# 1

# 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, electro-catalytic 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. Nano-electrodes 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.

## References

1 Jiao, L., Zheng, G.J., Minh, T.B. et al. (2009). Persistent toxic substances in remote lake and coastal sediments from Svalbard, Norwegian Arctic: levels, sources and fluxes. *Environmental Pollution* **157** (4): 1342–1351.

2 Barra, R., Popp, P., Quiroz, R. et al. (2005). Persistent toxic substances in soils and waters along an altitudinal gradient in the Laja River Basin, Central Southern Chile. *Chemosphere* **58** (7): 905–915.

3 Johnson, B.L., Hicks, H.E., Jones, D.E. et al. (1998). Public health implications of persistent toxic substances in the Great Lakes and St. Lawrence basins. *Journal of Great Lakes Research* **24** (3): 698–722.

4 He, H., Hu, G.J., Sun, C. et al. (2011). Trace analysis of persistent toxic substances in the main stream of Jiangsu section of the Yangtze River, China. *Environmental Science and Pollution Research* **18** (4): 638–648.

5 Guzzella, L., Poma, G., De Paolis, A. et al. (2011). Organic persistent toxic substances in soils, waters and sediments along an altitudinal gradient at Mt. Sagarmatha, Himalayas, Nepal. *Environmental Pollution* **159** (10): 2552–2564.

6 Man, M., Naidu, R., and Wong, M.H. (2013). Persistent toxic substances released from uncontrolled e-waste recycling and actions for the future. *Science of the Total Environment* **463**: 1133–1137.

7 Rosenfeldt, R.R., Seitz, F., Schulz, R., and Bundschuh, M. (2014). Heavy metal uptake and toxicity in the presence of titanium dioxide nanoparticles: a factorial approach using *Daphnia magna*. *Environmental Science & Technology* **48** (12): 6965–6972.

8 Guerrini, L., Rodriguez Loureiro, I., Correa Duarte, M.A. et al. (2014). Chemical speciation of heavy metals by surface-enhanced Raman scattering spectroscopy: identification and quantification of inorganic- and methyl-mercury in water. *Nanoscale* **6** (14): 8368–8375.

9 Jin, X.Z., Lee, H.K., Badejo, A.C. et al. (2016). Decline in sediment contamination by persistent toxic substances from the outfall of wastewater treatment plant: effectiveness of legislative actions in Korea. *Chemosphere* **153**: 426–435.

10 Neagu, D., Arduini, F., Quintana, J.C. et al. (2014). Disposable electrochemical sensor to evaluate the phytoremediation of the aquatic plant *Lemna minor* L. toward $Pb^{2+}$ and/or $Cd^{2+}$. *Environmental Science & Technology* **48** (13): 7477–7485.

11 Kim, H.N., Lee, M.H., Kim, H.J. et al. (2008). A new trend in rhodamine-based chemosensors: application of spirolactam ring-opening to sensing ions. *Chemical Society Reviews* **37** (8): 1465–1472.

12 Chakraborty, A., Bhattacharyya, S., Hazra, A. et al. (2016). Post-synthetic metalation in an anionic MOF for efficient catalytic activity and removal of heavy metal ions from aqueous solution. *Chemical Communications* **52** (13): 2831–2834.

13 Jaishankar, M., Tseten, T., Anbalagan, N. et al. (2014). Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology* **7** (2): 60–72.

14 Xiu, M., Pan, L., and Jin, Q. (2014). Bioaccumulation and oxidative damage in juvenile scallop *Chlamys farreri* exposed to benzo[*a*]pyrene, benzo[*b*]fluoranthene and chrysene. *Ecotoxicology and Environmental Safety* **107**: 103–110.

15 Besis, A., Tsolakidou, A., Balla, D. et al. (2017). Toxic organic substances and marker compounds in size-segregated urban particulate matter-implications for involvement in the in vitro bioactivity of the extractable organic matter. *Environmental Pollution* **230**: 758–774.

16 Wilson, J., Berntsen, H.F., Zimmer, K.E. et al. (2016). Effects of defined mixtures of persistent organic pollutants (POPs) on multiple cellular responses

in the human hepatocarcinoma cell line, HepG2, using high content analysis screening. *Toxicology and Applied Pharmacology* **294**: 21–31.

17 Lakroun, Z., Kebieche, M., Lahouel, A. et al. (2015). Oxidative stress and brain mitochondria swelling induced by endosulfan and protective role of quercetin in rat. *Environmental Science and Pollution Research* **22** (10): 7776–7781.

