with a 3D printed porous junction along the sample compartment side. The reference electrode was modified by electrodeposition of nanostructured Ag to increase the sensitivity for nitrate ions. Then, nitrate ions in synthetic brackish water samples (pH 8.0) were detected using linear sweep voltammetry with a LOD of 1.40 ppm and a sensitivity of 0.2086 μA ppm^{-1}. Measurements done with different electrode batches confirmed the intra- and inter-electrode reproducibility without much interference by ions (cations and anions) commonly found in such samples [36].

HuseyinIpekci and coworkers [37] developed a novel flexible sensor by depositing conductive Ag patterns to polyester fabrics. The Ag layer was prepared by inkjet printing followed by heat treatment. The performance of this sensor was assessed by chronoamperometry with H_2O_2. The high sensitivity (295 μA/mM.cm^2) and linear range (50–70 mM) indicate that this textile-based electrode might be used to make flexible electrochemical sensors for environmental applications. Diaz-Amaya and coworkers [38] fabricated an electrochemical inkjet aptasensor to identify Hg^{2+} in organic solvents with a LOD of 0.01 ppm in water and of 0.005 ppm in organic solvents. This value is much lower than the minimum sensitivity needed for monitoring according to the Environmental Protection Agency regulations. This sensor fills a gap in the market of portable and cheap tools for real-time environmental and biosafety monitoring.

5. Roles of different nanomaterials in electrochemical sensor platforms

Nanomaterials with different sizes, shapes, dimensions, composition, permeability, phases, and homogeneity have been studied to produce working electrodes, and many more will be developed in the future [16]. The electrochemical response of nanomaterials depends on their chemical composition (carbon, inorganic, organic, or hybrid nanomaterials) and their dimensionality (size and shape) compared with bulk materials. This section discusses the critical role of different nanomaterials in the electrochemical sensor features, for instance, stability, sensitivity, and selectivity.

5.1. Carbon nanomaterials

Carbon nanomaterials are a novel class of nanomaterials that are widely used in electrochemical sensors [39] particularly due to their elevated aspect ratio, chemical stability, and electrical conductivity. Functionalization is possible, because of the carbon structure high reactivity, to increase selectivity for the analyte of interest. In electrochemical gas sensors, MWCNTs with elevated surface-to-volume ratio and hollow structures promote the gas molecule adsorption and desorption. Sorption gas sensors, which are the largest group of gas sensors, mainly operate through adsorption, in which an adsorbed gas molecule donates or accepts an electron from the carbon nanomaterial. Pristine carbon nanotubes (CNT) lack selectivity as sensors because they

react with too many chemicals. This drawback can be overcome by functionalization with different chemical groups to improve their sensitivity and tailor their selectivity for specific analytes.

Carbon paste electrodes (CPEs) are ion-selective electrodes that are chemically inert, robust, renewable, and without an internal solution. They also display stable response and low ohmic resistance. CPEs are usually composed of graphite powder, ionophores that bind to the analytes, and pasty liquids (mineral oils) to promote the analyte mobility and binding to the electrode active surface. Inorganic and organic materials can be detected using CPEs after chemical modification [40]. CPE's major drawback is that their performance is influenced by the user's experience and this limits their applicability. Unlike solid GCEs, which show similar basic electrochemical features among products from the same manufacturer, each CPE is unique, its electrochemical properties may vary in function of the batch, and thus must be calibrated. This may not be a problem in a research environment but would be a significant burden in production [40].

Electrochemical biosensors-based metallic electrodes modified with carbon nanostructures are interesting analytical devices for real life utilization. Although CNTs have often used, graphene nanofibers, through careful adjustments of their structure, can display better electrochemical sensing performances. Metal electrodes can be modified by deposition of carbon nanomaterials to obtain improved electrical signals. For instance, an electrochemical biosensor based on screen-printed ITO electrodes modified with CNTs was fabricated to detect *Porphyromonas gingivalis* (a Gram-negative bacterium) in saliva [41]. Chronocoulograms were obtained (at 0.25 V) using artificial saliva samples with different *P. gingivalis* concentrations on CNT- and BSA-modified ITO electrodes after incubation in Tris buffer (pH 7.5) (0.1 mM GPR-AP, 2.0 mM TCEP, and 50 mM Gly-Gly) at 55 °C for 15 min. The device had a LOD of 5×10^5 CFU mL^{-1} in artificial saliva [41]. CNTs can transport electrons very quickly, are extremely sensitive, and can detect molecules at low concentrations [39].

Chemical processes have been extensively studied. For instance, in covalent functionalization, oxidization with strong acids (e.g. H_2SO_4, HNO_3, or H_2SO_4/HNO_3) is used to fix the carboxyl groups on the carbon nanomaterial surface. This may be followed by other modifications, such as esterification or amination [43]. Covalent functionalization can be also performed by radical grafting with alkyl or aryl peroxides, substituted anilines, and diazonium salts as starting materials. Carbon materials can be covalently and non-covalently functionalized to tailor the electrode electrochemical sensing performance. However, there are still many challenges in the fabrication of carbon materials to eliminate impurities and improve functionalization. Overcoming these hurdles will increase the sensor selectivity and control the densification defect.

5.2. Inorganic nanomaterials

Inorganic nanomaterials can be composed of a metal or a non-metal element, of a metal oxide, hydroxide, chalcogenide, or of phosphate compounds. In electrochemical sensing, noble metal nanoparticles (mainly Ag, Au, Pt, and Pd) might provide a less expensive and more robust alternative to enzymes, and are often chosen because they are biocompatible and display fast electron transfer. Transition metal nanoparticles (e.g. copper, nickel, and their alloys) are electrocatalysts for the conversion of various analytes in alkaline conditions. Metal oxide and ceramic nanoparticles (TiO_2, MnO_2, ZnO, and Fe_3O_4) can enhance the electrochemical sensor stability. Oxides of non-transition metals and internal transition metals (e.g. bismuth, tin, and lanthanides) are suitable for the electrochemical detection of gas molecules [44]. The conductivity of semiconducting metal oxide nanoparticles can be improved by doping with metal sulfides that have a smaller band gap and higher electrical conductivity compared with metal oxides. The nanostructure of the doped electrode active sites leads to excellent specificity and sensitivity. Metallic nanoparticles can be deposited on the electrode surface using different methods, such as electrodeposition and physical

adsorption [45].

