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Introduction

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Persistent toxic substances (PTS) are chemical species that possess the properties of bioaccumulation, degradation difficulty, and poison [1–6]. Usually, PTS primarily refer to persistent organic pollutants (POPs, including polycyclic aromatic hydrocarbons (PAHs); polybrominated diphenyl ethers (PBDEs); polychlorinated biphenyls (PCBs); and organochlorine pesticides (OCPs)) and heavy metal ions (HMIs, including Pb(II), Cd(II), Cr(VI), As(III), and so on) [7–9]; the details can be found in Chapter 2 (PTS in aquatic environment). The most popular PTS include POPs, which are organic chemical substances that could remain intact for a long period, accumulate in the tissues of living organisms (bioaccumulation), and have toxic effects. POPs usually come from various pesticides, industrial chemicals, and unintentional chemical by-products such as dioxins. POPs are now globally distributed, including in environments where they have never been used, and are linked to a range of health effects, such as cancer, allergies, and hypersensitivity, damage to the central and peripheral nervous systems, reproductive disorders, and disruption of the immune system. Other persistent, bioaccumulative, and toxic (PBTs) substances include organometallic substances, such as organomercury. The attributes of POPs and PBTs mean they will continue to do great damage to human health and the environment for a long period of time. These chemicals have seriously destructive effect on health and environment. It may include carcinogenicity, reproductive impairment, developmental and immune system changes, and endocrine disruption, thus posing a threat of lowered reproductive success and, in extreme cases, possible loss of biological diversity [10–13]. At present, there is concern due to these pollutants' ability to travel long distances through the atmosphere or oceans to places where these compounds have never been used before [14–18]. A PTS study in different chemical environment such as soils, sediments, water, and snow in geographical areas with a continuous matter cycling flux could provide insights into the biogeochemical cycling of the pollutants within hydrographical basins according to their anthropogenic influence [19].

The detection and monitoring of environmental pollutants is very important in the overall safety and security of humans, other animals, and plants. A variety

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of environmental media including water, sediment, and biomonitors have been utilized to monitor contaminants. For example, Mussel Watch monitoring uses bivalves and has been implemented successfully regionally and internationally [20]. Although these devices do not require large amounts of water samples to be collected and transported, technical operations are necessary to install them on site [21]. In these contexts, it would be invaluable to establish monitoring media, which could easily be collected and shipped at relatively low cost. Recently, a variety of analytical techniques for PTS monitoring have been reported, such as cold vapor atomic fluorescence spectrometry (CV-AFS), atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), synchrotron-based probing techniques, and so on [22–24]. While highly sensitive and selective, traditional chromatographic and spectroscopic analytical techniques are time consuming, expensive, and require much expertise. In a word, the above-mentioned methods involve use of expensive instruments and materials, require complicated procedures, and are not suitable for in situ analysis due to the ponderous and complicated instruments. Therefore, there is need for simple, rapid, specific, sensitive, and portable methods for analyzing environmental security threats.

Electrochemical sensors are an important and representative subclass of chemical sensors. In terms of electrochemical sensor, an electrode is used as the sensing element, and it is highly qualified for meeting the size, cost, and power requirements of environmental monitoring [25, 26]. High sensitivity, selectivity, and a wide linear range are important characteristics of electrochemical sensing systems. Additionally, it requires only minimal space and low power source, and low-cost instrumentation. This kind of device has been applied in a vast range of fields of clinical, industrial, environmental, and agricultural analyses. In the past several decades, electrochemical devices have been used for PTS monitoring, which could serve as a variety of water quality parameters (e.g. conductivity, dissolved oxygen, or pH). Consequently, electrochemical sensors have led to a wider range of environmental applications including the measurement of trace metals in natural waters [27–36], carcinogen monitoring (e.g. N-nitroso compounds or aromatic amines) [37–44], the development of biosensors for the detection of organic pollutants (e.g. pesticides, phenols) in ground water [45–53], and environmental protection and clean energy conversion [49, 54–58], providing a fast return of the analytical information in a timely, safe, and cost-effective manner. Such devices could offer direct and reliable monitoring (including assessment of the fate and gradient of the target analytes).

