Silver Nanoparticles in Sensors for Aquatic Environmental Analysis

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With rapidly increasing environmental pollution, there is an urgent need for the development of fast, low-cost, and effective sensing devices for the detection of various organic and inorganic substances. Silver nanoparticles (AgNPs) are well known for their superior optoelectronic and physicochemical properties, and have, therefore, attracted a great deal of interest in the sensor arena. The introduction of AgNPs onto the surface of two-dimensional (2D) structures, incorporation into conductive polymers, or within three-dimensional (3D) nanohybrid architectures is a common strategy to fabricate novel platforms with improved chemical and physical properties for analyte sensing.

silver nanoparticles
chemical reduction
voltammetric sensors
amperometric sensors
environmental analysis

1. Introduction

Today, nanotechnology represents a growing multidisciplinary sector which has brought a revolution in modern science, enabling materials of specific size, structure, and composition to be formed [1][2]. Nanodimensional structures (size domain less than 100 nm) represent a bridge between atomic and bulk matter, and possess novel physicochemical properties, high surface-to-volume ratio, high adsorption and catalytic capacity, advantageous properties not present in their macro-sized counterparts [3]. The remarkable advances and tunable attributes of nanomaterials have led to increasing attention to their applications in fundamental biological research, clinical diagnostics, food safety, and environmental monitoring.

Nowadays, environmental pollution is considered a major threat worldwide, especially to the aquatic ecosystem [4][5]. With the accelerated industrialization, increasing agricultural activities, and rapid urbanization, various toxic and poisonous substances can enter natural waterways, contaminate drinking water, and subsequently cause severe health problems. Among them, heavy metal ions, nitrogen-containing inorganic species, pharmaceuticals, hormones, and nitroaromatic compounds are particularly dangerous, because of their high toxicity, carcinogenicity, and low biodegradability [6][7][8]. To date, experts have developed distinctive analytical methods for the detection of different water pollutants, including gas chromatography/mass spectrometry (GC/MS), high-performance liquid chromatography (HPLC), atomic absorption spectroscopy (AAS), and inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis, which are used to detect water pollutants [9]. While the above methods have the advantage of being very sensitive, they are also expensive and require trained personnel, making them unsuitable for on-site analysis. To solve the above problems, nanostructured materials have been recognized as powerful analytical tools for the development of facile analytical strategies for assaying trace-level aquatic environmental pollutants, with the possibility of their quantification even at femtomolar levels [10].

2. Application of Silver Nanoparticles in Voltammetric and Amperometric Sensors

An electrochemical sensor is a device that consists of two basic parts: a receptor that specifically recognizes a substance of interest, and a transducer that converts the chemical response into a signal detectable by modern electrical instruments. Regarding the way in which the transduction process occurs, electrochemical sensors can be divided into amperometric, voltammetric, potentiometric, and conductometric [11].

The performance of all electrochemical sensors is strongly influenced by the working electrodes. In general, the redox reaction of the electroactive species at the bare electrodes (metal electrodes, glassy carbon electrodes, screen-printed or paste (carbon) electrodes, inkjet-printed electrodes) is often difficult due to the slower kinetics of the electrochemical reactions for a number of compounds and overpotential requirements. To improve the sensing mechanism, bare electrodes are usually modified with nanoengineered materials that exhibit excellent electrical conductivity and high catalytic activity such as silver [6]. Silver nanoparticles have been widely demonstrated as ideal candidates for sensing applications. Ideally, particles with a smaller size provide a larger fraction of silver atoms accessible to reactant molecules, making them a promising material for electrochemical sensors. However, AgNPs with a zero-net charge tend to coalesce into larger clusters with a lower surface-to-volume ratio. Therefore, to preserve the unique thermal and electrical properties of AgNPs, significant progress has been made towards the synthesis of AgNPs with controllable morphology, dimensions, surface charge, and physicochemical properties. To improve their sensing properties, AgNPs are often integrated into nanocomposite materials, e.g., by alloying with some another metal [12], embedded into single- [13] or multiwalled [14] carbon nanotubes, anchored on functionalized graphene (oxide) platforms [15][16], modified to form multifunctional ternary systems [17], or deposited in the form of a thin film on the electrode surface [18].

A current trend in the sensor field is directed toward solving analytical problems by developing low-cost, miniaturized, and portable devices that could be operated in the field. Electrochemical techniques, placed in order to achieve simple and sensitive analysis, are of particular interest because of their fast response and low detection limit (LOD).

2.1. Working Principles of Voltammetric and Amperometric Sensing Techniques

In general, three-electrode systems are employed for selective voltammetric and amperometric detection of environmental pollutants, which includes a working electrode (WE) where oxidation/reduction (OR) of the electroactive species (analyte) takes place, a reference electrode (RE) that provides a constant potential, and a counter electrode (CE) that is important for a complete circuit for the charge-transfer process (**Figure 1**). The counter electrode is usually a platinum wire, and the reference electrode is either a standard calomel electrode

(SCE) or saturated (sat.) Ag/AgCl electrode [19]. The electrodes are immersed in aqueous primary electrolyte solution to improve ionic conductivity and reduce migration during mass transfer of one or more targeted species. Voltammetric and amperometric sensors are two commonly used electrochemical devices and are, therefore, described in more detail below.

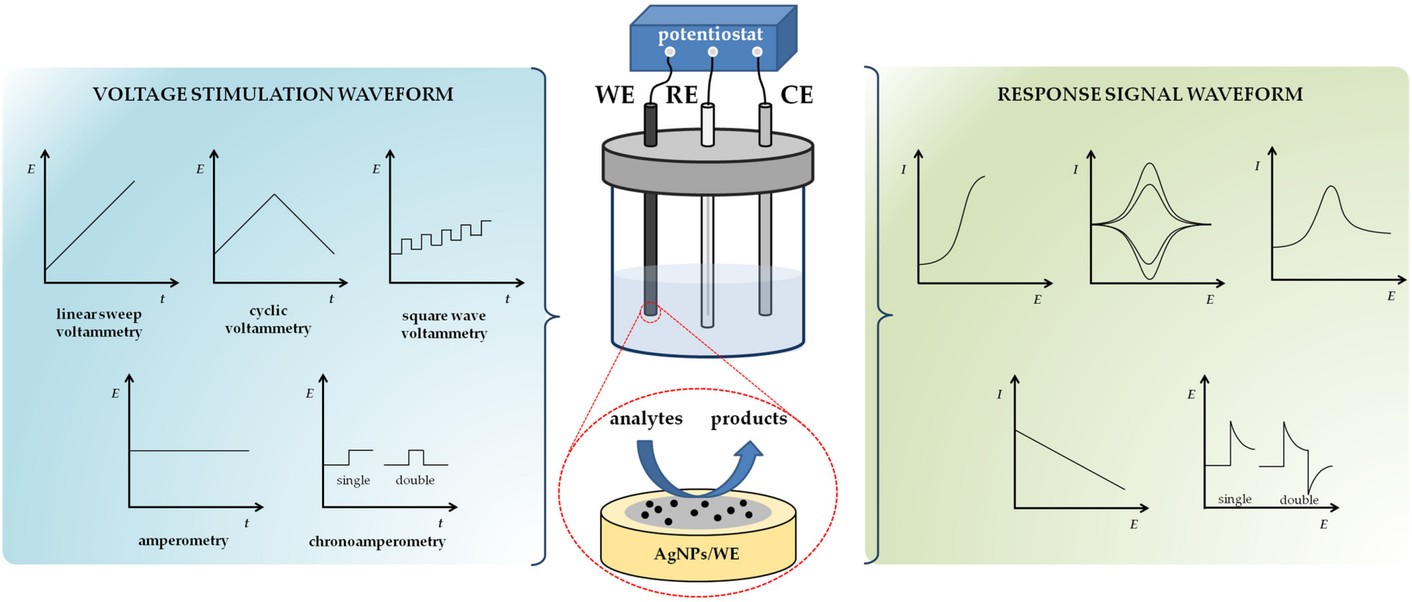

Figure 1. Schematic representation of voltammetric and amperometric techniques used for detection of emerging water pollutants. In the scheme, *E* stands for potential, *I* for current, and *t* for time.