Quantum dots (QD) are excellent fluorophores for improving the performance of photoelectrochemical sensors. The electroluminescence properties of inorganic QDs can be tailored by changing their shape, size, and composition, using advanced surface modification and complexation techniques. Electrochemiluminescence (ECL) sensors based on inorganic QDs have many advantages. Compared with conventional ECL luminophores (Ru(bpy)$_3^{2+}$), inorganic QDs exhibit good stability, functional flexibility, optical properties, and low cost. For instance, luminol is not suitable for biomolecule labeling because luminol ECL requires alkaline conditions (pH 13). Therefore, inorganic QDs have been exploited in many sensing methods to improve ECL detection efficiency [42]. However, the relatively high toxicity of inorganic QDs has limited their application in biological labeling and as electrochemical sensors. Therefore, organic QDs, such as carbon dots, graphene dots, and graphene oxide dots, have been investigated to fabricate ECL sensors because they are readily available starting materials, easy to use, and less toxic than inorganic QDs. Fig. 5b shows a schematic presentation for the synthesis of an ECL biosensor to detect *Escherichia coli O157:H7*. MIPs. This ECL biosensor is prepared by dopamine electropolymerization in the presence of E. coli on the electrode surface. E. coli bioconjugation with the primary anti-E. coli antibody (pAb) followed by incubation with the N-GQD-labeled secondary antibody produces intense ECL irradiation in the presence of K$_2$S$_2$O$_8$ [42].

5.3. Hybrid nanomaterials

Conductive polymers are potential electrochemical sensor candidates. Conductive polymers are organic compounds with an extended π-orbital system that allows the migration of electrons from one to the other polymer end. Using conductive polymers and screen printing, a wearable (tattoo) sensor was fabricated for biomedical and environmental applications [46]. Common classes of organic conductive polymers include polyacetylene, polypyrrole, polythiophene, polyterthiophene, polyaniline, polyfluoro, polyalkylthiophene, polytetrathiafulvene, polynapthalene, polyphenylene sulphide, and polyphenylene vinylene. Several methods have been described to synthesize new conductive polymer composites, such as template-oriented synthesis, steam polymerization, chemical functionalization, in-situ generations of conductive polymer composites. Besides these methods, electrochemical techniques are a convenient approach for preparing
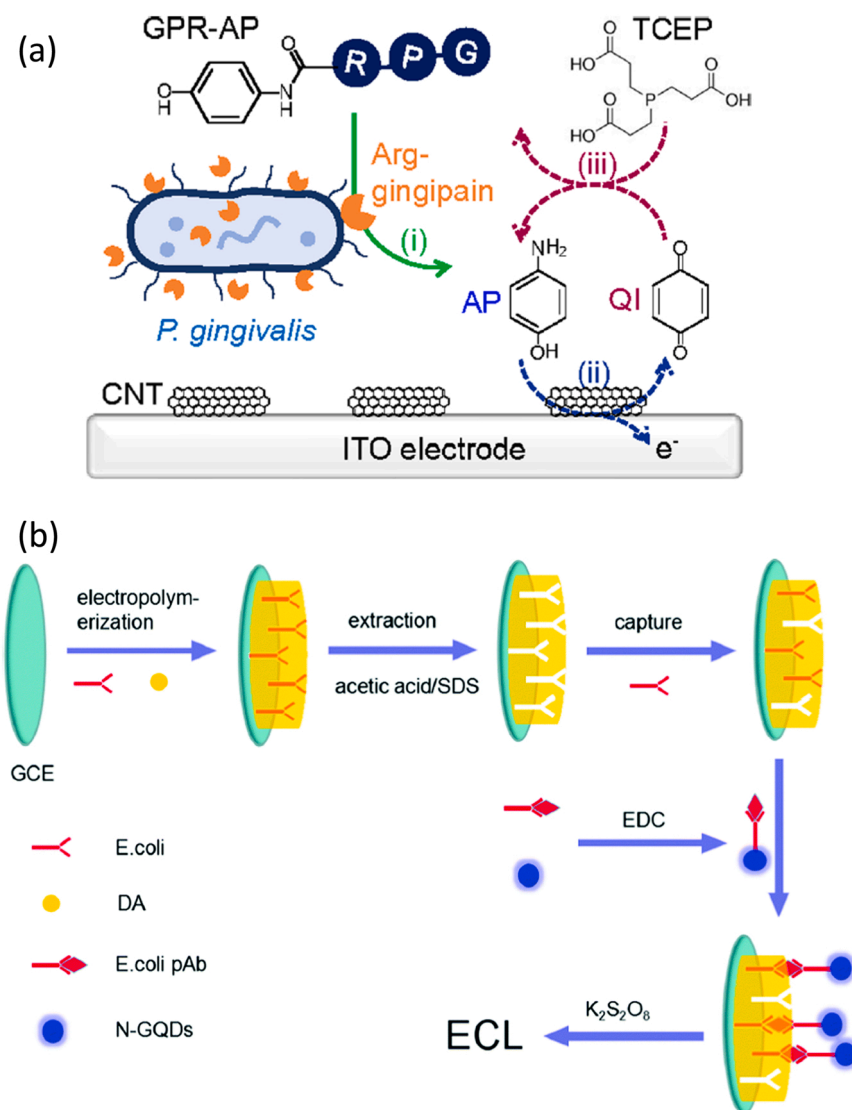

Fig. 5. Electrochemical sensors for the detection of bacteria and biofilms: (a) ITO electrode modified with CNTs for the detection of *Porphyromonas gingivalis* detection through the proteolytic cleavage of Arg-gingipain © American Chemical Society [41]; (b) GCE electrode coated with electrochemically deposited MIPs (capture layer) for the detection of detect *Escherichia coli* O157:H7. © American Chemical Society, [42].

conductive polymer composites because they allow controlling the morphology, thickness, chemical state, and conductivity for electrochemical sensing applications [47].

Researchers have been investigating the use of electrically conductive polymers based on electrically conductive nanomaterials, such as metallic nanoparticles, CNTs, and graphene, to fabricate electrochemical sensors [48]. For instance, an electrochemical sensor based on conductive microporous organic polymers with many -OH functional groups, acetylcholinesterase and Nafion on the CPE surface was used to monitor organophosphate pesticides (paraoxon and methylparathion) in lettuce (Fig. 6a). The sensor had good linear ranges for methylparathion and paraoxon (5.0×10^{-13} g•mL^{-1} - 1.0×10^{-8} g•mL^{-1} and 1.0×10^{-13} - 1.0×10^{-9} g•mL^{-1}, respectively) [49].

