Manuscript Details

Manuscript number	CCR_2020_633_R1
Title	Sensors for the environmental pollutant detection: are we already there?
Article type	Review Article

Abstract

Sensors integrating chemical, biological, materials, electronics sciences, and etc., are considered as a promising technology that can bring great convenience and change to the world. Pollutant detection is one of the significant missions of sensors in the background of serious global environmental problems. As an accurate, selective, simple and inexpensive detection method, sensors are very suitable for environmental detection. Environmental samples, however, are very complex and unexpectedly relative to other ecosystems, which makes sensors a long way to go in practical application. Thus far, sensors have been developed with greater sensitivity, simpler and more efficient detection, better environmental adaptation, and etc. for pollutants detection. This review critically and comprehensively highlights the sensing strategies, and points the way of sensor development in environmental application. The sensitive and efficient, simple and miniaturized, low-cost, in-situ sensor strategies are comparatively reviewed in consideration of sensor development in pollutants detection.

Keywords	Sensors, environmental pollutant, detection, practical application, development

Corresponding Author	Guangming Zeng
Corresponding Author's Institution	College of Environmental Science and Engineering, Hunan University
Order of Authors	Yi Zhang, Yuan Zhu, Zhuotong Zeng, Guangming Zeng, Rong Xiao, Yingrong Wang, Yi Hu, Lin Tang, Feng chonglin
Suggested reviewers	Hou Wang, Jonathan Chou, Pierce Lee, Roman Guan, Hua Zhang

Submission Files Included in this PDF

File Name [File Type]

Cover letter.docx [Cover Letter]

CCR response.docx [Response to Reviewers]

Highlights.docx [Highlights]

Graphical abstract.docx [Graphical Abstract]

CCR Manuscript(1).doc [Manuscript File]

Figures.docx [Figure]

Table.docx [Table]

Declaration of competing interests.docx [Conflict of Interest]

Author statement.docx [Author Statement]

Data in brief.docx [Data in Brief]

To view all the submission files, including those not included in the PDF, click on the manuscript title on your EVISE Homepage, then click 'Download zip file'.

Research Data Related to this Submission

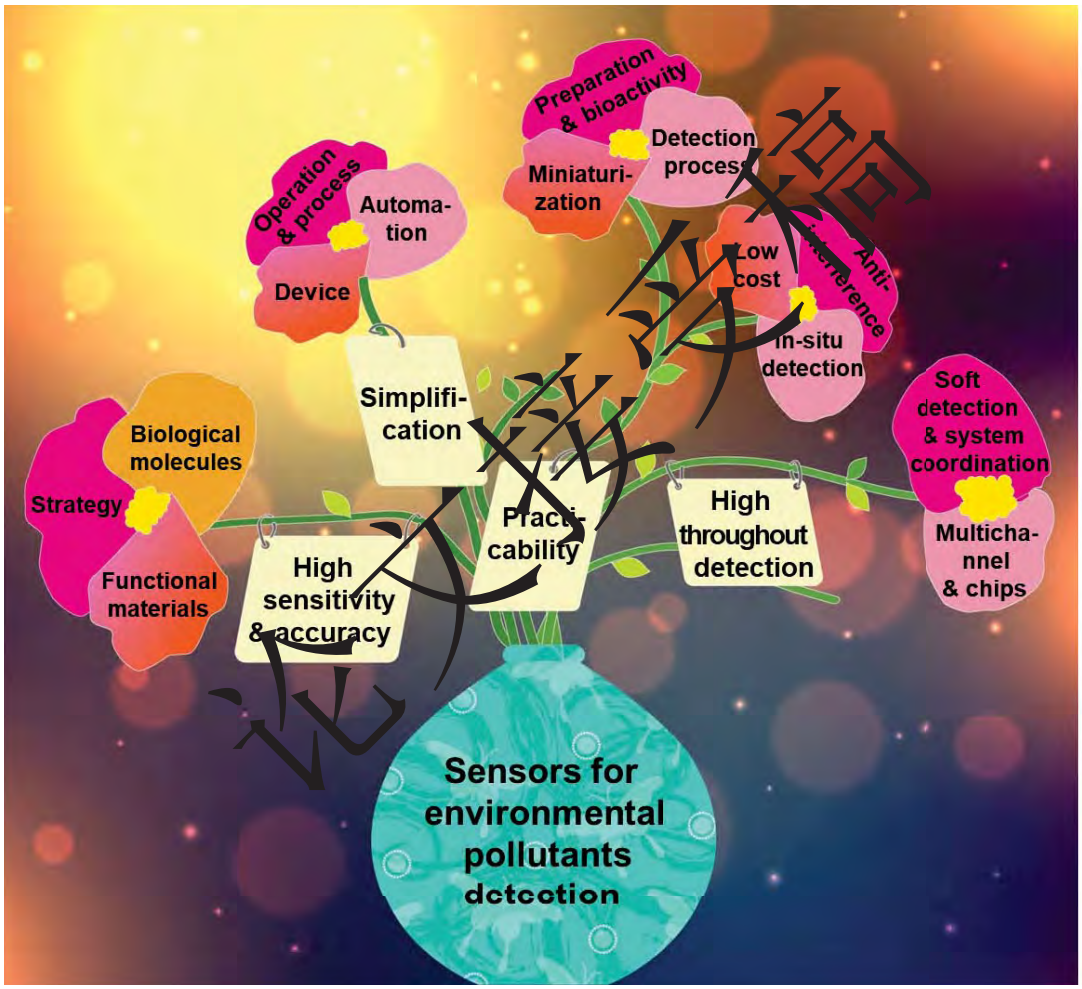
There are no linked research data sets for this submission. The following reason is given:
No data was used for the research described in the article