The working principle of voltammetry is based on the variance of the time-dependent excitation potential (linear, in pulses, or in squares), and the current output is correlated with the concentration of the analyte (**Figure 1**) [5]. In voltammetry, the measured current is composed of the Faradic current and the charging current (also known as non-faradic component). The Faradaic current results from electron transfer between the analyte and the electrode surface, and is directly proportional to the concentration of the target species. The charging current is not an analytical signal; it is the result of the perturbations in the electrode potential that lead to the charging/decharging of the electrical double layer. Cyclic voltammetry (CV) is one of the most important and widely used voltammetric techniques, where the current output is the result of a linear potential change (in the form of a triangular wave) within a given potential window. The peak current for a reversible system with diffusion control is described by the Randles–Ševčik equation (Equation (1)) [20]:

$$I_p = \left(2.69 \times 10^5\right) n^{3/2} A D^{1/2} C \nu^{1/2} \tag{1}$$

where I_p stands for peak current (A), *n* is the number of electrons exchanged in the reaction, *A* is electroactive area of the electrode (cm^2), *D* is the diffusion coefficient (cm^2 s^{-1}), *C* is the concentration of the electroactive molecule in the electrolyte (mol dm^{-3}), and *ν* is the scan rate (V s^{-1}). In this Equation, the constant of 2.69 × 10^5 has units of C mol^{-1} V$^{-1/2}$. Another technique in which the current is determined by a linearly varying electrode potential, this time in one direction, i.e., it is ideal for studying irreversible redox reactions, is linear sweep voltammetry (LSV). The other way to apply the potential is to use a pulse method—a series of pulses with a linear baseline (differential pulse voltammetry, DPV) or a square pulse amplitude applied to a stair–step waveform (square wave voltammetry, SWV). The common denominator of the stripping techniques is the preconcentration/removal of the analyte on and off the WE probe by controlling the applied voltage stress for highly sensitive quantification of the target molecule. Due to the analyte preconcentration, a much lower LOD is achieved compared to other electroanalytical methods. The deposition step can be done in three different ways: (i) by applying a negative voltage in anodic stripping voltammetry (ASV), (ii) by applying a positive voltage in cathodic stripping voltammetry (CSV), and (iii) by adsorption of the analyte in adsorptive stripping voltammetry (AdSV).

In amperometry, a constant potential is applied to the WE, and the current is measured as a function of time (**Figure 1**) [21]. Operating in this mode, the recorded currents can be averaged over a longer period of time, which allows more accurate quantification, i.e., amperometric sensors display high sensitivity and selectivity as well as a wide detection range. In chronoamperometry (voltage applied in steps to WE), the current output obtained is related to the bulk analyte concentration via Cottrel Equation (Equation (2)) [22]:

$$I = \frac{nFAD^{1/2}C}{\pi t} \tag{2}$$

where I corresponds to the diffusion current (A), n is the number of the electrons involved in the redox reaction, F is the Faraday constant, D represents the diffusion coefficient (cm^2 s^{-1}), C is the concentration of the electroactive species (mol dm^{-3}), and t is the total electrolysis time (s). Amperometry is ideal for detection of analyte(s) in flow systems (complex matrices), as well as a highly sensitive platform for rapid analysis of targeted molecule in a simple solution. The portability of amperometric sensors also makes them ideal for in-field studies.

2.2. Electrochemical Sensors for Detection of Heavy Metal Ions

The heavy metals (HMs) are a group of naturally occurring metals and metalloids whose density is five times greater than that of water and which are toxic even in trace amounts. Among them, mercury (Hg), lead (Pb), cadmium (Cd), chromium (Cr), and arsenic (As) are biologically nonessential elements and are classified as priority metal pollutants. On the other hand, copper (Cu) is an important component of various enzymes in humans and aquatic organisms, but has toxic effects at high concentrations. Extensive anthropogenic activities (industrial and domestic use of raw materials and metal-containing products) have resulted in widespread environmental pollution. The major problem with HMs in the environment is that they are not subject to biodegradation [23], but rather bioaccumulate in different tissues by complexing with various protein functional groups. Therefore, the release of hazardous metal species into the environmental waters from industrial or municipal waste has become a global concern.

2.2.1. Electrochemical Sensors for Divalent HMs

Mercury (Hg). Mercury is a pervasive, persistent, and extremely toxic pollutant that enters the environment through gold mining and coal power plants. Long-term exposure to mercury in humans causes irreversible damage to the kidneys, central nervous system, endocrine system, and cardiovascular respiratory system. Mercury is equally toxic in all three possible oxidation states (0, +1, and +2); however, because Hg(II) has the highest water solubility, the development of sensitive and selective methods to monitor the presence of this particular species is of great public health and environmental importance [24]. Therefore, this chapter summarizes voltametric and amperometric probes based on nanosilver material for the detection of divalent mercury.

A simple, environmentally friendly and disposable voltammetric platform for the detection of Hg(II) using folic acid (FA)-stabilized AgNPs was proposed by Eksin and coauthors [25]. FA (vitamin B9) can effectively bind to the AgNPs surface via amine groups and generate a negative particle charge via the carboxylic moiety, which provides electrostatic particle stabilization. Electrochemical characterization of the pencil graphite electrode (PGE) improved with FA-AgNPs was performed by CV and electrochemical impedance spectroscopy (EIS) techniques, while DPV was used for quantitative identification of the analyte (detection limit of 8.43 µM under the optimized conditions). The main advantage of the FA-AgNPs-PGE sensing platform is the time savings; only 2 h are required to perform the entire procedure—from electrode preparation to analysis. A dual optical and electrochemical sensor for rapid sensing of toxic mercury based on *Agaricus bisporus* (AB) synthesized AgNPs was proposed by Sebastian et al. [26]. In optical detection, a visible change in the color of the suspension was followed by a decrease in the absorption maxima, indicating particle aggregation by Hg(II)-AgNP-AB complexation as a highly selective mercury sensing mechanism. The same approach was used in the electrochemical sensing, where a reversible redox couple was formed in the presence of mercury in acetate buffer solution (ABS, pH = 6.0). The enhancement of the current signal is favored by the presence of small AgNP-AB (mean diameter of 14.13 nm), which significantly increases the effective surface area of the platinum electrode (PE) substrate. The analytical performance of the AgNPs-AB/PE sensor manifested in well-defined DPV plots (scan rate of 100 mV s^{-1}), with peak current linear to mercury at micromolar concentration. Another dual sensor for the detection of Hg(II) in water specimens based on biosynthesized AgNPs was fabricated by Punnoose et al. [27].

Cadmium (*Cd*). Cadmium is a heavy metal often referred to as the metal of the 20th century, because of its widespread use in industry—galvanizing and electroplating, rechargeable Ni-Cd batteries, electrical conductors, and in the manufacture of alloys, pigments, and plastics. Cd is released into the environment through anthropogenic sources such as smelting and mining, and is considered as a prevalent environmental contaminant [28]. High exposure to cadmium causes severe damage to kidneys, lungs, and liver, and increases the risk of cancer. Therefore, many researchers are focusing of the development of selective and sensitive methods to quantify cadmium in the environmental and drinking water. An extract of *Allium sativum* (garlic) has been shown to be an excellent green agent for the synthesis of AgNPs and for the removal of hazardous cadmium [29]. Divalent cadmium induces aggregation of the AgNP-AS; a mechanism successfully used in optical sensing (color change), fluorescence response (enhancement of fluorescence intensity with increasing cadmium concentration), and electrochemical sensing (prominent CVs in the presence of the analyte). DPV current outputs (recorded in 0.1 M

ABS) were linear with analyte concentration in the range of 10–90 μM, corresponding to a detection limit of 0.277 μM cadmium.

Lead (Pb). Lead is a highly poisonous metal found in the Earth's crust [30]. The widespread use of lead in households and industry has resulted in extensive contamination of water sources caused by the perennial deterioration of paints, corrosion of metal water pipes, and leaching of ceramic containers used in the manufacture of lead-containing batteries. Thus, the significant environmental damage, human exposure, and serious public health issues require the development of rapid and efficient methods for Pb detection. Ganash and Alghamdi [31] proposed a sensitive and selective strategy for the electrochemical detection of lead ions based on a nanocomposite modified carbon paste electrode (CPE). The WE was prepared by mixing polyaniline (PANI), graphite, and paraffin oil, and the green-synthesized AgNPs were drop casted onto the electrode surface. Compared with bare CPE, PANI/CPE, and AgNPs/CPE, the prepared AgNP/PANI/CPE exhibited the lowest charge transfer resistance (R_{ct}) and the highest conductivity. The electrochemical detection was performed in three steps: (i) accumulation at open-circuit potential (8 min); (ii) preconcentration step at a potential of −0.3 V (100 s) vs. saturated Ag/AgCl; and (iii) application of SWV technique (ABS, pH = 5.5, in the potential range of −0.7 V to −0.2 V) to oxidize zero-valent lead. This simple sensor exhibited good recoveries (104%, 110%, and 116% for wastewater, biologically treated wastewater, and tap water samples, respectively, assessed by spiking with known Pb concentration) and excellent reproducibility (RSD values of less than 10% obtained for other HMs). Highly crystalline Ag@Pt core-shell nanoparticles for selective detection of lead in environmental water samples were synthesized by a bioinspired method, using extract of *Psidium guajava* leaves, ascorbic acid, and microwave irradiation [32]. The prepared nanocatalyst (14.5 nm core diameter and 4.55 nm shell thickness) was successfully decorated on a plain graphite paste electrode (GPE). Compared to the bare electrode, the implementation of the nanohybrid material enlarged the effective surface area (from A = 0.066 cm^2 to A = 0.145 cm^2) and resulted in faster electron transfer (58% reduction in the electron transfer resistance). To achieve ultratrace detection, the analyte was first electrodeposited at a potential of −1.2 V vs. sat. Ag/AgCl for 300 s, after which SWASV was performed (0.1 M acetate buffer, pH = 5; stripping potential of −0.43 V). The fabricated sensor successfully detected lead in the sewage water sample (0.48 μM), and the result was further verified using AAS with a deviation of only 3.0%. Amino acid synthesized NiO-Ag particles with ball-flower (BF) morphology were found to be highly selective for lead ions due to their large active surface area and high conductivity [33]. The usage of L-glutamine was pivotal for the synthesis and anisotropic growth of the nanocomposite. Namely, the formation of functional flower structured BF-NiO-Ag particles was initiated by the complexation of metal ions with carboxyl groups, and the generation of steric particle stabilization by amino acid side chains. Detection of lead ions in an electrolyte buffer solution (0.1 M ABS, pH = 6.0) was performed by DPV; the dependence of the reduction peak current was found to be linear with Pb(II) concentrations ranging from 1.5 nM to 10 nM. The analytical application of the BF-NiO-Ag/GCE sensor was investigated in pipe water and groundwater samples with satisfactory average recoveries and relative standard deviations, while selectivity was confirmed in the presence of 100-fold transition metal ions.