18 Kümmerer, K., Haiß, A., Schuster, A. et al. (2016). Antineoplastic compounds in the environment—substances of special concern. *Environmental Science and Pollution Research* **23** (15): 14791–14804.

19 Grimalt, J.O., Fernandez, P., Berdie, L. et al. (2001). Selective trapping of organochlorine compounds in mountain lakes of temperate areas. *Environmental Science & Technology* **35** (13): 2690–2697.

20 Goldberg, E.D. (1975). The mussel watch—a first step in global marine monitoring. *Marine Pollution Bulletin* **6** (7): 111.

21 Cunha, I., Moreira, S., and Santos, M.M. (2015). Review on hazardous and noxious substances (HNS) involved in marine spill incidents—an online database. *Journal of Hazardous Materials* **285**: 509–516.

22 Daşbaşı, T., Saçmacı, Ş., Ülgen, A., and Kartal, Ş. (2016). Determination of some metal ions in various meat and baby food samples by atomic spectrometry. *Food Chemistry* **197**: 107–113.

23 Guimaraes, J.R.D., Roulet, M., Lucotte, M., and Mergler, D. (2000). Mercury methylation along a lake–forest transect in the Tapajós river floodplain, Brazilian Amazon: seasonal and vertical variations. *Science of the Total Environment* **261** (1): 91–98.

24 Iwashita, A., Nakajima, T., Takanashi, H. et al. (2007). Determination of trace elements in coal and coal fly ash by joint-use of ICP-AES and atomic absorption spectrometry. *Talanta* **71** (1): 251–257.

25 Taillefert, M., Luther, G.W. III,, and Nuzzio, D.B. (2000). The application of electrochemical tools for in situ measurements in aquatic systems. *Electroanalysis* **12** (6): 401–412.

26 Bakker, E. and Telting-Diaz, M. (2002). Electrochemical sensors. *Analytical Chemistry* **74** (12): 2781–2800.

27 Howell, K.A., Achterberg, E.P., Braungardt, C.B. et al. (2003). Voltammetric in situ measurements of trace metals in coastal waters. *TrAC—Trends in Analytical Chemistry* **22** (11): 828–835.

28 Howell, K.A., Achterberg, E.P., Braungardt, C.B. et al. (2003). The determination of trace metals in estuarine and coastal waters using a voltammetric in situ profiling system. *Analyst* **128** (6): 734–741.

29 Promphet, N., Rattanarat, P., Rangkupan, R. et al. (2015). An electrochemical sensor based on graphene/polyaniline/polystyrene nanoporous fibers modified electrode for simultaneous determination of lead and cadmium. *Sensors and Actuators B: Chemical* **207**: 526–534.

30 Ruecha, N., Rodthongkum, N., Cate, D.M. et al. (2015). Sensitive electrochemical sensor using a graphene–polyaniline nanocomposite for simultaneous detection of Zn(II), Cd(II), and Pb(II). *Analytica Chimica Acta* **874**: 40–48.

31 Gumpu, M.B., Sethuraman, S., Krishnan, U.M., and Rayappan, J.B.B. (2015). A review on detection of heavy metal ions in water—an electrochemical approach. *Sensors and Actuators B: Chemical* **213**: 515–533.

32 Cui, L., Wu, J., and Ju, H. (2015). Electrochemical sensing of heavy metal ions with inorganic, organic and bio-materials. *Biosensors and Bioelectronics* **63**: 276–286.

33 Afkhami, A., Ghaedi, H., Madrakian, T., and Rezaeivala, M. (2013). Highly sensitive simultaneous electrochemical determination of trace amounts of Pb(II) and Cd(II) using a carbon paste electrode modified with multi-walled carbon nanotubes and a newly synthesized Schiff base. *Electrochimica Acta* **89**: 377–386.

34 Farghaly, O., Hameed, R.A., and Abu Nawwas, A.A.H. (2014). Analytical application using modern electrochemical techniques. *International Journal Electrochemical Science* **9** (1).

35 Cui, L., Wu, J., and Ju, H.G. (2014). Nitrogen-doped porous carbon derived from metal–organic gel for electrochemical analysis of heavy-metal ion. *ACS Applied Materials & Interfaces* **6** (18): 16210–16216.

36 Laffont, L., Hezard, T., Gros, P. et al. (2015). Mercury(II) trace detection by a gold nanoparticle-modified glassy carbon electrode using square-wave anodic stripping voltammetry including a chloride desorption step. *Talanta* **141**: 26–32.