Electroanalytical sensors are concerned with the interplay between electricity and chemistry, namely, the measurements of electrical quantities, such as current, potential, or charge, and their relationship to chemical parameters, such as the concentration of PTS. Most of the electrochemical devices used for environmental monitoring fall within three categories and ultimately depend upon the specific analyte, nature of the sample matrix, and the sensitivity and selectivity requirements [32, 59]. Amperometry and voltammetry are the main methods in electrochemical sensing. The use of a potential applied between a reference electrode and a working electrode could cause the oxidation or reduction of an electroactive species. Thus, the applied potential will serve as the driving force for the electron-transfer reaction. The resulting current is a direct measure of the rate of the electron-transfer reaction and is proportional to the target analyte concentration. The most common example is the oxygen Clark electrode that has been widely used for monitoring the level of oxygen in the water column and sediment pore water. Potentiometry is another method in electrochemical sensing. In potentiometric sensors (primarily ion-selective electrodes), the analytical information is obtained by converting an ion-recognition event into a potential signal. A local equilibrium is established across the recognition membrane, leading to a change in the membrane potential. The analytical information is obtained from the potential difference between the ion-selective electrode and a reference electrode. Potentials are a function of species activity, not concentration. Typical examples are potentiometric devices for in situ monitoring of pH and concentration of CO_2 or S^{2-}. Conductimetry is the third method in electrochemical sensing. Conceptually, it is the simplest of the electroanalytical techniques but is inherently nonspecific. The concentration of the charge is obtained through measurement of solution resistance. Usually, voltammetry and conductimetry are two main techniques applied in monitoring PTS, and the details can be found in Chapter 3.

The nanoelectrochemical method involves the electrodes and materials applied in monitoring of PTS at the micro–nano scale. In terms of the electrodes in the detection of PTS, the ultra-microelectrode has unique electrochemical properties when compared with conventional counterparts. The use of ultra-microelectrodes (with diameter smaller than 20 μm) has been employed for minimizing errors associated with fluctuations in natural convection. Such relative independence of microelectrode sensors from convective flow reflects the larger natural convection boundary layer compared to the Nernst layer. In addition, the decreased ohmic distortions at ultra-microelectrodes allow direct electrochemical measurements to be made in aquatic systems (e.g. inland water) of low ionic strength. This also obviates the need for supporting electrolyte, thereby minimizing possible impurities. For example, Brendel and Luther demonstrated the utility of a voltammetric microelectrode for obtaining depth profiles of dissolved iron, manganese, oxygen, and S^{2-} in marine environments [60]. Besides, the intrinsic sensitivity, simplicity, and portability of electrochemical methods have been receiving much more attention in the monitoring of PTS [61–64]. Owing to the small electrode area of the micro–nano electrodes, the electric double layer capacitance and the electrode time constant are small, resulting in a fast electrode response rate. Compared to conventional electrodes, micro–nano electrodes are suitable for electrochemical measurement techniques, such as square wave voltammetry (SWV), pulse voltammetry, and fast scan voltammetry. Additionally, the small electric double layer capacitance endows micro–nano electrodes with a small charging current and fast decay rate. Consequently, the charging current interference is minimized in the electrochemical analysis process, significantly improving the sensitivity and reducing the limit of detection. The intrinsically small diameters and high aspect ratios allow them to be applied in the field of electrochemical monitoring of PTS. Recently, our group and Compton's group have made some achievements in the detection of HMIs with the help of micro–nano electrodes [65–79], which will be discussed in detail in Chapter 10.