2.2.2. Electrochemical Sensors for Trivalent and Hexavalent HMs

Arsenic (As). Arsenic is a metalloid that occurs naturally in minerals, usually in association with sulfur and metals (arsenopyrite, cobaltite, enargite, etc.). Due to the complex combination of natural processes (soil erosion, volcanic eruptions, bacterial decomposition) and anthropological activities (mining activity, usage of arsenic-containing pesticides), various forms of arsenic circulate in the environment through geological cycle (air, soil, and water). In its two inorganic forms, i.e., trivalent arsenites and pentavalent arsenates, arsenic is highly toxic; however, As(III) has been shown to be more harmful and more difficult to remove from water sources [34]. Long-term exposure to arsenic-containing water can lead to adverse health problems, from skin lesions to many types of cancer. Considering its toxicity, detection of arsenic is extremely important. Recently, electrochemical methods, especially stripping voltammetry, have made great progress in detection trace amounts of As(III) in water samples [35].

The citrate-stabilised AgNPs dispersed on the surface of the Au electrode were proposed as an effective tool for the selective electrochemical determination of arsenic in river water [36]. Compared to the bare Au electrode, the voltammogram recorded on the modified electrode generated a well-defined peak at a potential of −0.28 V, which was attributed to the three electron reduction of As(III) to a zero-valent form. The DPASV currents (recorded in 0.1 M HNO_3; E_d = −0.6 V; t_d = 5 min) were linear with increasing As(III) concentrations in the micromolar range (0.05–0.2 μM), with a detection limit of 0.0138 μM. To improve analytical performance in arsenic detection, polypyrrole nanowire (PpyNW) was coated with AgNPs, sandwiched between a pair of gold electrodes, and used as a selective sensing platform [37]. As(III) was detected by the two-step stripping voltammetry technique: (i) reduction of the As(III) at the electrode surface by enrichment of As(0) at a potential of −0.3 V for 10 s, respectively, and (ii) reoxidation of As(0) from the electrode surface (PBS, pH = 4.0), resulting in a current response directly proportional to the analyte (0.01–0.10 μM concentration range). Compared to the previously reported AgNPs/Au sensor [36], the detection limit of the PpyNW/AgNPs electrode was lowered to the ppb region [37]. The excellent plasmonic properties and unique electrochemical activity of AgNPs were used as a sensing strategy to fabricate a multimodal arsenite sensing assay [38]. For this purpose, AgNPs were first coated with asparagine (Asn), and then modified with reduced glutathione (GsH) and dithiotreitol (DTT). The effect of the capping agent on the binding ability of As(III) was investigated; it was found that the AgNPs encapsulated with Asn were insensitive to the analyte, whereas GSH-AgNPs showed a weak signal. Due to the abundant oxygen and sulphur-containing groups, the GSH/DDT/Asn-AgNPs probe interacts with As(III), resulting in aggregation of the probe in solution or on the surface of the gold electrode, boosting both the optical and electrochemical signals. From the DPV results, the linear working range for the concentration of As(III) was between 0.01 ppb and 40 ppb, with a LOD of 5.2 ppt (S/N = 3). In addition, the concentration of As(III) measured with the dual-mode sensor agreed well with the results of the standard ICP-MS method.

Chromium (Cr). This transition metal can occur in several oxidation states between 0 and VI, with the trivalent and hexavalent states being the most abundant and, thus, the forms most commonly encountered in the environment and in industrial settings [39]. Cr(III) is an essential trace element, but it can be harmful to humans in high concentrations. On the other hand, the carcinogenic Cr(VI) is one of the most concerned toxic heavy metals due to its extensive use in industries (leather tanning, electroplating). The hazards of Cr(VI) are reflected not only in cell damage (it possess strong ability to penetrate biofilms, disrupt the DNA transcription process, and cause chromosomal aberrations and cell apoptosis), but also in bioaccumulation through the food chain. Hence, it is a pertinent issue to effectively monitor hexavalent chromium concentrations to ensure the safety of the environmental and drinking water sources.

2.3. Electrochemical Sensors for Nitrogen-Containing Inorganic Species

Nitrogen compounds are one of the most important nutrients in nature. They occur as part of the nitrogen cycle in soil and aquatic systems in various organic (proteins, amino acids, urea, living or dead organisms) and inorganic (gaseous nitrogen, ammonia, ammonium ions, nitrite, and nitrate) forms [21]. Due to extensive anthropogenic activities, the concentration of nitrogen-containing substances in the natural environment has increased dramatically. Regulations for the maximum allowance concentrations of nitrogen-based inorganic species are related to the specific water source. Since groundwater and surface water are very important sources of drinking water, the development of an accurate, sensitive, and low-cost platform for in situ monitoring of various nitrogen-containing species has been and continues to be of great importance.

2.3.1. Electrochemical Sensors for Nitrite (NO_2^-) and Ammonium (NH_4^+) Detection

Nitrite anions (NO_2^-) are common inorganic pollutants found in soil, drinking water, and biological systems. Control of nitrite concentration is of great importance because its presence in the human body affects the rate of oxygen transport in the blood by irreversibly converting hemoglobin to methemoglobin. In addition, nitrite anions can also react with amines to produce carcinogenic nitrosamine species [40][41]. Therefore, the World Health Organization (WHO) has limited the nitrite concentration in drinking water to 65.2 μM [42]. Nowadays, there is considerable interest in the monitoring of nitrites as well as the development of a simple and reliable low-cost nitrite sensors [43]. The irreversible mechanism of electrocatalytic nitrite oxidation at the electrode modified with nanosilver material in neutral and weakly acidic solutions can be simply described by Equation (5) [44]:

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \qquad (3)$$

Graphene and graphene-derivative-based composites have also attracted considerable attention in the electrochemical detection of nitrites in water samples [8]. Core-shell Au@Ag nanoparticles (average diameter of 60 nm), synthesized on carboxylated graphene (CG) sheets and drop casted on GCE surface, provided a specific platform for dual detection of nitrite and iodide [16]. The electrochemical behavior of the target species was thoroughly investigated (0.1 M PBS, pH = 7.4), partly to exclude the formation of insoluble AgI on the surface of the nanohybrid material. The DPV technique was chosen for the simultaneous determination of the analytes because it yields distinct peaks in low concentration ranges. In the quantification of nitrite, the oxidation currents at a potential of +0.95 V increased linearly with the increase in analyte concentration, without any significant shift in peak position. For I^-, two prominent anodic peaks occurred, one corresponding to the oxidation of iodide to triiodide (I_3^-) form (+0.55 V), and the other to the further oxidation of triiodide to elemental iodine. Although the presence of two iodide oxidation peaks indicates that the presented sensor is more effective for accurate detection of I^-, it provides a broader linear range for the quantification of nitrite.

2.3.2. Electrochemical Sensors for Nitrate (NO_3^-) and Ammonia (NH_3) Detection

Nitrate (NO_3^-) is one of the most common nitrogen-containing contaminants in aquatic systems. Adverse human activities have permanently altered the global nitrogen cycle, and excess nitrate from agricultural lands leaches through the soil into groundwater, lakes, and rivers, and eventually enters into drinking water [8][45]. Excess of nitrate disrupts aquatic ecosystem dynamics and leads to eutrophication processes, water quality degradation, and biodiversity destruction. In animal species and humans, excessive nitrate intake leads to the formation of nitrosamines, and subsequently to cancer. Therefore, the development of a low-cost and portable instrument that can perform routine measurements in various water matrices is highly desirable. The most promising analytical tool that can meet these requirements are voltammetric and amperometric sensors.