Highlights:

1. This review summarizes and classifies the novel or interesting sensing strategies for environmental pollutants in recent years for better understanding of environmental sensors in view of the characteristics of environmental detection.
2. The review provides an insight into the remaining challenges and future perspectives in sensors for practical application.

Graphical abstract

It is the first time that sensors are systematically overviewed in environmental pollutants detection and the gaps between laboratory researches and practical applications are pointed out in this review. The recent applications of various sensors in the environmental detection have been summarized and highlighted.



Sensors for the environmental pollutant detection: are we already there?

Yi Zhang[‡, a, b, c], Yuan Zhu[‡, a, b], Zhuotong Zeng [‡, d], Guangming Zeng[*, a, b], Rong Xiao[*, d], Yingrong Wang[a, b], Yi Hu[a, b], Lin Tang[*, a, b] and Chongling Feng[e]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, China

[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, China

[c] Department of Chemistry, University of Science and Technology of China Hefei, 230026, China

[d] Xiangya Medical College, South Central University, Changsha 410013, China

[e] Research Center of Environmental Science and Engineering, Center South University of Forestry and Technology, Changsha, 410004, China

∗ Corresponding: Tel: +86 0731 88822754. Fax: +86 0731 88823701. E-mail: zgming@hnu.edu.cn (G.M. Zeng), xiaorong65@csu.edu.cn (R. Xiao), tanglin@hnu.edu.cn (L. Tang)

‡ These authors contributed equally to this work

Contents

ABSTRACT: Sensors integrating chemical, biological, materials, electronics sciences, and etc., are considered as a promising technology that can bring great convenience and change to the world. Pollutant detection is one of the significant missions of sensors in the background of serious global environmental problems. As an accurate, selective, simple and inexpensive detection method, sensors are very suitable for environmental detection. Environmental samples, however, are very complex and unexpectedly relative to other ecosystems, which makes sensors a long way to go in practical application. Thus far, sensors have been developed with greater sensitivity, simpler and more efficient detection, better environmental adaptation, and etc. for pollutants detection. This review critically and comprehensively highlights the sensing strategies, and points the way of sensor development in environmental application. The sensitive and efficient, simple and miniaturized, low-cost, in-situ sensor strategies are comparatively reviewed in consideration of sensor development in pollutants detection.