37 Švorc, Ľ., Rievaj, M., and Bustin, D. (2013). Green electrochemical sensor for environmental monitoring of pesticides: determination of atrazine in river waters using a boron-doped diamond electrode. *Sensors and Actuators B: Chemical* **181**: 294–300.

38 Zaidi, S.A. and Shin, J.H. (2015). A novel and highly sensitive electrochemical monitoring platform for 4-nitrophenol on $MnO_2$ nanoparticles modified graphene surface. *RSC Advances* **5** (108): 88996–89002.

39 Rahman, L.-U., Shah, A., Lunsford, S.K. et al. (2015). Monitoring of 2-butanone using a Ag–Cu bimetallic alloy nanoscale electrochemical sensor. *RSC Advances* **5** (55): 44427–44434.

40 Gao, G.G., Xu, G.B., Li, J.L. et al. (2014). Low-level expression of purine bases in BALB/3T3 cells monitored by ultrasensitive graphene-based glass carbon electrode. *Analytical Biochemistry* **467**: 40–46.

41 Kuss, S., Trinh, D., and Mauzeroll, J. (2015). High-speed scanning electrochemical microscopy method for substrate kinetic determination: application to live cell imaging in human cancer. *Analytical Chemistry* **87** (16): 8102–8106.

42 Mazhabi, R.M. and Arvand, M. (2014). Disposable electrochemical DNA biosensor for environmental monitoring of toxicant 2-aminoanthracene in the presence of chlorine in real samples. *Journal of Chemical Sciences* **126** (4): 1031–1037.

43 Yilmaz, N., Eksin, E., Karacicek, B. et al. (2017). Electrochemical detection of interaction between capsaicin and nucleic acids in comparison to agarose gel electrophoresis. *Analytical Biochemistry* **535**: 56–62.

44 Wu, L., Lu, X., Fu, X. et al. (2017). Gold nanoparticles dotted reduction graphene oxide nanocomposite based electrochemical aptasensor for selective, rapid, sensitive and congener-specific PCB77 detection. *Scientific Reports* **7**: 5191.

45 Martínez Huitle, C.A., Rodrigo, M.A., Sirés, I., and Scialdone, O. (2015). Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: a critical review. *Chemical Reviews* **115** (24): 13362–13407.

46 Zhang, B., Wang, Z., Zhou, X. et al. (2015). Electrochemical decolorization of methyl orange powered by bioelectricity from single-chamber microbial fuel cells. *Bioresource Technology* **181**: 360–362.

47 Brillas, E. and Martínez Huitle, C.A. (2015). Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. *Applied Catalysis B: Environmental* **166**: 603–643.

48 Saranya, M., Ramachandran, R., Samuel, E.J.J. et al. (2015). Enhanced visible light photocatalytic reduction of organic pollutant and electrochemical properties of CuS catalyst. *Powder Technology* **279**: 209–220.

49 Vasudevan, S. and Oturan, M.A. (2014). Electrochemistry: as cause and cure in water pollution—an overview. *Environmental Chemistry Letters* **12** (1): 97–108.

50 Villasenor, J., Capilla, P., Rodrigo, M. et al. (2013). Operation of a horizontal subsurface flow constructed wetland–microbial fuel cell treating wastewater under different organic loading rates. *Water Research* **47** (17): 6731–6738.

51 Soler, L. and Sánchez, S. (2014). Catalytic nanomotors for environmental monitoring and water remediation. *Nanoscale* **6** (13): 7175–7182.

52 Liu, Q., Zhou, Q., and Jiang, G. (2014). Nanomaterials for analysis and monitoring of emerging chemical pollutants. *TrAC—Trends in Analytical Chemistry* **58**: 10–22.

53 Souza, F.L., Aquino, J.M., Irikura, K. et al. (2014). Electrochemical degradation of the dimethyl phthalate ester on a fluoride-doped Ti/$\beta$-$PbO_2$ anode. *Chemosphere* **109**: 187–194.

54 Cao, X., Jie, Y., Wang, N., and Wang, Z.L. (2016). Triboelectric nanogenerators driven self-powered electrochemical processes for energy and environmental science. *Advanced Energy Materials* **6** (23): 1600665.

55 Mook, W., Aroua, M., and Issabayeva, G. (2014). Prospective applications of renewable energy based electrochemical systems in wastewater treatment: a review. *Renewable and Sustainable Energy Reviews* **38**: 36–46.