The analytical performance of electrochemical nitrate sensors is highly dependent on the efficiency of the catalysts, which can be strongly influenced by the pH of the water matrices and the composition of the working electrode used [46]. In other words, the mechanism of electrocatalytic reduction of nitrates on various metallic (Pt, Pd, Cu, Au, Ag, Zn, Fe, Ru, Bi, Sn, Au(Hg), etc.) and chemically modified electrodes is a complex process that can lead to the formation of nitrites or various gaseous nitrogen species [47]. Considering that most of the environmental waters have a (near) natural pH, electrochemical reduction in neutral solution has been studied in detail, developing voltammetric and amperometric sensors using different types of nanosilver as catalysts.

2.4. Electrochemical Sensors for Phenolic Compounds

Phenolic compounds are a group of small molecules containing a hydroxyl group attached to the carbon atom of an aromatic ring. Based on their chemical structure and number of carbon atoms, phenolic compounds can be divided into several classes. Due to their toxicity and persistency, phenolic compounds are also the most polluting components in the environment, especially in water sources [6]. Therefore, numerous studies aim at simple and effective detection of phenolic compounds via designing voltammetric and amperometric sensor surfaces.

Among phenol-based compounds, *phenol* is the most toxic species and is classified as a priority pollutant [48]. An eco-friendly synthetic approach using five different plant leaf extracts (*Basil*, *Geranium*, *Eucalyptus*, *Melia*, and *Ruta*) as reducing and stabilizing AgNPs agents for water quality monitoring has been reported [49]. XRD analysis revealed common Miller indices for the crystalline FCC structure, while the size of nanosilver grains, calculated by the Scherrer formula, yielded crystallites between 21 nm (AgNP-M) and 50 nm (AgNP-E). Thus, applying DPV technique, the GCE sensor modified with AgNPs-*Melia* particles was highly selective towards phenol even in the presence of bisphenol A and catechol, exhibited a LOD value of 0.42 µM and retained 93.11% of its initial response after four consecutive weeks of measurement. In another work, Zhu and Yang [50] reported an amperometric sensor based on the AgNPs/CNT for simultaneous detection of phenol and *o*-cresol in shale gas wastewater. The electrodeposition from 0.5 mM $AgNO_3$ (applied potential range from −0.7 V to 1.4 V in 0.1 M PBS/1.0 M ascorbic acid) was used for the successful modification of the acid-pretreated CNTs onto the oxygen functional groups. Under optimal conditions (0.1 M PBS; pH = 6.5; scan rate 20 mV s^{-1}), the electrocatalytic response of the AgNPs/CNTs/GCE sensor showed two prominent and well-separated oxidation DPV throughs, indicating the applicability of the sensor for discrimination of phenolic compounds. Moreover, the amperometric response (examined under the same conditions) responded linearly in the micromolar linear range for both analytes, and with a low LOD value of 0.01 μM for both target species, respectively. Another electrochemical sensor based on AgNPs/MWCNT-coated GCE, this time for the simultaneous detection of four phenolic compounds, was proposed by Athie Goulart and coworkers [51].

Hydroquinone (1,4-benzenediol, HQ) and catechol (1,2-benzenediol, CC) are two positional isomers of phenolic compounds found as environmental contaminants in many industries (cosmetics, textiles, chemicals, pharmaceuticals, etc.). Two different fabrication designs have been proposed for the simultaneous electrochemical detection of HQ and CC using PANI doped with phthalocyanine-stabilized AgNPs [52] and AgNPs-decorated magnetic Fe_3O_4-rGO composite [17], both layered over GCE surface. In the first report [52], a novel hybrid architecture, combining semiconducting and catalytic properties of a macrocyclic molecule (tetraamino cobalt phthalocyanine, TACoPc), with (highly) conducing AgNPs and PANI, showed well-defined CV redox peaks of HQ (+0.68 V) and CC (+0.76 V) vs. standard hydrogen electrode (SHE). Electrochemical detection of analytes (in 0.1 M H_2SO_4 primary electrolyte solution) provides a linear micromolar concentration range (DPV), good stability (3.3% and 2.31% changes from the 1st to the 200th cycle for the oxidation of HQ and CC, respectively), and good selectivity to 100-fold concentration of inorganic interferents (Na^+, Ca^{2+}, K^+, Mg^{2+}, Cl^-, nitrates).

Nitrophenols (o-NP; p-NP; 4-NP) are not released from natural sources, but are manufactured and used as a precursors and/or intermediates in the synthesis of nitro dyes and analgesic drugs (acetophenenetidine and paracetamol). A simple voltammetric platform based on uncapped silver nanoclusters (AgNCS) decorated GCE for direct oxidation of 4-nitrophenol was proposed for the first time by the Maduraiveeran group [53]. The AgNCS/GCE sensor demonstrated significantly improved LSV current output and less positive anodic peak potential shift (compared to bare GCE), with direct electrocatalytic oxidation of 4-NP at the potential of +0.63 V/sat.Ag/AgCl and low onset potential (+0.5 V). After the 100th measurement, no significant change in the LSV current peak and the peak potential shift occurred, confirming excellent sensor stability. The cubic-shaped AgNPs supported on rGO platform were used as a GCE modifier for the selective detection of hazardous 4-NP [54]. Activity and stability of the catalyst were confirmed by a chronoamperometry study performed at potentials of −0.3 V and −0.6 V, respectively, in 0.1 M PBS by successive addition of 5 μL of 4-NP. The Ag-rGO/GCE sensor displayed excellent reproducibility (RSD value of 2.87% after five consecutive measurements) and stability (difference in reduction of 13.38% compared to the initial value after 15 days of storage under ambient conditions).

2.5. Electrochemical Sensors for Pharmaceuticals

The surging growth of the pharmaceutical industry has inevitably led to an increase in the misuse and release of pharmaceuticals into the aquatic environment. The main classes of pharmaceuticals found in environmental samples and wastewater include antibiotics, antipyretics, and anti-inflammatories. Due to their toxicity and accumulation in living organisms, their presence poses a serious environmental problem. Therefore, there is a need for accurate, sensitive, portable, and cost-effective technologies to monitor fresh water or wastewater sources for pharmaceutical contaminants [4][55][56].

Paracetamol (*N*-acetyl-*p*-aminophenol or acetaminophen, AP) is a potent antipyretic used worldwide mainly for fever reduction and pain relief. High doses and long-term use of acetaminophen can lead to liver disease and nephrotoxicity [5]. Electrochemical methods have proven to be simple, rapid, and accurate methods for the quantitative detection of acetaminophen in clinical diagnosis and quality of acetaminophen-based drugs. An extract of *Araucaria Angustifolia* was used for the first time as a simple and environmentally benign procedure for fabrication of AgNPs [57]. Since the nature and concentration of reducing and stabilizing biomolecules are not the same in every part of the plant, the synthesis parameters were carefully studied and strictly optimized. It was found that AgNPs optimal sensing performance were synthesized at slightly elevated temperature (45 °C), using a 0.50 mmol L^{-1} solution of silver(I) nitrate and an extract:water ratio of 1:0. Transmission electron microscopy (TEM) images of the biosynthesized material revealed almost spherical particles with an average diameter of 91.0 ± 0.5 nm. The as-prepared AgNPs and exfoliated graphene nanoplatelets were deposited on the surface of GCE to fabricate a voltammetric sensor for the detection of paracetamol. The sensor showed excellent analytical features in terms of good repeatability and reproducibility (1.8% and 4.0%, respectively), linear SWV response to the analyte in the micromolar concentration range, and a low detection limit of 8.50×10^{-8} M. GCE modified with carbon black (CB); AgNPs and PEDOT:PSS was used for the detection of paracetamol and levofloxacin in river samples [58]. Spherical silver nanoparticles with the median diameter of 10.6 nm were prepared by borohydride reduction. A dispersion of AgNPs (250 µL), CB (1.0 mg), conductive polymer (10 µL), and ultrapure water (740 µL) was drop casted onto the electrode surface. Electrochemical determination by SWV (0.1 M PBS, pH = 6.0) gave a linear concentration range from 0.62 µM to 1.7 µM, with a LOD value of 0.012 µM. The AgNPs-CB-PEDOT:PSS/GCE sensor showed good stability, reproducibility, and repeatability, and no interference occurred in the electrochemical detection of the analyte in the presence of glucose, caffeine, and urea molecules. rGO decorated with a suspension of Ag-Pd bimetallic nanoparticles (1 mg mL^{-1}) and 1% chitosan solution (CS) was dropped onto the GCE surface to fabricate a voltametric sensor for the determination of acetaminophen [59]. The CS/Ag-Pd@rGO/GCE sensor showed high stability (96.3% of the initial value after 20 days storage at 4 °C) and good selectivity (1000-fold concentration of NaCl, KCl, $CuSO_4$, and $CaCl_2$ did not affect the paracetamol determination). A nanohybrid structure of AgNPs integrated into a porous 3D metal–organic framework (ZIF-67) and deposited on GCE demonstrated enhanced electrocatalytic activity toward dopamine (DA) and acetaminophen [60]. Such a specific morphology (dodecahedral crystallite imaged by TEM) enlarges the active composite site and increases the specific surface area. The DVP responses of DA and AP on Ag-ZIF-67p-modified GCE (0.10 M PBS, pH = 7.0) revealed two separated anodic peaks with good linear relationships between anodic peak currents and DA/AP concentrations.