Keywords: Sensors, environmental pollutant, detection, practical application, development

1. Introduction

Environmental pollution is one of primarily global problems affecting human sustainable development. Environmental pollutant detection is an indispensable basic link and requisite for environmental pollution control. Judging from the development trend of detection technology and demand, an ideal detection method should be highly sensitive and accurate, simple and efficient, flexible and practical. Many efforts have been tried to use various analysis methods, e.g. spectrophotometry, high performance liquid chromatography (HPLC), gas chromatography (GC), mass spectrometry (MS) etc. in environmental pollutant detection. Spectrophotometry is simple but the detection accuracy is slightly deficient. HPLC, GC, and MS have good detection accuracy, but they are relatively cumbersome in operation and are not suitable for in-situ detection [1,2]. Alternatively, sensor seems a promising method owing to its inherent properties, e.g. sensitivity, selectivity, simple operation, and in-situ detection [3,4]. Sensor, as a sensitive and fast detection tool with specific response, has sparked a great interest in the development of various sensing strategies for the goal of real-time online in-situ detection, which involves chemical, biological, materials, electronics and other cross-disciplinary sciences. Over the past few decades, sensing technology has been evolving. From chemical sensor to biosensor, and from single detector to chip technique and high-throughput detection, electrochemical sensors, fluorescent sensors, colorimetric method, surface plasmon resonance (SPR) sensors, field-effect transistor (FET) sensors etc. successively emerged [5,6]. The labels of sensitivity, simple operation, low cost, miniaturization and portability etc., are

promoting people's understanding of sensors for environmental pollutant detection.

Environmental pollutant detection by contrast with the detection in medical, food safety etc., has to face to more changeable environments, more complex and unpredictable composition [7,8]. Therefore, sensor techniques must rise up to the challenge in developing a stable, reliable strategy with certain environmental resistance for qualitative and quantitative analysis with high sensitivity and selectivity. Moreover, cost is another noteworthy concern that can decisively affect sensor application due to the wide, huge implementation scale and volume in environmental monitoring. A practical sensing strategy with reasonable and low cost matches the needs of environmental pollutant detection to promote its application. The sensitivity and accuracy are the ambition for sensor development and environmental pollutants sensors are no exception, in order to meeting a variety of low/trace requirements and environmental safety warning needs. Additionally, the strengthening in automation, miniaturization and so on, and the development in high throughput detection conform to the trend of future sensing. That is to say, the development of sensors in environmental pollutant detections should be comprehensively examined from the aspects of sensor detection performance, efficiency, simplification and practicability of sensor technology.

Indeed, as a promising and efficient detection method, many researchers have made great efforts to develop various sensing strategies directly or indirectly related to environmental analysis. However, so far as we know, it has never

systematically overviewed the sensing methods in environmental pollutant detection, which seems not clear-cut of the research direction, inevitably. Hence, the novel or interesting sensing strategies in recent years were collected and classified for a review, revolving around the practical application in environmental pollutant detection. According to the characteristics of practicality, this review consists of accuracy (especially considering the tremendous advances to the sensor brought by nanotechnology, detection strategy, etc.), simplification (involving simper device, simper operation and process, automation), practicability (involving miniaturization, efficient detection process, anti-interference performance, etc.), high throughput detection (which links to detection efficiency, involving multichannel detection and chips, soft sensing and systems coordination), and outlook. In this case, the aim of this review is showing a cognitive system and overall framework to facilitate the understanding how to apply sensing strategies in environmental monitoring and their trends, which is beneficial to push the sensing method out of laboratory and into practical application in environmental monitoring as an excellent