56 Qian, F., Wang, H., Ling, Y. et al. (2014). Photoenhanced electrochemical interaction between Shewanella and a hematite nanowire photoanode. *Nano Letters* **14** (6): 3688–3693.

57 Mueller, S.C., Sandner, P.G., and Welpe, I.M. (2015). Monitoring innovation in electrochemical energy storage technologies: a patent-based approach. *Applied Energy* **137**: 537–544.

58 Hodnik, N., Dehm, G., and Mayrhofer, K.J. (2016). Importance and challenges of electrochemical in situ liquid cell electron microscopy for energy conversion research. *Accounts of Chemical Research* **49** (9): 2015–2022.

59 Xu, T., Jia, X., Chen, X., and Ma, Z. (2014). Simultaneous electrochemical detection of multiple tumor markers using metal ions tagged immunocolloidal gold. *Biosensors and Bioelectronics* **56**: 174–179.

60 Brendel, P.J. and Luther, G.W.I. (1995). Development of a gold amalgam voltammetric microelectrode for the determination of dissolved Fe, Mn, $O_2$, and S(-II) in porewaters of marine and freshwater sediments. *Environmental Science & Technology* **29** (3): 751–761.

61 Radhakrishnan, S., Krishnamoorthy, K., Sekar, C. et al. (2014). A highly sensitive electrochemical sensor for nitrite detection based on $Fe_2O_3$ nanoparticles decorated reduced graphene oxide nanosheets. *Applied Catalysis B: Environmental* **148**: 22–28.

62 Ramnani, P., Saucedo, N.M., and Mulchandani, A. (2016). Carbon nanomaterial-based electrochemical biosensors for label-free sensing of environmental pollutants. *Chemosphere* **143**: 85–98.

63 Viswanathan, S. and Manisankar, P. (2015). Nanomaterials for electrochemical sensing and decontamination of pesticides. *Journal of Nanoscience and Nanotechnology* **15** (9): 6914–6923.

64 Hu, L., Fong, C.C., Zhang, X. et al. (2016). Au nanoparticles decorated $TiO_2$ nanotube arrays as a recyclable sensor for photoenhanced electrochemical detection of bisphenol A. *Environmental Science & Technology* **50** (8): 4430–4438.

65 Liu, Z.G. and Huang, X.J. (2014). Voltammetric determination of inorganic arsenic. *TrAC—Trends in Analytical Chemistry* **60**: 25–35.

66 Yang, M., Jiang, T.J., Wang, Y. et al. (2017). Enhanced electrochemical sensing arsenic(III) with excellent anti-interference using amino-functionalized graphene oxide decorated gold microelectrode: XPS and XANES evidence. *Sensors and Actuators B: Chemical* **245**: 230–237.

67 Yang, M., Chen, X., Liu, J.H., and Huang, X.J. (2016). Enhanced anti-interference on electrochemical detection of arsenite with nanoporous gold in mild condition. *Sensors and Actuators B: Chemical* **234**: 404–411.

68 Xu, W., Zhang, Y.X., Guo, Z. et al. (2012). Conduction performance of individual Cu@C coaxial nanocable connectors. *Small* **8** (1): 53–58.

69 Chen, X., Cui, C.H., Guo, Z. et al. (2011). Unique heterogeneous silver–copper dendrites with a trace amount of uniformly distributed elemental Cu and their enhanced SERS properties. *Small* **7** (7): 858–863.

70 Meng, F.L., Zhang, L., Jia, Y. et al. (2011). Electronic chip based on self-oriented carbon nanotube microelectrode array to enhance the sensitivity of indoor air pollutants capacitive detection. *Sensors and Actuators B: Chemical* **153** (1): 103–109.

71 Zhu, B.J., Yu, X.Y., Jia, Y. et al. (2012). Iron and 1,3,5-benzenetricarboxylic metal–organic coordination polymers prepared by solvothermal method and their application in efficient As(V) removal from aqueous solutions. *The Journal of Physical Chemistry C* **116** (15): 8601–8607.

72 Li, J., Guo, Z., Liu, J.H., and Huang, X.J. (2011). Copper nanowires array: controllable construction and tunable wettability. *The Journal of Physical Chemistry C* **115** (34): 16934–16940.

**73** Liu, Z.G., Chen, X., Jia, Y. et al. (2014). Role of Fe(III) in preventing humic interference during As(III) detection on gold electrode: spectroscopic and voltammetric evidence. *Journal of Hazardous Materials* **267**: 153–160.

**74** Liu, Z.G., Chen, X., Liu, J.H., and Huang, X.J. (2014). Robust electrochemical analysis of As(III) integrating with interference tests: a case study in groundwater. *Journal of Hazardous Materials* **278**: 66–74.