MOFs are compounds in which metal ions or clusters are linked to organic ligands to form 0–3D structures. MOFs are exploited for sensors based on luminescent, electrochemical, and colorimetric signals. They are attractive electrode materials for electrochemical sensing for the following reasons: i) MOFs can be used to enhance the surface area for analyte adsorption and transport due to their porous matrices; ii) MOFs have pores or channels of different shapes and sizes that are needed for size-exclusion effects and detection selectivity; iii) MOFs offer different functional sites (metal centers, linker groups, or active visitors in the channels) for analyte adsorption and activation or direct electron transfer between redox-active sites and analytes; and iv) MOFs can be

structurally modified to study the sensor mechanisms and structure-property correlations [50,51]. Low electrical conductivity and stability in aqueous solutions (due to due to the coordination bond reversibility) are the main MOF drawbacks for use in electrochemical sensors. Moreover, as their size is often in the micrometer range, MOFs display poor adhesion affinity for the electrode surface. To overcome these limitations, MOFs must be combined with polymeric materials or metallic nanoparticles that exhibit high electrical conductivity [52,53].

Several studies investigated MOFs for sensing applications. Redox hopping supports charge transport between porphyrin units in a MOF-525 thin film [50]. These units catalyzes nitrite oxidation due to their electrocatalytic properties (Fig. 6b), leading to an amperometric sensing response (linear concentration range and LOD of 20–800 µM and 2.1 µM, respectively). In another study [51], $V_{10}O_{28}$ nanoclusters immobilized on Zr-MOF (NU-902) allowed reducing the charge transport and electrocatalytic activity for dopamine sensing. Charge binding was observed through reversible redox reactions of $V_{10}O_{28}$ which was a potent electrocatalyst for dopamine detection (Fig. 6c). The amperometric sensor made using $V_{10}O_{28}$@NU-902 displayed a linear range of 25–400 µM and a LOD of 2.1 µM. Similarly [52], bimetallic Au-Pd nanoparticle deposition on a Zr-MOF (UiO-66-NH2) allowed the ultra-sensitive detection of nitrite (Fig. 6d), as indicated by the linear response concentration range (0.05–5666 µM) and LOD (0.01 µM). In an earlier work, Ti-MOF (NH₂-MIL-125(Ti)) was used as catalytic thin films to
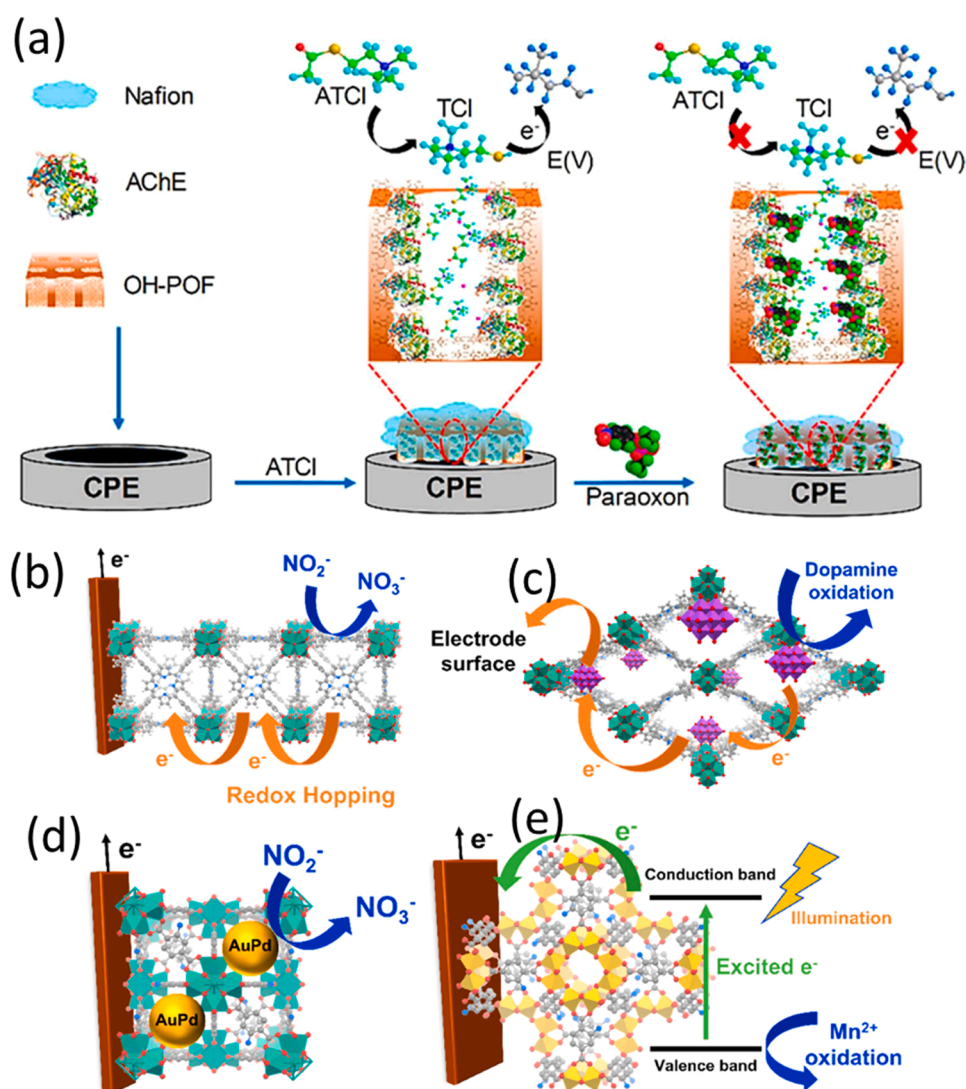

Fig. 6. Electrode modification using nanomaterials with enhanced electrochemical response: (a) Nafion/ microporous organic polymers (OH-POF). © Elsevier [49]. (b) Thin films made of a redox-active uniform Zr-based porphyrin metal-organic framework (MOF-525) for nitrite detection. © Elsevier [50]; (c) $V_{10}O_{28}$ clusters deposited on Zr-MOF (NU-902) for dopamine detection. © American Chemical Society [51], (d) Immobilized Au-Pd nanoparticles on UiO-66-NH₂ for nitrate detection. © Elsevier [52]. (e) catalytic thin films of Ti-MOF (NH2-MIL −125(Ti)) for photoelectrochemical detection of Mn²⁺ ion. © Elsevier [53] and © MDPI [54]. Cyan: Zr; yellow: Ti; violet: V; red: O; blue: N; gray: C; white: H.

oxidize and to photoelectrochemically detect Mn^{2+} in tea samples [53] (Fig. 6e).