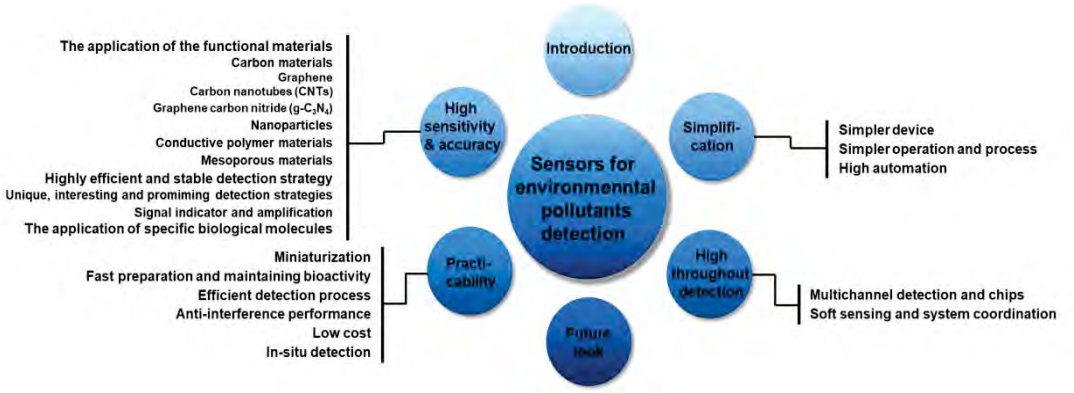


Figure 1. The structure of the review.

detection method (Figure 1).

2. High sensitive and accurate environmental sensors

Sensors developed with functional nanomaterials, highly sensitive efficiency, stable detecting strategies and specific biological molecules that can greatly enhance the sensitivity and accuracy of sensors in environment pollutants detection are enumerated.

2.1 The application of functional materials in environmental sensors

The rapid progress of material technique in recent years has a great impact on the sensors, which made a continuous improvement of sensor performance for environment pollutants monitoring. With the application of new materials, incredible changes have befallen the detectability of sensors, i.e. several orders of magnitude improvements were obtained in sensitivity and accuracy. Some new materials, for example, carbon materials (e.g. graphene [9,10], carbon nanotubes [11,12]), Graphitic carbon nitride [13,14], nano metals and their oxide materials [15,16], conductive polymer materials [17,18] and mesoporous materials [19,20] have been extensively used in pollutant monitoring sensors with their fantastic inherent characteristics.

2.1.1 Carbon materials

The application principles of carbon materials for sensor developments are basically the same. And therefore, the typical and frequently used carbon materials (e.g. grapheme, carbon nanotubes (CNTs) and graphitic carbon nitride (g-C_3N_4) are reviewed in this section.

2.1.1.1 Graphene

As a high electron mobility (> 15000 $cm^2/V·s$) and low electrical resistivity (~ 1 Ω·m), one-atom-thick, two-dimensional sp^2-hybridized carbon material, graphene is known to significantly improve electrical conductivity of electronic components. While, it is worth mentioning that graphene itself possesses inertness to reaction, which weakens the applicability of graphene in sensor fabrication. Therefore, the graphene/reduced graphene oxide (rGO) is functionalized to expand its applicability and applied in many sensing strategies with high sensitivity. Metal nanoparticle (e.g. gold [21], bismuth [22,23]), carbon nanotube [24], mesoporous material [25], electrical conductivity of polymers (e.g. polypyrrole (PPy) [26], polyaniline (PANI) [27] and polystyrene [28]) were used to achieve the functionalization. Generally, the graphene/rGO introduced in various sensing strategies can be summarized four modes including: (i) modifying the functionalized graphene/rGO onto an electrode for direct detection [22,23,29]; (ii) further assembling probe for detection after the functionalized graphene/rGO attaching on an electrode; (iii) modifying the non-functionalized graphene/rGO onto an electrode for direct detection [30]; (iv) further assembling probe for detection after the non-functionalized graphene/rGO attaching on an electrode, e.g. gold nanoparticles (AuNPs) were directly further electrodeposited onto the rGO electrodeposited GCE to attach the DNA probes for ultrasensitive detection of Hg^{2+} with a detection limit of 1.0×10^{-21} M [31]. Although significantly enhanced the sensitivity, the strategies of the above former two modes were involved in cumbersome fabrication. And the latter two, in comparison, simplified those tedious procedures but had a little defective in evenness of the

electrodeposited lays on the substrates. In general, most strategies have subjected to certain barriers to go out of the laboratory because of the relative cumbersome modifying and immobilizing process of graphene/rGO. A further challenge using the materials in field of environmental monitoring is the difficulty in finding a simple route to easily obtain the graphene/rGO functionalized sensing units, which determines the flexibility and operability of the sensing strategies of choice for application.