2.6. Electrochemical Sensors for Nitroaromatics

Due to their high solubility in water and low vapor pressure, nitroaromatic compounds (e.g., nitrobenzene, nitrotoluene, nitroaniline, nitroaromatic drugs) have been found to be significant environmental pollutants and have been associated with toxicity, carcinogenesis, and mutagenesis.

Pandiyarajan et al. [61] prepared AgNPs-supported, graphitic-like C_3N_4 nanocomposite via chemical reduction to detect *nitrobenzene* (NB) in aqueous samples. The AgNPs were stabilized with *N*-[3-

(trimethoxysilyl)propyl]ethylenediamine (EDAS) via an amine group to improve the anchoring of AgNPs onto the graphitic nitride sheets and prevent the aggregation of the particles. The nanocomposite has an electrochemical detection function for analyte, with SWV reduction peaks showing a linear dependence on NB concentration in broad concentration range. The sensitivity of the EDAS/(g-C_3N_4-Ag) nanocomposite was found to be 0.594 A M^{-1} cm^{-2}, with a LOD value of 2 μM. Bimetallic gold–silver alloy nanodots (AuAgNDs) with a size of less than 3 nm, encapsulated in a silicate sol–gel (SSG) matrix functionalized with amine groups, were found to be a more environmentally friendly electrocatalyst for the monitoring of NB [12]. The AuAg alloy expressed a characteristic SPR band between the AuNPs and AgNPs, and a unique electrocatalytic behavior compared to monometallic-coated GCE sensors. Furthermore, the synergistic effect of the small AuAg alloy size, combined with the preconcentration of the analyte due to SSG porosity, resulted in a threefold improvement in NB reduction peak current. A linear dependence of the SWV reduction peak current was noticed with a correlation coefficient of R^2 = 0.998, and a sensitivity of 0.045 μA/μM towards nitrobenzene reduction. Shivakumar and coworkers [62] devised a sensitive voltammetric sensor for the detection of NB on *Eucalyptus bark* synthesized AgNPs immobilized on the GCE surface. It was found that the modified electrode made an effective electrocatalytic contribution to reduce NB and to diminish the analyte overpotential; therefore, the peak cathodic current increased compared to the bare GCE. The DPV responses obtained were linear at different concentrations of the analyte (5–45 μM range) in N_2-saturated 0.1 M PBS, with a sensitivity of 2.262 μA $μM^{-1}$ cm^{-2} and a calculated LOD value of 0.027 μM (S/N = 3). The modified electrode was successfully used as a sensor for detecting NB in real water matrices, with recoveries between 98.42% and 102.18% (tap water), and 97.92% and 99.84% (lake water), respectively. A wider linear range and a lower LOD value for the electrocatalytic reduction of NB was achieved with *Camellia japonica* leaf-extract-synthesized AgNP-coated GCE [63]. The typical amperometic current–time behavior (applied potential of −0.42 V; 0.05 M PBS; pH = 7.0) was obtained with the continuous nitrobenzene addition under constant stirring; the reduction peak current changed linearly with respect to the concentration of the analyte in the lower and upper concentration ranges. This behavior can be attributed to the adsorption of nitrobenzene reduction products on the surface of the green catalyst, changing the reduction kinetics. However, the importance of this sensor lies in its dual role, as it is also suitable for photocatalytic degradation of dye Eosin-Y. The development of a sustainable method to remediate Hg(II) as Hg(0) using graphene quantum dots coated carbon cloth (CC/GQDs) and utilization of Hg(0) and AgNPs/CC/GQDs composite as a sensitive electrochemical sensor for nitrobenzene was reported [64]. This sensing platform not only reduced the overpotential for analyte reduction by more than 100 mV, but also exhibited a 4-fold increase in the oxidation current compared to the bare electrode. The NB DPV reduction current (0.2 M PBS, pH = 7.0) increases linearly with analyte concentration within a wide linear range (R^2 = 0.9943), rendering the lowest nitrobenzene LOD value of 30 pM. The applicability of the presented sensor was tested in spiked real matrices (20 and 10 ppm of Hg(II)), and the total Hg(II) removal efficiencies of 24% (lake water), 20% (tap water), 48% (river water), and 11% (sea water), respectively, were obtained.

2.7. Electrochemical Sensors for Natural and Synthetic Estrogens

Hormones are key messengers that convey essential information in living organisms and are used to regulate physiological processes [65]. Among them are estrogens, a group of chemically similar steroid hormones found in animals and humans. Both biogenic (estrone (E1), 17-β-estradiol (E2), estriol (E3), and estretol (E4)) and synthetic estrogens (dienestrol, 17-α-ethinylestradiol) are released into the environment through pharmaceutical and agricultural industries, making them emerging pollutants found in the aquatic environment and even in drinking water [66]. Because they interfere with normal physiological processes, biogenic and synthetic estrogens are also classified as endocrine disrupting chemicals (EDCs). Prolonged exposure to EDCs through food and drinking water can lead to reproductive disorders and tumors in humans. Therefore, strict monitoring of their presence in food and environmental water specimens using selective and sensitive methods is essential for human health [7].

Among natural estrogens, *17-β-estradiol* is the main bioactive molecule that enters into the environment through sewage and animal feed production [67]. Graphene-coated silver nanoparticles (GN@Ag) anchored over graphitic carbon nitride (g-C_3N_4) have been proposed as an outstanding hybrid nanocomposite material for electroanalytical quantification of E2 [68]. In ultrasound-assisted reflux fabrication approach, the graphene–silver NPs were randomly dispersed over g-C_3N_4 sheets (imaged via SEM and TEM, respectively). Such prepared voltammetric GN@Ag/g-C_3N_4/GCE sensor exhibited excellent conductivity and enabled rapid electron transfer, showing excellent CV response to the oxidation of E2 as well as linearity over a wide micromolar concentration range. This simple sensing platform was remarkably stable (91% of initial current response obtained after 21 days) and applicable in real water matrices with recoveries between 95% and 104%. A voltammetric sensor based on molecularly imprinted polymer (MIP) and 2-mercaptobenzoxazole (2-MBO)-capped AgNP composite material was presented as a novel sensing platform for the highly sensitive and selective determination of E2 in real water samples [69]. First, the GCE was modified with nanosilver (electrodeposition from 0.5 mM $AgNO_3$ with addition of a capping agent in 0.1 M PBS under the potential range of −0.7 V to 1.4 V for 7 cycles). Second, electrochemical polymerization of poly(*p*-aminophenol, *p*-APh) was performed in the presence of the E2 molecule as an MIP template (10 mM p-APh, 1 mM E2, and PBS-acetone mixture, pH = 3.0, scan rate of 100 m V s^{-1} controlled between −0.40 V and +0.95 V for 10 cycles). The number of potential cycles during polymerization (5, 10, 15, or 20), polymerization scan rates (50, 100, 150, and 200 mV s^{-1}), effects of pH, and incubation time were studied: the number of scan cycles of 10 proved to be optimal for sensor preparation; the scan rate of 100 mV s^{-1} gave the highest peak current; neutral pH was suitable for E2 detection; and 15 min was the required incubation time. SWV measurements (n = 3) showed that the 17β-estradiol MIP sensor responded to the increasing E2 concentrations from 10 pM to 100 nM, and had a LOD value of 1.86 pM. An electrochemical MIPs-nanocomposite sensor, this time made of ternary poly-imidazole (PImi)-graphene oxide (GO)-AgNPs hybrid material for the selective detection of E2 in river water, was fabricated by the same authors as in the previously published work [70]. The nanosilver material serves as a catalyst and charge carrier, imidazole-based MIP (*p*-type-electron acceptor) provides specific binding cavities for the analyte, and the role of GO (*n*-type-electron donor) in the composite material is to provide additional functional units to bind the template. The imprinted polymer-modified GCE (optimized for Imi to E2 molar ratio, scan rate, scan cycle, pH range, template removal, and the electrode incubation) exhibited relatively small SWV responses after the E2 incubation of 9 min, suggesting that diffusion of ferry/ferrocyanide redox probe to the sensor surface was blocked due to the large amount of analyte detected. The synergistic effect of the MIPs, GO, and AgNP ternary nanocomposite with enlarged high surface-to-volume ratio showed exceptional analytical sensor features, yielding a femtomolar LOD value.