**75** Zhou, C., Yang, M., Li, S.S. et al. (2017). Electrochemically etched gold wire microelectrode for the determination of inorganic arsenic. *Electrochimica Acta* **231**: 238–246.

**76** Yang, G.M., Chen, X., Li, J. et al. (2011). Bubble dynamic templated deposition of three-dimensional palladium nanostructure catalysts: approach to oxygen reduction using macro-, micro-, and nano-architectures on electrode surfaces. *Electrochimica Acta* **56** (19): 6771–6778.

**77** Fu, X.C., Chen, X., Guo, Z. et al. (2010). Three-dimensional gold micro-/nanopore arrays containing 2-mercaptobenzothiazole molecular adapters allow sensitive and selective stripping voltammetric determination of trace mercury(II). *Electrochimica Acta* **56** (1): 463–469.

**78** Xu, W.H., Wang, L., Guo, Z. et al. (2014). Copper nanowires as nanoscale interconnects: their stability, electrical transport, and mechanical properties. *ACS Nano* **9** (1): 241–250.

**79** Huang, X.J., Aldous, L., O'Mahony, A.M. et al. (2010). Toward membrane-free amperometric gas sensors: a microelectrode array approach. *Analytical Chemistry* **82** (12): 5238–5245.

**80** Zhang, X., Peng, Y., Bai, J. et al. (2014). A novel electrochemical sensor based on electropolymerized molecularly imprinted polymer and gold nanomaterials amplification for estradiol detection. *Sensors and Actuators B: Chemical* **200**: 69–75.

**81** Zhu, C., Yang, G., Li, H. et al. (2014). Electrochemical sensors and biosensors based on nanomaterials and nanostructures. *Analytical Chemistry* **87** (1): 230–249.

**82** Abo Hamad, A., AlSaadi, M.A., Hayyan, M. et al. (2016). Ionic liquid-carbon nanomaterial hybrids for electrochemical sensor applications: a review. *Electrochimica Acta* **193**: 321–343.

**83** Chen, A. and Chatterjee, S. (2013). Nanomaterials based electrochemical sensors for biomedical applications. *Chemical Society Reviews* **42** (12): 5425–5438.

**84** Yola, M.L., Eren, T., and Atar, N. (2015). A sensitive molecular imprinted electrochemical sensor based on gold nanoparticles decorated graphene oxide: application to selective determination of tyrosine in milk. *Sensors and Actuators B: Chemical* **210**: 149–157.

**85** Wu, L., Xiong, E., Zhang, X. et al. (2014). Nanomaterials as signal amplification elements in DNA-based electrochemical sensing. *Nano Today* **9** (2): 197–211.

**86** Zhang, Y., Zeng, G.M., Tang, L. et al. (2015). Electrochemical sensor based on electrodeposited graphene-Au modified electrode and nanoAu carrier amplified signal strategy for attomolar mercury detection. *Analytical Chemistry* **87** (2): 989–996.

87 Song, S., Qin, Y., He, Y. et al. (2010). Functional nanoprobes for ultrasensitive detection of biomolecules. *Chemical Society Reviews* **39** (11): 4234–4243.

88 Gatoo, M.A., Naseem, S., Arfat, M.Y. et al. (2014). Physicochemical properties of nanomaterials: implication in associated toxic manifestations. *BioMed Research International* **2014**: 1–8.

89 Guo, Y., Xu, K., Wu, C. et al. (2015). Surface chemical-modification for engineering the intrinsic physical properties of inorganic two-dimensional nanomaterials. *Chemical Society Reviews* **44** (3): 637–646.

90 Peijnenburg, W.J., Baalousha, M., Chen, J. et al. (2015). A review of the properties and processes determining the fate of engineered nanomaterials in the aquatic environment. *Critical Reviews in Environmental Science and Technology* **45** (19): 2084–2134.

91 Smith, S.C. and Rodrigues, D.F. (2015). Carbon-based nanomaterials for removal of chemical and biological contaminants from water: a review of mechanisms and applications. *Carbon* **91**: 122–143.

92 Yang, C.C. and Mai, Y.W. (2014). Thermodynamics at the nanoscale: a new approach to the investigation of unique physicochemical properties of nanomaterials. *Materials Science and Engineering: R: Reports* **79**: 1–40.

93 Yokel, R.A. (2016). Physicochemical properties of engineered nanomaterials that influence their nervous system distribution and effects. *Nanomedicine: Nanotechnology, Biology and Medicine* **12** (7): 2081–2093.