2.1.1.2 CNTs

CNTs, one-dimensional nanomaterials [32,33], are another variety of popular and important carbon material utilized in sensing strategies to strengthen the functionality of sensing components [34,35] for environment pollutants monitoring. Multi-wall carbon nanotubes (MWCNTs) considered excellent inherent conductivity and huge specific surface area [36,37], were used to develop a tyrosinase modified MWCNTs-CoPc-silk fibroin film sensor for bisphenol A (BPA) detection with a detection limit of 3.0×10^{-8} M [38]. According to the number of layers of graphene sheet, the hollow cylindrical tubes with great aspect ratios (length/diameter) are classified into: single-wall carbon nanotubes (SWCNTs) and MWCNTs. MWCNTs is thicker and longer than SWCNTs, e.g. the length of MWCNTs andSWCNTs are in the ranges from 0.3 to 500 mm and 0.4 to 50 mm, respectively. MWCNTs possess better dispersibility than SWCNTs after functionlization. However, the pore volume and electric capacity of SWCNTs were higher than those of MWCNTs [39,40]. All the same, considering their substantially similar properties and contributions in sensors, we did not

deliberately classify the two differences between them and ignored herein [41]. Similarly to graphene, CNTs generally need to have a functionalization (e.g. carboxylation, amination) before further application. For example, thiophenol functionalized SWCNTs were self-assembled on the gold electrode surface to reduce interfacial capacitance of basal electrode for directly trace stripping analysis of mercury in various environmental samples [17]. Certainly, CNTs can also be directly used to fabricate sensing unit by deposition without functional group modification, e.g. a nanocoax sensor for volatile organic chemicals (VOCs) detection based on CNTs [42]. While as an inert material, CNTs have good compatibility with other substances, especially biological molecular materials such as proteins and DNAs, which were combined to CNTs surfaces owing to hydrophobic interactions [43], amino-affinity [44] and π–π stacking interactions [45], and were modified on the electrodes for high sensitive sensors construction. Moreover, the twisted CNTs also could provide spatial reaction sites to enhance reaction rate [46,47]. Not only direct improvement of the performance of electrodes, CNTs are also easily to upgrade by combining with other materials. SWCNTs were filled into the channels of the mesoporous silica to improve the electroconductivity of due to nano size and excellent inherent conductivity [48]. This strategy could be extended for high sensitive monitoring of environment pollutants. More attentions have been paid on their flexible applications in electrode modification, while CNTs also were appeared in expression of signal in sensing system. The lightweight [49] and large specific surface CNTs were used as the carriers of the enzyme linked signal amplification tools of the sensing strategies [50-

52]. Additionally, SWCNTs were designed as a fluorescence quencher in a "switch-on" DNA sensing strategy of Hg^{2+} detection [53]. CNTs have drawn a growing interest due to flexible and diverse applicability in sensing strategies. Nevertheless, it is noteworthy that their disorder distribution on the attachments, which leads to a certain of difference of reproduce in the micro-interface.

2.1.1.3 graphitic carbon nitride (g-C_3N_4)

G-C_3N_4, as the metal-free and graphite-like polymeric carbon nitride, has attracted an explosion of interest in recent years owing to the unique electronic structures and optical properties, low cost, high stability. It has wide application in sensors. The easily prepared bulk g-C_3N_4 possessed sluggish charge transfer and poor water-dispersibility was employed for electrochemical sensor fabrication and exhibited poor Hg^{2+} detection performance [54]. Some shortcomings should be overcome before its practical sensors. As a consequence, g-C_3N_4 nanosheets were synthesized for improving the surface area and decreasing the interactions among the layers of g-C_3N_4. Ma *et al* [55] prepared the highly dispersed ultrathin g-C_3N_4 nanosheets with sonication-exfoliation under an acid condition for sensor fabrication. The surface area of the 2D g-C_3N_4 nanosheets increased 305 m^2/g, comparing with the bulk g-C_3N_4 surface area of 9 m^2/g. The edges of the ultrathin g-C_3N_4 nanosheets exposed more -NH_2 after ultrasonic treatment for better immobilization. Further, in order to enhance the electron transfer for improving the performance of sensor application, doping (e.g. B [56], C [57], P [58] etc.) was a widely used method to modulate the electronic structure of g-C_3N_4. Sulfur-doped g-C_3N_4 was modified on the fluorine-doped tin