6. Electrochemical gas sensors for air analysis

In gas monitoring with electrochemical gas sensors, the studied gas is oxidized or reduced at an electrode and then the resulting current is measured. To date, several amperometric gas sensors have been fabricated to monitor gaseous emissions (i.e. NO, NO_2, CO, HCN, HCl, HBr, O_3, HF, H_2S, alcohols, aldehydes) at ppb concentrations [55,56]. Electrochemical gas sensors are classified in three groups: potentiometric, amperometric, and conductometric sensors. Each sensor can have a specific layout and an unique set of electrolytes, geometries, membranes, and electrodes to detect the chemical properties of the gas analyte and to withstand the operating conditions. Their design and materials are selected mainly in function of the applications and desired analytical performance [57].

In amperometric gas sensors, the current between the functional and counter electrodes is recorded over time and in function of the target gas concentration, a common feature of all gas sensors. The use of counter, working and reference electrodes in contact of a water-sulfuric acid mixture as electrolyte has been a crucial innovation in amperometric sensors. This sensor layout gives a separate gas diffusion barrier for the orifice and the porous membrane. These low-cost sensors offer sufficient statistical accuracy and affordable detection versatility. However, their performance is limited in hot and dry conditions due to solvent evaporation [55]. Ionic liquid amperometric sensors were developed as potentially environmentally friendly electrolytes compared with strongly acidic electrolytes. Indeed, room-temperature ionic liquids have specific properties, such as low vapor pressure, excellent electrochemical stability and thermal properties, low toxicity, thin films, biocompatibility, and shorter reaction time for the sensor material [58]. Gold and copper electrodes have been successfully integrated in ionic liquid amperometric sensors that are used to rapidly identify toxic gases (e.g. H_2S, NH_3, HCl) [59].

Amperometric CO sensors measure a chemical reaction within the sensor that produces an electrical output proportional to the level of CO. These includes includes the fellowing reactions on the electrode surface: (a) working electrode [CO + H_2O = CO_2 + 2 H^+ + 2e-], (b) counter electrode [$_{1/2}O_2$ + 2 H^+ + 2e- = H_2O], and a reference electrode. When the three electrodes come into contact with the electrolyte, the following cell reaction [CO + $_{1/2}O_2$ = CO_2] occurs [55]. This reaction is completed when the electrochemical products are desorbed at the electrode surface. Similarly, in diesel engine vehicles, an amperometric sensor based on a lean burn ratio is used to detect oxygen. When the mass transfer through the electrolyte is restricted by the gas diffusion current to the electrode where the electrochemical reaction is undergoing, the limiting current is reached. Specifically, a diffusive gas flow limits the mass transfer through the electrolyte, where the electrochemical reaction proceeds independently of the applied voltage and proportionally to the gas's partial pressure. The choice of materials for electroanalytical processes is crucial because the sensor lifetime and reaction properties can be significantly limited if the reaction products are sensor poisons [55].

In conductometric gas sensors, electrical conductivity changes upon exposure to the target gas. The metal oxide layers deposited on the electrode surface influence the transducer activity. The receptor function depends on the target gas-electrode surface interactions and can be changed by adding metal oxide mixtures or noble metals. The CO or H_2 gases are detected as follows: oxygen is adsorbed on the material grains when exposed to air [60]. The metal oxide surface conductivity is influenced by surface stoichiometry because it is increased by oxygen vacancies and decreased by the absorbed ions. When molecules (e.g. NO_2) are adsorbed onto the vacancies, electrons flow out of the conduction band and conductivity decreases, while CO or H_2 reacts with the adsorbed O_2 in the oxygenated atmosphere, releasing electrons and

increasing the conductivity. The response of these sensors is regulated by the chemical reaction rate at low temperatures and by the molecular diffusion rate at high temperatures [61].

Potentiometric gas sensors can detect low concentrations of pollutant gases in vehicle exhaust or atmospheric air at temperatures ranging from 450° to 900°C [62], particularly NOx, CO, H_2, NH_3, and hydrocarbons for commercial applications. A recent study described a carbon-based electrochemical device in which a proton-conducting graphene oxide membrane was combined with a sensing electrode (a tungsten oxide nanorod-reduced graphene oxide, WO_3 @rGO, composite) for hydrogen sensing (Fig. 7) [57]. This device showed a good response (>50 mV at 100 ppm H_2, slope of 82 mV/decade) at ambient temperature, a LOD for hydrogen of ~11 ppm, and higher selectivity for hydrogen than ethanol, CO, and acetone. The cathodic and anodic hydrogen and oxygen reactions occurred at the interface between the WO_3 @rGO composite and the graphene oxide membrane [57].

Wearable gas sensors usually consist of sensor components that are developed or attached to the body surface (skin) using a patch, pin, tattoo, or garments. Polyimide, polyethylene terephthalate, silk, stretchable polydimethylsiloxane, acrylic, and Ecoflex are generally used as substrates for wearable gas sensors. mainly because they are flexible, stretchable, and cheap. Tattoo foils are used to detect various harmful gases in the body [63]. A paper-based electrochemical sensor has been fabricated to monitor in real-time exhaled air (see Fig. 8). In this sensor, a screen-printed carbon electrode was modified with Prussian blue, and carbon was used as a counter electrode. Testing by amperometric measurements (potential of 0.0 V against Ag/AgCl as reference electrode) indicated that H_2O_2 is reduced by Prussian blue oxidation and produces a cathodic signal [63]. Drop casting, soaking, spin coating, printing, vacuum filtration, hand writing, and other methods have been used to fabricate wearable gas sensors on paper substrates. However, paper substrate-based sensors are not suitable for the detection of volatile organic compounds due to their solid hygroscopic nature because the absorbed moisture causes major conductivity changes [64]. Table 1.

Thanks to remarkable technological advances, gas detectors for many hazardous gases are now widely used for household, indoor, aviation, and industrial applications. Resistance-based sensors are frequently chosen, but their high operating temperatures result in significant energy consumption. This makes them unsuitable for some technical applications, particularly as portable sensors. Microelectromechanical gas sensors display smaller energy consumption, dimensions, and electrical components compared with resistive-based sensors. Yet, their energy consumption is higher than that of self-heated gas sensors [73]. Currently, gas sensors are incorporated in smartphones for a variety of purposes, including public safety, healthcare, and food and environmental monitoring [74]. As chemiresistive sensors cannot be used in smartphones or batteries due to their higher operating temperatures, it is important to develop low-power, low-cost, portable gas sensors for wireless and wearable devices. Researchers have tried to decrease gas sensor energy consumption using low-power light-emitting diodes, noble metals, and hybrid materials [75].