94 Li, X., Liu, W., Sun, L. et al. (2015). Effects of physicochemical properties of nanomaterials on their toxicity. *Journal of Biomedical Materials Research Part A* **103** (7): 2499–2507.

95 Podila, R. and Brown, J.M. (2013). Toxicity of engineered nanomaterials: a physicochemical perspective. *Journal of Biochemical and Molecular Toxicology* **27** (1): 50–55.

96 O'Mahony, A.M. and Wang, J. (2013). Nanomaterial-based electrochemical detection of explosives: a review of recent developments. *Analytical Methods* **5** (17): 4296–4309.

97 Putzbach, W. and Ronkainen, N.J. (2013). Immobilization techniques in the fabrication of nanomaterial-based electrochemical biosensors: a review. *Sensors* **13** (4): 4811–4840.

98 Govindhan, M., Adhikari, B.R., and Chen, A. (2014). Nanomaterials-based electrochemical detection of chemical contaminants. *RSC Advances* **4** (109): 63741–63760.

99 Laborda, F., Bolea, E., Cepriá, G. et al. (2016). Detection, characterization and quantification of inorganic engineered nanomaterials: a review of techniques and methodological approaches for the analysis of complex samples. *Analytica Chimica Acta* **904**: 10–32.

100 Bhakta, S.A., Evans, E., Benavidez, T.E., and Garcia, C.D. (2015). Protein adsorption onto nanomaterials for the development of biosensors and analytical devices: a review. *Analytica Chimica Acta* **872**: 7–25.

101 Biju, V. (2014). Chemical modifications and bioconjugate reactions of nanomaterials for sensing, imaging, drug delivery and therapy. *Chemical Society Reviews* **43** (3): 744–764.

102 Goenka, S., Sant, V., and Sant, S. (2014). Graphene-based nanomaterials for drug delivery and tissue engineering. *Journal of Controlled Release* **173**: 75–88.
103 Yang, D., Hou, Z., Cheng, Z. et al. (2015). Current advances in lanthanide ion ($Ln^{3+}$)-based upconversion nanomaterials for drug delivery. *Chemical Society Reviews* **44** (6): 1416–1448.
104 Yang, Y., Wang, S., Wang, Y. et al. (2014). Advances in self-assembled chitosan nanomaterials for drug delivery. *Biotechnology Advances* **32** (7): 1301–1316.
105 Hu, Q., Katti, P.S., and Gu, Z. (2014). Enzyme-responsive nanomaterials for controlled drug delivery. *Nanoscale* **6** (21): 12273–12286.
106 Nalwa, H.S. (2014). A special issue on reviews in nanomedicine, drug delivery and vaccine development. *Journal of Biomedical Nanotechnology* **10** (9): 1635–1640.
107 Liu, J., Huang, Y., Kumar, A. et al. (2014). pH-sensitive nano-systems for drug delivery in cancer therapy. *Biotechnology Advances* **32** (4): 693–710.
108 Zhang, G., Zeng, X., and Li, P. (2013). Nanomaterials in cancer-therapy drug delivery system. *Journal of Biomedical Nanotechnology* **9** (5): 741–750.
109 Liang, R., Wei, M., Evans, D.G., and Duan, X. (2014). Inorganic nanomaterials for bioimaging, targeted drug delivery and therapeutics. *Chemical Communications* **50** (91): 14071–14081.
110 Meng, Y., Aldous, L., Belding, S.R., and Compton, R.G. (2012). The formal potentials and electrode kinetics of the proton/hydrogen couple in various room temperature ionic liquids. *Chemical Communications* **48** (45): 5572–5574.
111 Shah, B. and Chen, A. (2012). Novel electrochemical approach for the monitoring of biodegradation of phenolic pollutants and determination of enzyme activity. *Electrochemistry Communications* **25**: 79–82.
112 Chatterjee, S. and Chen, A. (2012). Voltammetric detection of the $\alpha$-dicarbonyl compound: methylglyoxal as a flavoring agent in wine and beer. *Analytica Chimica Acta* **751**: 66–70.
113 Chen, A., Rogers, E.I., and Compton, R.G. (2009). Abrasive stripping voltammetry in room temperature ionic liquids. *Electroanalysis* **21** (1): 29–35.
114 Lei, J. and Ju, H. (2012). Signal amplification using functional nanomaterials for biosensing. *Chemical Society Reviews* **41** (6): 2122–2134.