3. Discussion

3.1. Electrochemical Sensor Technology

Electrochemical sensor technology has become an important aspect of modern analytical chemistry, and great efforts are being made to develop novel and cost-effective sensing platforms that provide a fast, accurate, and repeatable response to the analyte of interest. Compared to ubiquitous colorimetric sensors, the main advantage of electrochemical detection is the ability to measure in turbid samples [71]. Moreover, working electrodes can also be made in a planar and/or flexible mode [72][73][74][75], i.e., they can be easily miniaturized and integrated into more hierarchical devices [76]. Electrochemical sensors can be used in various fields, including pharmaceuticals, medicine, chemistry, synthesis, materials engineering, and biotechnology [77][78][79]. In addition, electrochemical sensors based on disc (3D) or planar (2D) electrodes decorated with AgNPs have proven to be simple but reliable analytical tools for the rapid and selective detection of emerging water pollutants (i.e., heavy metal ions, nitrogen-containing inorganic species, phenolic compounds, nitroaromatics, pharmaceuticals, and natural and synthetic hormones), which is highlighted.

3.2. Wet Chemical Synthesis of AgNPs for Sensing Applications

For the fabrication of highly selective and sensitive voltammetric and amperometric electrochemical sensors, the usage of silver nanomaterials with precise particle size, shape, crystalline facets, and morphology is essential. Hence, controlled synthesis is a paramount for achieving excellent electrocatalytic activity for practical sensing application. AgNPs are usually synthesized using a chemical reduction from soluble silver(I) precursors (mostly $AgNO_3$), and many of these synthetic processes are carried out under harsh reaction conditions applying toxic hydrazine [80] or borohydride [81][82][83] reducing agents and/or (volatile) organic solvents [84]. Although there has been more recent focus towards green synthesis [85][86][87], in 64 of the 86 electrochemical sensors presented the reduction of silver(I) to zero-valent form was assisted by electric current or inorganic reducing agents. It is important to emphasize that if the chemical reduction process using strong inorganic agents is precisely controlled, i.e., if no hazardous chemicals are released into the environment during the synthesis [88], such an approach does not necessarily contradict to the principles of green synthesis. Moreover, AgNPs of smaller size and cleaner particle shapes can be produced with strong reducing agents: (i) nanoball-shaped AgNPs (d = 5–6 nm) via the polyol process [89], (ii) spherical crystals (mean diameter of 10.6 nm) obtained via borohydride reduction [90], or (iii) globular particles with a diameter of ~20 nm via ethanolamine reduction [91]. On the other hand, biosynthesized AgNPs generally exhibit irregular morphologies, are polydisperse, and often form larger particle agglomerates [92][93][94]. Nevertheless, even strong reducing agents can render AgNPs of various morphologies (quasi-spherical, cubic, twinned structure, and triangles) and larger size distributions when deposited on highly wrinkled and folded graphene nanosheets [95], or when the Ag(I) precursor is previously encapsulated with a massive chelating ligand [96], while a precisely controlled green approach can produce remarkably small particles (d = 5 nm) with high catalytic efficiency [97]. AgNPs of precise size and shape can also be formed and fine-tuned using electric current [98][99][100][101]. In electrochemical sensors based on electrodeposited silver nanomaterial [102][75], the addition of silver material was found to play a key role in the trace-level quantification of both trivalent and hexavalent chromium through formation and stabilization of functional bimetallic metal oxides [102], and in the formation of dual-region WE for simultaneous detection of inorganic nitrogen-containing species (nitrate/ammonia) through a signal current channel [75].

3.3. Electroanalytical Techniques for Characterization of AgNPs-Modified Electrodes and Analyte Quantification

In general, cyclic voltymmetry and impedance measurements are used to study the changes in the interfacial phenomena between the sensor body and solution when different electrode coating materials are used. In other words, CV and the EIS technique are indispensable tools to observe in detail the stepwise evolution of the electrochemical sensor fabrication pathway. To implement both techniques the usage of a ferri/ferrocyanide redox probe is needed, and measurements are usually performed in aqueous 0.1 M KCl [103][104][105][106][107] or in a phosphate buffer solution [108][109]. With the introduction of AgNPs as electrode modifier material, both the increase of current peak and the reduction in peak separation are noticeable with cyclic voltammetry [89]. The AgNPs modification of the bare electrode is also evident in electrochemical impedance spectroscopy, where the value of electron transfer resistance, which corresponds to the semicircle diameter of the Nyquist diagram, is significantly lower compared to the bare electrode (**Figure 2**). Furthermore, the diffusion-limited process is represented by the linear portion of the Nyquist plot at lower frequencies, while the process is related to the part of the diagram at higher frequencies. In summary, the specific role of the nanosilver material in the exchange of the electron transfer rate between the electroactive species (redox couple) and the modified sensing surface is attributed to the enhancement of the maximum peak current (CV analysis) and the diminution of the impedance (EIS analysis) .

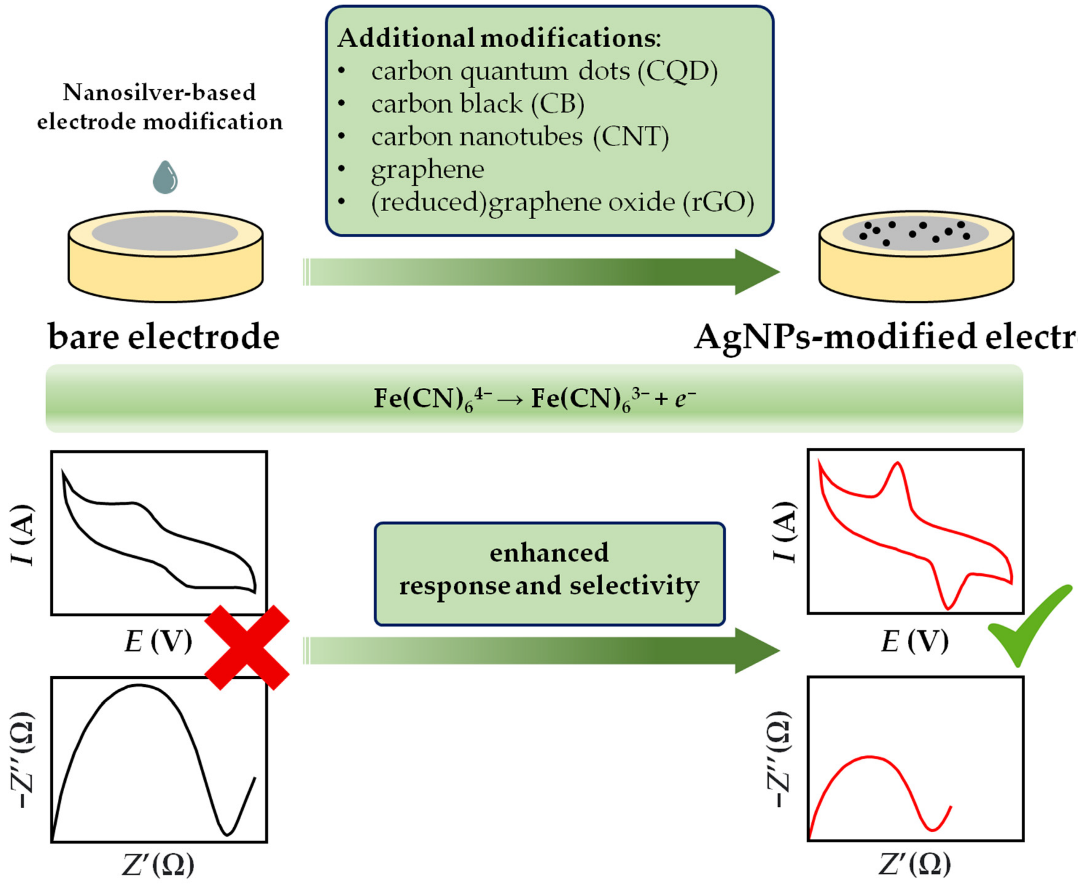

Figure 2. Schematic illustration of AgNPs electrochemical signal boost through the changes in current (CV) and impedance (EIS) responses on bare and nanosilver-modified electrodes.

Voltammetry and amperometry are particularly attractive techniques for the analysis of complex sample matrices such as various environmental waters (groundwater, lakes, rivers, streams, seawater, etc.) The choice of voltammetric technique depends primarily on the location of the sample and the expected concentration of the analyte. Although CV can be used to determine analyte concentration [110][111][112][75], DPV or SWV methods have been shown to be better for quantitative analysis. SWV is known for its superior sensitivity and measurement speed compared to DPV technique [113]. For greater sensitivity, analyte preconcentration can be performed by adsorptive square wave stripping voltammetry [114][115].

3.4. Mechanisms of AgNPs-based Voltammetric and Amperometric Sensors

The detection mechanism of nanosilver-based voltammetric and amperometric sensors for water pollutant monitoring summarized is based on several different mechanisms: (i) AgNPs aggregation; (ii) AgNPs displacement; (iii) AgNPs electronic conductive channels enhancement/inhibition via selective site recognition; and (iv) OR reaction of inorganic/organic water pollutants.