7. Electrochemical sensors for water quality monitoring

Inorganic compounds (e.g. metals), carcinogens, and organic pollutants (e.g. pesticides) can be detected in water samples and on-site using electrochemical sensors. Electrochemical sensors can be used also to monitor the water physical (i.e. color, odor, taste, temperature, turbidity, electrical conductivity) and chemical features (i.e. acidity, alkalinity, chlorine presence, hardness, and dissolved oxygen). The performance of electrochemical sensors depends on their capacity to provide correct and real-time data in specific environments, without affecting the sample [4].

Molinero-Abad and coworkers [76] developed an anodic stripping voltammetry method to measure Pb^{2+} at sub-nanomolar concentrations
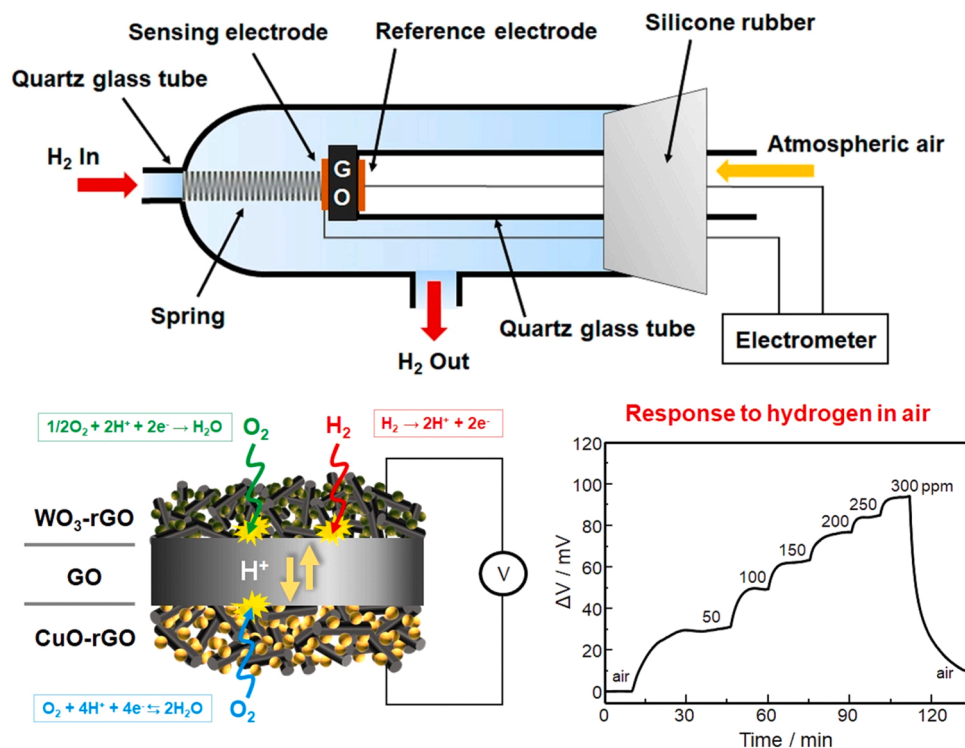
Fig. 7. Potentiometric sensor based on a proton-conducting graphene oxide membrane (WO$_3$ @rGO/GO/Cu-rGO) as electrode materials hydrogen detection in the gas phase. © Elsevier, [57].

using disposable sensing devices. This system is based on three screen-printed electrodes (counter, working, and reference) where the working electrode was modified with reduced graphene oxide and gold nanoparticles. This modification allowed measuring Pb^{2+} in seawater (LOD $= 3 \times 10^{-10}$ M) without changing the sample pH. Liao et al. [77] used smartphone electrochemical sensors to detect in water Pb^{2+} and chemical oxygen demand at low concentrations (45 nM and 9 mg/L, respectively). Bujes-Garrido and Arcos-Martínez [78] developed a low-cost, one-use, wearable screen-printed electrochemical sensor to detect chloride ions by voltammetry by testing different flexible materials. The sensor displayed a LOD of 0.2 mM and a relative standard deviation < 3%. Qi et. al. [79] tested an electrochemical biosensor based on luminescent bacteria (*Vibrio fischeri*) to monitor Cu^{2+} at increasing concentrations (1 mg·L^{-1}, 3 mg·L^{-1}, 6 mg·L^{-1}) in an aqueous solution in real time. The electrical signal increased with Cu^{2+} concentration. Conversely, no optical signal was obtained with 1 mg·L^{-1} Cu^{2+}. This indicated that the electrical signal was generated by Cu^{2+} chemical reaction at the electrode surface.

Ansari and Arvand [80] developed electrochemical sensors using CPEs functionalized with electrospun CoFe$_2$O$_4$/GO nanofibers that could identify rutin (0.001–0.1 nM) and flavonoids (1.0–100 nM) in water samples. Mazzei and coworkers [81] studied electrochemical sensors based on alkaline phosphatase inhibition for the detection of pesticides (malathion and 2,4-dichlorophenoxylacetic acid). In optimal operating conditions (Tris/0.1 M HCl, pH=8.0, 30–60 min of incubation), the sensors had a LOD of 0.5 µg/L. Chen et al. [82] fabricated an electrochemical sensor in which a graphene/polymer film was deposited on a GCE for phenol monitoring in water. A clear reduction peak was observed upon exposure to hydroquinone in phosphate buffer, pH = 6.5 (LOD of 3×10^{-4} M). Recently, Suvina and coworkers [83] developed an electrochemical sensor in which LaCoO$_3$/graphene nanosheets were deposited on a GCE. This sensor allowed the non-enzymatic detection of catechols at concentrations from 9 nM to132 µM. Nagaraj et al. [84] developed an electrochemical sensor in which an alumina nanochannel was supported on a screen-printed electrode. This sensor showed high

sensitivity for the real-time monitoring of ibuprofen (an anti-inflammatory drug) in various water samples (LOD: 0.25 pg·mL^{-1}).