On the other hand, using nanomaterials to modify electrodes to improve the electrochemical sensing performance has been proved the most popular method [80–86]. Nanomaterials may be decorated with polymers and bioactive molecules (e.g., monoclonal antibodies) in order to enhance biocompatibility and to achieve precise targeting; they are increasingly being employed in the development of electrochemical DNA biosensors due to their unique electrocatalytic properties. Functionalized nanomaterials offer excellent prospects for interfacing biological recognition events with electronic signal transduction in the design of a new generation of bioelectronic devices that exhibit novel functions [87]. Additionally, it has been observed that chemical composition, surface condition, crystal structure quality, crystallographic axis orientation, etc. are critical parameters of nanomaterials, which cumulatively influence electron transport mechanisms [88–95]. Two major advantages of nanomaterials are their potential to be utilized as noninvasive diagnostic tools and the capacity for combining multiple modalities within a single probe. This enables far higher sensitivities to be achieved, which leads to further clarity and deeper insights into in vivo processes [31, 81, 82, 96–100]. Nanomaterials are also ideally suited to be applied as drug-delivery systems, which may facilitate the development of a new generation of theranostics with exquisitely sensitive chemical and biological sensing capabilities [101–109]. The ability to identify particular cell species or specific anatomical sites within the human body may bode very well for the use of nanobiosensors in medical diagnostics. Given their sensitivity, flexibility, and miniaturization, these sensors may serve as a new paradigm for clinical and field-deployable analytical instruments. The intent of this review is to impart insights into nanomaterials-based electrochemical sensors, and to illustrate their potential benefits in various key biomedical applications. Electrochemistry provides powerful analytical techniques encompassing the advantages of instrumental simplicity, moderate cost, and portability. Modern electrochemical methods are sensitive, selective, rapid, and facile techniques applicable to biomedical fields, and indeed in most areas of analytical chemistry. A number of electrochemical strategies have been explored in the development of nanomaterials-based electrochemical sensors for biomedical applications. In nanoelectrochemical sensing, voltammetric techniques have been extremely useful in measuring blood levels, metabolites, and the urinary excretion of drugs following low doses, especially when coupled with chromatographic methods. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) have evoked great interest as they can be used for the elucidation of electrode processes and redox mechanisms [110]. Differential pulse voltammetry (DPV) [111] and SWV [112] are particularly useful in the determination of trace amounts of electroactive compounds in pharmaceuticals and biological fluids. Stripping voltammetry has also been widely utilized due to its ability to preconcentrate analytes for ultrasensitive detection [113]. Amperometry is another common electrochemical technique that has been widely employed in electrochemical sensors and biosensors. More details can be found in Chapter 3. Electrochemiluminescent (ECL) and photoelectrochemical assays are also promising prospective technologies in that they possess the advantage of enabling both optical and electrochemical detection. Various signal amplification strategies based on functional nanomaterials, coupled with different electrochemical methods, have recently gained considerable interest toward the emergence of high-performance analytical tools for the ultrasensitive detection of trace amounts of a wide variety of analytes, including DNA and micro-RNA assays in clinical and environmental applications [114].

In this book, PTS in aquatic environment is first introduced in Chapter 2. Common electrochemical principles, such as voltammetry and conductimetry for PTS detection, are discussed in Chapter 3. Design concepts of nano-electrochemical sensing interface, including adsorption capability-enhanced electrochemical signal, selective adsorption for selective recognition, electrocatalytic performance for enhanced sensitivity, and controllable preparation of specific crystal facet to boost sensitivity are presented in Chapter 4. The popular carbon-based nanomaterials modification for enhanced selectivity and sensitivity toward PTS is recommended in Chapter 5. Facet and phase-dependent electroanalysis performance of nanocrystals is utilized in PTS monitoring to investigate the mechanism of electrochemical detection at atomic level, as shown in Chapter 6. Mutual interferences between HMIs on the electrochemical nanointerfaces are demonstrated in Chapter 7. Metal oxide and its composite nanomaterials for electrochemical monitoring of PTS are presented in Chapter 8. A new method, nanogap for detection of PTS, is shown in Chapter 9. Nanoelectrodes are used in the determination of PTS, as demonstrated in Chapter 10. Electrochemical-assisted preconcentration for the spectral detection of PTS is presented in Chapter 11. At the end of the book (Chapter 12), conclusions and future perspectives are given based on the present study. All these contents have been reviewed in detail and the reader could find them in the corresponding chapters. Nanoelectrochemical methods provide a new and powerful paradigm in terms of novel and augmented functionality that encompasses a wide variety of applications in environment analysis research. This brief survey of various electrochemical sensing strategies may facilitate the development of advanced applications in environment electroanalysis field.

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