(i) Aggregation of AgNPs triggered by the addition of the analyte is a common optical sensing approach that can be converted to voltammetric [116] and amperometric sensors [117]. This strategy is feasible usually in the form of dual- [116][118] or multisensing [119][120][121][122] platforms, with optical, fluorescent, and electrochemical response towards the detection of HMs. In contrast to the colorimetric assay, electrochemical aggregation of functional silver material results in voltammetric/amperometric signal amplification or inhibition, depending on the chemistry of the nanoparticle stabilizer and the target analyte. For the aggregation-induced sensing mechanism, the role of biogenic synthesized AgNPs is highlighted because biogenic molecules are rich in electron-donor groups that successfully act as analyte-chelating ligands. AgNPs synthesized using fungus *Agaricus bisporus* [116] and the *Mimosa diplotricha* leaf extract [118] were found to be potent sensors towards hazardous mercury, boosting the DPV responses through strong stabilizer complexation. Green AgNPs also play a prominent role as multisensor probes for mercury [119], cadmium [120], arsenic [123], and chromium [122].

(ii) Electrochemical sensors based on the displacement of functional nanomaterials are considered a novel tool for highly selective and sensitive detection of analytes. In two examples of the reviewed scientific papers, the mechanism of mercury detection was associated with the removal of the surface-bound stabilizer (calixarene moiety), leaving the AgNPs uncapped [117], or with galvanic displacement of silver by mercury [124]. As thermodynamically unstable species, the bare nanoparticles tend to aggregate into larger clusters, or form a amalgam [117]. This leads to signal inhibition, which is visible in the optical mode by a reduction in the SPR band in the UV-Vis spectrum, and in the amperometric mode by a reduction in current output. In the galvanic displacement method, the AgNPs interact with divalent mercury ions in the solution and convert the zero-valent silver into ionic silver species, resulting in loss of stripping signal. Since only small amounts of the analyte are required to displace measurable amounts of silver, this sensor can quantify inorganic mercury in the picomolar range.

(iii) Aggravation or enhancement of the electron transfer pathway of AgNPs-modified WE leads to the amplification or decrement of voltammetric performance. Two voltammetric platforms based on MIPs supported by AgNPs-decorated GCE have been developed for highly selective and sensitive detection of natural estrogen in environmental and drinking water with picomolar and femtomolar detection limits [101][125]. The detection of the analyte is catalyzed by the AgNPs (signal amplification or inhibition), while the analyte capture and selective recognition were performed by the MIPs. In the presence of E2, more imprinted cavities of the poly(*p*-aminophenol) (MIP-pAPh) were occupied, resulting in direct amplification of the current response by AgNPs signal amplification [101]. The reverse sensing mechanism was proposed for the AgNP/GO/MIP (poly-imidazole; PImi) functional platform [125]. In addition to the imidazole moiety (*p*-type-electron acceptor), additional functional sites of GO (*n*-type electron donor) were available for analyte binding, which blocked the diffusion of the ferri/ferrocyanide redox probe at the electrode/solution interface, reducing the SWV current responses.

(iv) Voltammetric and amperometric sensors, which detect inorganic/organic pollutants based on their OR response, are the most represented electrochemical sensor class. AgNPs increase the active surface area of the bare and/or modified electrode, facilitate electron transfer, and serve as active catalytic sites for oxidation/reduction of the aquatic pollutant. It has been reported that the reaction rate constant (k) is proportional to the total effective surface area of the nanosilver material [126]. Therefore, the homogeneity of particle size and shape of AgNPs anchored on sensing platforms is of utmost importance for catalytic efficiency. The adsorption of the analyte (the first step in the sensing mechanism) is more promoted on small particles with larger effective surface area, which facilitates the OR process of electroactive species on the modified electrodes [127]. The interactions between the

AgNPs, electrode support and/or other electrode modifiers, and the target analyte, depends on the nature of the surface-active species. On the one hand, stabilizers can be interpreted as a barrier between the AgNPs and the electrode material, controlling the electron transfer kinetics and, thus, affecting the analytical performance of the sensor, especially in terms of achieving lower detection limits [103]. Therefore, clean and uncovered active surface sites of nanoclusters are preferred for catalytic and sensing applications [128]. However, since unprotected AgNPs tend to aggregate, the presence of a stabilizer is extremely important. The catalytic activity of green-capped AgNPs can be altered by the size of the stabilizer (bulky ligands or small molecules) [129][130], and by the adsorption of intermediary molecules (formed during the sensing mechanism) onto the biostabilizers, as was the case in the amperometric quantification of nitrobenzene [131]. The determination of nitrites based on their irreversible electrochemical oxidation via two-electron transfer was reported for various AgNPs-functionalized electrodes, i.e., nanospheres decorated GCE [93], core-shell Au@Ag structure anchored over carboxylated graphene/GCE [132], AgNPs-(r)GO platform [133][134], AgNPs/rGO nanohybrid in conjunction with PPy [135] and PANI [136] conducting polymers, AgNPs/ZnO nanocomposite [137], and AgNPs/HNT/MoS_2 platform [138]. In contrast, one-electron transfer was demonstrated in nitrite sensing with a nanosilver-polymer composite (chitosan, PEDOT:PSS) [139], and also with an AgNPs-MWCNTs hybrid platform [140]. AgNP/SWCNT/CPE was used to detect DNL by the irreversible oxidation of phenolic groups to (semi)quinone species [141]. The overall chemical–electrochemical mechanism involves a transfer of two protons and two electrons, but the final product depends on the applied potential and the electrode modifier used. Oxidation products of E3, obtained using GCE coated with AgNP/CNB [89] and AgNPs-rGO [142], correspond to ketone derivatives. For ultrasensitive detection of AM and AT drugs, an oxidation mechanism involving rapid electron transfer from the analytes through the COOH-CNTs/Ag/NH_2-CNTs ternary sandwich architecture to the GCE was proposed [115]. The overall electrochemical oxidation (single SWASV profile) of the electroactive center 1,4-dihydropyridine (AM) occurs through a two-electron/two-proton process, whereas the pyrrole center of AT exhibits two-electron/one-proton transfer. The reversible oxidation of CC and HQ phenolic compounds to *o*- and *p*-benzokinone species via a two-electron/two-proton transfer was mediated by the cobalt active site of the AgNPs/TACoPc/PANI ternary composite using the DPV technique [143] and with AgNPs/Fe_3O_4-rGO hybrid material [144]. Quantitative determination of BPA via electrooxidation to 2,2-bis(4-phenylquinone) was successfully performed with an AgNPs-rGO composite on a ITO substrate [72], and with an AgNPs-rGO/PLL-coated GCE [80]. Conversely, several phenolic compounds were detected using the reduction mechanism. The nitro groups of 4-nitrophenol [108][128][145], 2,6-dinitrophenol [146], 4-nitrotoluene [147], nitrofurantoin [107], and nitrobenzene [148][94][131] were irreversibly converted into hydroxylamine or aminophenol groups by an electrochemical mechanism involving four protons and four electrons. Moreover, nitrobenzene was detected on a silicate sol–gel matrix GCE functionalized with AgAu alloy, depending on the electrochemical reduction of the nitro group involving six protons and six electrons [149]. Gold electrode coated with AgNPs [150][84], in conjunction with the SWV technique, proved to be a highly efficient combination for the detection of nitrates in seawater due to their two-electron reduction to nitrites. In addition, nitrate was detected on a Cu(II)-terephthalate decorated SPCE via a Cu^{2+}/Cu^{+} redox couple [151]. The adsorption of nitrates is promoted on the Cu(I) active site by copper–oxygen coordination interactions, which is further supported by the charge transferability of MOFs and the enhanced transfer of two electrons to the catalytic AgNP sites.

3.5. Design of AgNPs-based Voltammetric and Amperometric Sensors for Detection of Aquatic Pollutants

The choice of bare electrode substrate (supporting material) is of paramount importance in manufacturing process of electrochemical sensors. The common denominator in the use of pure metal electrodes (Au or Pt), or bare carbon-based electrodes (GCE, GPE, PGE, CPE, SP(C)E, etc.), is the difficult electron transfer between the electroactive analyte molecule and the sensing electrode materials. This leads to low selectivity towards the analyte (the redox reaction is possible at potentials substantially higher than thermodynamic potentials), and inability to distinguish the target molecule from interfering species in real matrices. Therefore, modification of bare electrodes with (hybrid) nanomaterials, especially noble metallic nanoparticles, offers a unique combination of excellent catalytic and sensory properties [110][152][153]. Silver nanoparticles outperform gold and platinum nanomaterials as a low-cost and efficient electrocatalysts for practical sensing applications. Moreover, the synergistic effects of bimetallic [154][132][155], AgNPs/metal oxide composites [156][137] can be also used to promote and/or enhance catalytic sensing.