Ramírez-Chavarría and coworkers developed a cheap and easy-to-use device based on the reverse transcriptase-loop mediated isothermal amplification (RT-LAMP) technology and an electrochemical sensor based on screen-printed electrodes to identify two SARS-CoV-2 genes (N and ORF1ab) in water samples. They showed that the electrochemical test strip can specifically detect and quantify RT-LAMP amplicons up to ~ 2.5×10–6 ng/µL, with high reproducibility. Chlorine and antibacterial agents are used to control biofilm growth; however, high chloride concentrations can result in the generation of toxic byproducts. Saljooqi et al. [85] fabricated an electrochemical sensor using a GCE modified with a magnetic Fe$_3$O$_4$ @Au-PPy/GO composite to detect triclosan, an antibacterial agent. This sensor showed high sensitivity, good stability, reproducibility, and low LOD (2.5 nM) for triclosan. Electrochemical aptamer sensors with graphene nanomaterials and with 2D nanomaterials have been used to detect Gram-positive (e.g. *Staphylococcus aureus*) and Gram-negative bacteria (e.g. *E. coli*), respectively [86,87]. Bimakr et al. [170] developed an open-circuit impedance spectroscopy method using graphite and stainless steel as electrode materials for the real-time detection of biofilms that can serve as disinfectants (Fig. 9). They found that biofilm detection sensitivity was increased by 10-fold when using stainless steel compared with graphite (2×10^{-5} and 2×10^{-6}% capacitance change/cell cm^{-2} ratio). Table 2 shows some applications of voltammetric sensors for monitoring different water pollutants.

8. Electrochemical sensors for soil analysis

Soil monitoring involves the analysis of soil quality, constituents, and physical condition. Soil is exposed to many threats, such as compaction, contamination, loss of organic matter and biodiversity, slope stability problems, erosion, salinization, and acidification. Compared with traditional laboratory methods, electrochemical sensors can measure quickly and may be cheaper to purchase and use in the field (e.g. farms).
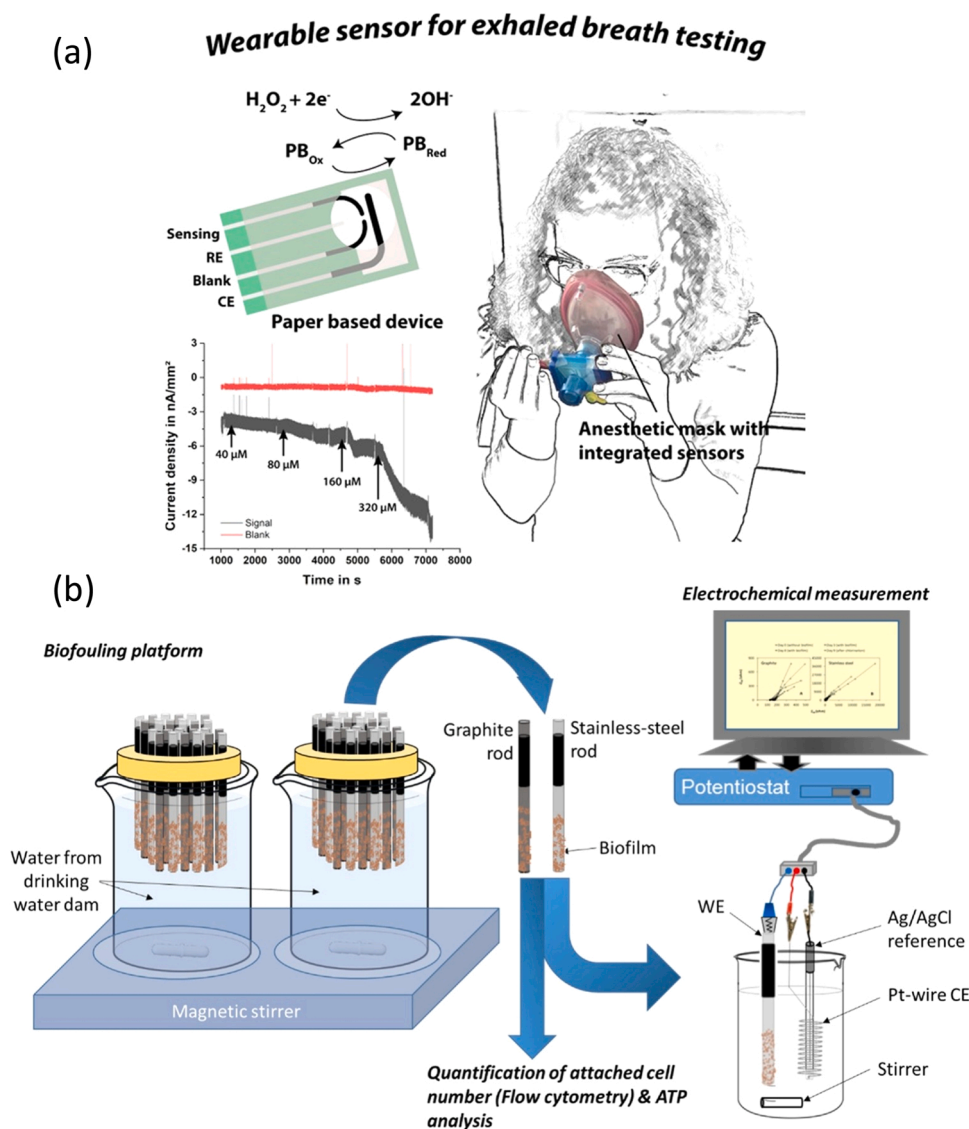
Fig. 8. Electrochemical sensors for environmental applications: (a) A wearable paper-based sensor to continuously monitor hydrogen peroxide in breath based on Ag/AgCl-, carbon-, and Prussian blue (PB)-modified electrodes. © American Chemical Society, [63]. (b) gtaphetic rods and stainless steel electrodes for biofilm detection in water samples. © Elsevier [65].

Table 1
Nanomaterial-based electrochemical sensors for gas and vapor monitoring.

| Gas/vapor	Sensing nanomaterial@electrode	Electrode fabrication	Detection technique	Detection range	Detection limit	Ref.
NO_2, NH_3, CO, CH_4	ZnO NPs@low-power micro light plate	InGaN-based LED integrated at a few 100 nm from the sensor material	Conductometric sensor	25 ppb 1 ppm	25ppb	[66]
Trimethylamine	Polyethyleneimine/ZnO nanosheets@gold electrode	One-pot wet-chemical synthesis followed by annealing	Conductometric sensor	10–300 ppb	10 ppb	[67]
Humidity	SnO_2 nanowires@gold electrodes	Chemical vapor deposition	Conductometric sensor	$8.59 \times 10^5 - 2.80 \times 10^7 \ \Omega$	$2.80 \times 10^7 \ \Omega$	[68]
Ethanol vapor	In_2O_3 nanowires@gold electrode	Solvothermal	Conductometric sensor	100–1000 ppm	100 ppm	[69]
H_2S, C_2H_5OH, H_2	GO/polyimide film@Ti/Au layer electrode	Drop-casting, thermal evaporation	Conductometric sensor	1–20 ppm	20 ppm	[70]
Dust particles (PM10, PM 2.5)	SHARP (GP2Y10) sensors	-	Conductometric sensor	0.2–0.3 mass fraction with a particle diameter	1 mg/m^3	[71]
Airborne influenza viruses	Electrochemical paper immunosensors	Sampling by a portable electrostatic particle concentrator	Non-pulsed high electrostatic fields	101–106 PFU/ mL	2.13 PFU/ mL	[72]
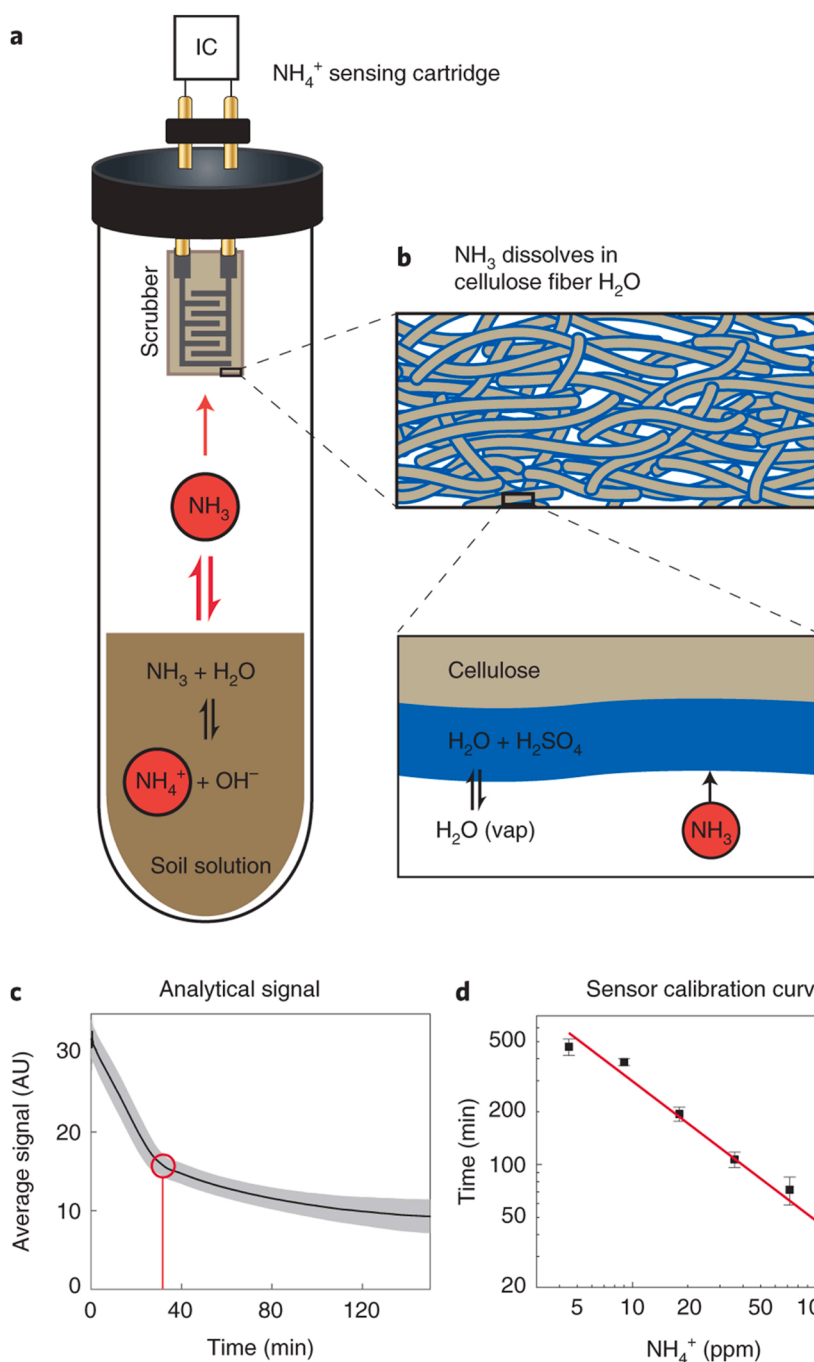
Fig. 9. Cheap point-of-use sensors to measure soil nitrogen. (a) Gas-phase NH_4^+ sensor cartridge made of a container, 1 mL of 15 M NaOH, and disposable chemPEGS as NH_4^+ scrubber in soil connected to an integrated circuit (IC) for impedance analysis. (b) Volatilized NH_3 (g) dissolves in the water layer adsorbed on the chemPEGS, neutralizes H_2SO_4, and increases the ionic impedance. The neutralization reaction extracts the residual NH_4^+ from the soil solution to maintain the NH_3 equilibrium in the air space. The time required to drastically slow or complete the neutralization was used as the analytical signal. (c) Signal (red circle) obtained with 144 ppm NH_4^+ in soil; the error is in gray. (d) Sensor response to increasing NH_4^+ concentrations (4.5–144 ppm) in soil samples after fertilization with NH_4NO_3 [100].

Soil moisture content is affected by climatic conditions and varies with the seasons. Moreover, moisture content is decreased in contaminated soil. Soil pH and salinity strongly influence the macro- and microelement bioavailability, migration, and many processes (e.g. C, N, P, and S cycling, soil fertility, and metal availability). Many electrochemical ion-selective electrode sensors have been developed to determine the soil pH. Patil and coworkers [96] fabricated a conductometric microsensor to monitor pH changes based on dodecylbenzene sulfonic acid-doped polyaniline and an epoxy resin (SU-8) nanocomposite film. Its sensitivity with red and bentonite soil samples was 34 and 89 μS/pH-water, respectively. Aljoumani and co-workers [97] detected the soil salinity by electrical conductivity measurement. The sensor could estimate the pore water electrical conductivity of sandy soils at a frequency from 10 to 500 MHz. Researchers have also used potentiometric sensors based on oxidized cobalt, molybdenum metal electrodes, and valinomycin-based

membranes to detect dihydrogen, hydrogen, and phosphate ions, Na^+, Mg^{2+}, Ca^{2+}, Al^{3+} and Li^+ in the range 10^{-1} to 10^{-5} mole/L [98,99]. Grell and coworkers [100] developed electrical sensors that can accurately determine soil NH_4^+ levels in the field (detection range: 3–144 ppm; LOD: 3 ± 1 ppm) at low cost and with a large dynamic range (Fig. 9).