Due to its diverse structural and morphological forms, carbon is remarkably important and one of the mostly widely used electrode materials [157]. In 54% of the voltammperometric sensors presented , GCE was used as the core material. The main advantages of GCE are its resistance to acidic and alkaline environments and the improved adhesion of the AgNPs to the glassy carbon material [158]. Only a few examples of GCE modified exclusively with AgNPs for the detection of nitrites [110][159][93], nitrobenzene [106][131], and 4-nitrophenol [128] have been found; the vast majority of GCE-based electrochemical sensors are modified with composite silver (nano)materials. One of the frequently used strategies in the development of novel sensor surfaces is the anchoring of AgNPs on the surface of 2D nanomaterials, mostly graphene-derived, due to their large surface area, high chemical stability, and mechanical strength [160][161]. The GO platform is rich in oxygen-containing functional groups, which greatly improves its hydrophilicity and functionality. Therefore, GO is easily dispersed in both water and organic solvents to obtain a homogeneous dispersion, and can be easily applied to electrode substrates by simple immersion or drop casting technique [133][91]. In addition, GO has an enhanced ability to capture target molecules due to its rich edge oxygen chemistry, a property that has been used to develop a nitrite sensing platform [133]. To increase the sensitivity of the sensor, the strategy of combining AgNPs with a more conductive reduced GO form (restoration of sp^2 hybrid carbon networks) was developed [80][144][95][142]. Thus, (r)GO serves as an outstanding platform for the immobilization of various electroactive species through covalent or noncovalent bonds. In addition to (r)GO sheets, other 2D layered structures with semiconducting properties such as activated C_3N_4 [105][148][162], MOFs [151][163], and transition metal dichalogenides [164] have also emerged as prospective candidates for improved catalyst supports for simultaneous voltammetric detection of HMs, selective oxidation of nitrite, amperometric nitrate detection, and selective dopamine quantification, respectively. 3D MWCNTs, especially functionalized by acid treatment, possess excellent thermal and electrical conductivity, which, combined with their large surface area, significantly improves the catalytic properties for the oxidation of ammonium and nitrite species [140][112][165], and the detection of phenolic compounds [99][166] in real water matrices. In only one scientific paper, SWCNTs were used in conjunction with AgNPs as a sensing surface for the quantification of the synthetic estrogen dienestrol in river water [141]. Another approach to increase the sensitivity is to use the CPs in the nanosilver-based sensing hierarchy in the form of an AgNPs@p-1,8-DAN layer [167] or an AgNPs/CB/PEDOT:PSS film [90] built over disc GCE, or ternary hybrid structures of nanosilver on the (r)GO platform with PPy [135] or PANI [168]. Due to their (high) conductivity, redox reversibility, long-term environmental stability, high solution process ability, and simple synthetic procedures with controllable thickness on the sensing electrode, CPs are often employed in voltammperometric sensor design. Synthetic MIPs based on GCE sensing platforms are the best alternative to circumvent the stability and cost issues associated with biological receptors traditionally used for the detection of (bio)molecules [169]. Since the size, shape, and orientation of the recognition sites of the cavities imprinted in MIP directly reflect the properties of the analyte, the molecular imprint technology is more than efficient for the development of highly selective sensors. MIPs in combination with AgNPs and AgNPs/GO composites have proven to be exquisite sensing platforms—picomolar and femtomolar LOD values have been achieved for the detection of the endocrine-disrupting 17-β-estradiol in real water matrices [101][125].

In addition to GCE, another robust carbon-based 3D electrode—CPE—can be quickly fabricated, modified with various (nano)materials, and its surface is easy to clean. Although their sensitivity is (usually) lower than that of GCEs, CPEs decorated with AgNPs have proven to be a reliable tool for amperometric detection of synthetic estrogen (nM LOD) [141], amperometric quantification of nitrites in aquatic solutions (μM LOD) [138], selective voltammetric reduction of *p*-nitroaniline in wastewater (nM LOD) [170], and electrochemical sensing of lead ions in tap water and wastewater specimens (μM LOD) [171]. Another simple and inexpensive form of a carbon-based electrode, with advantages such as high mechanical strength, good quality, stability, and reproducibility, is the PGE [172]. This user-friendly electrode can be used as disposable electrode, eliminating the time-consuming cleaning of solid electrodes. A PGE sensing probe modified with an AgNP-ZnO nanocomposite has been successfully used for the determination of nitrites in lake water and pickled water samples [137], and one decorated with biosynthesized AgNPs was selective towards divalent mercury [111].

Noble metal electrodes, such as gold and platinum material, find application in a variety of electrochemical processes due to their high electrical conductivity, mechanical stability, and chemical resistance. Nevertheless, only a few electrochemical sensors based on nanosilver-decorated noble metal electrodes have been presented . Gold (Au) disc electrodes predominate in the development of voltammetric sensors for the detection of arsenic in river water and lake water [173][100][123], but are also suitable as substrates for the selective and sensitive detection of nitrates in seawater matrices [150][84]. Platinum (Pt) electrodes, decorated with AgNPs biosynthesized utilizing *Agaricus bisporus* mushroom extract [116] and *Mimosa diplotricha* plant leaf extract [118], were found to be an excellent solution for the selective and sensitive detection of toxic Hg(II) in lake water, tap water, and river water specimens, respectively. In addition, a Pt disc electrode decorated with bark green AgNPs (*Moringa oleifera* bark extract) was utilized to detect hazardous Cu(II) from electroplating plant effluents [121], while AgNPs produced with garlic extract were used for the quantification of Cd(II) in lakes [120].

Planar screen-printed (carbon) electrodes are suitable for on-site analyses because they are built on the same substrate with a three-electrode setup (WE, RE, and CE). Planar SPE surfaces can be modified in the same way as disc electrodes by using a: (i) hybrid of AgNPs and Cu(II)–terephthalate MOFs for the quantification of nitrate in drinking water [151], (ii) silver nanoseed/carbon nanofiber modifier for simultaneous detection of Cu(II) and Pb(II) in groundwater matrices [81], (iii) a curcumin-stabilised AgNPs-$FeCo_2O_4$ nanosheets-rGO complex architecture for the detection of 4-NP in industrial wastewater [174], (iv) a ternary Ag/Co_3O_4/chitosan composite for the removal of 4-nitrophenol in sewage [175], (v) bimetallic silver-gold-oxide nanoparticles for simultaneous determination of trivalent and hexavalent chromium in tap water [176]. In addition to carbon-based planar surfaces, AgNPs-decorated glass [177], ITO substrates [72][178], and FTO glass substrates [179] were successfully employed for the selective detection of nitrite, nitrate, BPA, and hazardous copper, respectively.

3.6. Summary and Future Perspective

In summary, the use of silver nanomaterial-decorated electrodes as voltammperometric sensors offers several advantages based on the electroanalysis output: (i) efficient catalysis; (ii) rapid mass transfer of the target analyte from the bulk solution to the sensing surface and vice versa; (iii) large sensor surface area; and (iv) the ability to precisely tune the electrode microenvironment. Although electrochemical sensing technologies may achieve quantification of analytes even at femtomolar levels, they still lack quality assurance and reliability for long-term measurements in complex water matrices.

Therefore, to ensure an advanced and self-sufficient next generation of nanosilver-based voltammetric/amperometric probes, future research must focus on the: (i) the development of low-cost and submersible sensor platforms for real-time detection of pollutants in water matrices; (ii) fabrication of lighter weight and small-sized devices—miniaturization and planar (all-printed all-solid state) electrode design; (iii) construction of wireless and portable sensors for measurements at remote locations with minor facilities; (iv) sensitivity and selectivity augmentation overcoming interference and fouling challenges; and (v) development of self-sustained devices.

4. Conclusions and Outlooks

Electrochemical sensing in combination with nanosilver-based materials and various electroanalytical techniques offers attractive opportunities to meet the requirements for accurate detection of emerging water pollutants. The high conductivity of AgNPs facilitates rapid charge transfer during detection of the target species, while superior catalytic efficiency can be easily tuned by changing the particle size, shape, and temperature of the reaction mixture. Compared to other metal-based nanoparticles, AgNPs have relatively lower cost and toxicity, ensuring their great potential for practical applications. Modification of electrode substrates with silver hybrid architectures by introducing 2D carbon (graphene and its derivatives, carbon black, carbon cloth), 3D carbon nanomaterials (quantum dots, carbon nanotubes), and MOFs or CPs as support materials forms adventurous sensing surfaces for detection of various analytes. Molecular imprinting is by far the most sensitive targeting technology, enabling rapid and ultrasensitive quantification of analytes by fine-tuning the recognition sites in the MIP cavities.

So far, different synthesis strategies have been developed to prepare Ag-based nanocomposite materials decorated WE, from simple immersion and drop casting to in situ reduction method. By combining the advantages of the different synthesis methods and the various modification techniques, high-performance detection is possible for practical in-field applications. Although numerous studies on the synthesis and environmental applications of AgNPs-based electrochemical sensors have been conducted recently, the development of highly selective and sensitive platforms with the possibility of miniaturization and integration into portable devices for real-time measurements and sustainable use of water resources remains a challenge.

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