9. Technical challenges

Electrochemical sensors will play a major role in environmental monitoring. However, researchers must continue to develop innovative solutions to bring more smart sensors into our daily life. For this they have to overcome some major obstacles:

Table 2

Some applications of electrochemical sensors for monitoring water pollutants.

Analyte	Sensing materials/ Electrodes	Electrode fabrication/modification	Detection techniques	Linear range	Limit of detection	Ref
Nitrate /Nitrite	Cu/MWCNT/rGO/ GCE	Oxide-modified GCE	Square wave voltammetry	0.1–75 μM	20 nM/30 nM	[88]
Mercury(II)	MB–DNA–Au NPs	Gold electrode	Differential pulse voltammetry	0.2–100 ppb	0.064 ppb	[89]
Arsenic(III)	Au NPs–Te-hybrid	Au/Te hybrid electrode	Square-wave anodic stripping voltammetry	0.1–10 ppb	0.0026 ppb	[90]
Cyanide	MWCNT–iron(II)	GCE	Square wave voltammetry	40 nM to 150 mM	8.3 nM	[91]
Sulfites	SOx–PB NPs–PPY	Ag/AgCl (standard electrode) + Pt wire (auxiliary electrode)	Square wave voltammetry	0.5–1000 mM	0.1 mM	[92]
Polychlorinated Biphenyl	Aptamer–MWCNT	GCE through an amide linkage	Cyclic voltammetry	0.16–7.5 mM	10 nM	[93]
Hydroquinone Catechol	rGO–TT–CNT	Modified GCE	Differential pulse voltammetry	0.01–200 mM	7.61 nM	[94]
Bisphenol A	MWCNT	Modified GCE	Cyclic voltammetry	0.099–5.8 mM	0.032 mM	[95]

(1) It remains difficult to produce electrochemical sensors that can detect analytes at different concentrations, with low LOD (fM or aM) and good stability. The sensitivity of conventional electrodes (e.g. gold or GCEs) is often limited due to their sluggish redox kinetics. More research is needed to develop cheap and highly stable electrode materials for harsh environments.

(2) Maintaining the sensor signal repeatability and stability is a major challenge, especially when analyzing real environmental samples. On-site monitoring of environmental analytes is far more complicated than laboratory work with synthetic samples due to the complex air, water, and soil environment (e.g. many organic and inorganic compounds, pH, turbidity). The identification of many environmental pollutants remains difficult.

(3) The sensor signal and stability can limit their application in remote locations and extreme temperatures. Therefore, all developed electrochemical sensor systems must be validated against accepted international standard protocols. As the basic mechanisms of interaction between the electrode surface, analytical species, interfering species, and organic components are unclear, experimental and analytical data are required to fully understand the electrochemical recognition process kinetics and thermodynamics.

(4) When working with electrochemical sensors, electrode surface contamination is a serious problem that needs to be addressed. Microenvironmental contaminants cause electrode fouling or poisoning and often alter the voltammetric response, leading to inter-laboratory differences. There are several methods to clean the electrode surface for more cost-effective and automated electrochemical monitoring. However, regular instrument checks and calibrations are required to ensure correct sample monitoring. Environmental sample pre-treatment with membranes may reduce these interferences. Nevertheless, functional membrane materials with excellent selectivity for analytical species and innovative sensor methods for electrode assembly must be developed for practical applications.

(5) It is challenging to design and fabricate portable, wearable, and implantable sensor platforms to simultaneously analyze multiple components for environmental monitoring because of the need to reduce production costs, device size, and energy consumption. To improve the device performance, additional efforts should concentrate on sensing nanomaterials. Moreover, the integration of novel materials and structures must be scalable for commercial device manufacturing, otherwise, their use will be limited to laboratory experiments without real socioeconomic impact.

(6) Advances in electronics and microfabrication techniques have promoted the use of microchips for continuous sample monitoring. Integrated lab-on-a-chip sensors with low background current and high sensitivity are used in high-throughput screening techniques. This paves the way to the development of novel, cheap, automated, and portable electrochemical sensors for real-time environmental monitoring. However, due to the tiny volume of solution that may be contained in the channel/chamber, the electrode material, and platform design are critical for reducing hydrolysis in the chip.

(7) Paper-based electrodes also are a viable option for low-cost, single-use determination of heavy metals; however, their stability, reproducibility, and sensitivity in field measurements may need to be improved. The different properties of the used substrates, complicated processes, and stringent conditions of small-scale production of low-cost paper-based electrochemical sensors strongly influence reproducibility and accuracy. Two major areas of research concern i) the modification of the paper-based sensor surface to allow the selective identification of the target analyte, and ii) controlling the paper-based material for industrial production.

These challenges concern not only environmental monitoring but also all other applications of electrochemical sensors, from food safety monitoring to the electronics industry. The use of nanomaterials for electrochemical sensor fabrication has contributed and will still help to tackle these challenges.

10. Conclusion

Electrochemical sensors are promising tools for water, air, and soil monitoring, scientific investigations, food safety, military applications, electronics, and other industries. The breakthroughs allowed by nanomaterials are a tremendous advance that concerns all these industries. For real progress, researchers must continue to find novel solutions to fabricate smarter sensors to be used in our daily lives. The electrochemical sensor capacity to selectively sense multiple parameters is crucial for smart quality monitoring. We are confident that the continuous advances in nanoscience and nanotechnology will allow developing more precise and greener electrochemical sensors with longer lifetime and lower maintenance requirements in the near future. The integration of nanocomposite materials into microchips has been facilitated by the development of new tools for integrating electrode materials, such as nanomaterial incorporation, selective coatings, and inkjet printing, that have paved the way for novel electrode designs and architectures. Several studies concluded that the measurement repeatability, long lifetime, and self-calibration offset the variances in nanomaterial-based electrochemical sensors. In addition, there are few miniature versions of portable electrochemical devices with high sensitivity for environmental monitoring. Therefore, developing portable, low-cost nano-electrochemical sensors for environmental monitoring might soon become a major research axis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

All data used are only avilable in this article.

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