oxide electrode showed a low hydrazine detection limit (0.06 μM) [59]. In addition, g-C_3N_4 compositing with nanomaterials is a common method for the physical and chemical properties improvements. Metal nanoparticles combined with g-C_3N_4 could form metal-semiconductor heterojunctions and facilitate electron transfer between them. Chen *et al* [60] constructed the electrochemiluminescence immunosensor based on Au NPs and g-C_3N_4 for carcinoembryonic antigen detection. The hybrid between Au NPs and g-C_3N_4 effectively solved the passivation problem of g-C_3N_4 in electrochemiluminescence. The 2D MoS_2 composited with g-C_3N_4 could break the high electron-hole recombination efficiency barrier in photoelectrochemical assay owing to their ideally matched energy levels [61]. The nanocomposite was applied for photoelectrochemical biosensor development for 5-hydroxymethylcytosine with a low detection limit of 2.6 pM. The application of g-C_3N_4 is restricted in electrochemical sensors due to the inherently poor electrical conductivity. Nonetheless, benefiting from the luminescent, photoelectrochemical and catalytic properties, g-C_3N_4 becomes the excellent candidate for sensors based on photoelectric conversion and catalysis.

2.1.2 Nanoparticles

Given that the nanoparticle is one of the most common nanostructure and numerous applications of various nanoparticles in sensing strategies, herein only the major characteristics were summarized in applications. Nano size attributing to large surface-to-volume ratio, high surface reaction activity, and strong adsorption ability, is the most commonly feature considered in sensing strategy, which is an effective

way to improve detection performance of sensing strategies and never stops evolving. Get the truth from little things. Some typical and widely used nanoparticles are introduced and reviewed in the section. In the first place, AuNPs can be described as an all-round player for sensor constructions, which have excellent biocompatibility to biomolecules, stable and simple immobilization/assembly via the coupling between gold and sulfydryl/amino-group, and usable optical properties due to optical transition or SPR, as well as strong signal transmission and amplification capability. AuNPs provide a great multi-functionalization platform for a large amount of biological and organic ligands to selectively combine and detect trace analytes. AuNPs combined with nanomaterials in various sensing strategies, e.g. CNTs [46] electrodeposited graphene [31], realized heavy metals detection (Pb^{2+} (femtomolar level), Hg^{2+} (attomolar level)). From the point of view of optical properties, AuNPs were directly used in colorimetric or SPR strategies for specific detection of target contaminants. In colorimetric strategies, the color change between red and blue is related to the manner of AuNPs/AuNPs-biomolecular complex in dispersion or agglomeration state in solution. According to this feature, AuNPs were designed in various sensing strategies to detect pollutants such as Hg^{2+}, Pb^{2+}, Cr^{3+}, phenols, dopamine, and so on [62]. In addition to the sensing strategies developed in conjunction with other specific response systems, AuNPs also can use to directly construct an arsenic sensor based on the minimum adsorption bond energy between AuNP and As^{3+} [63]. Visible light absorbed by AuNPs in localized SPR were used to fabricate a mercuric sensor because the absorbance change was associated with the combined mercury [64].

AuNPs are suitable for sensing strategy, besides the above, the applications related to strengthening the signal expression will be explained in a special section later.

Besides nano size effect, there is another interesting and unique property, i.e. intrinsic paramagnetism in a certain kind of magnetic nanoparticle containing iron, cobalt, nickel, and lanthanide [65,66]. Accordingly, an attractive, simple and distinctive approach of electrode modification via paramagnetism appeared, which can reduce extra cumbersome physical coupling and chemical modification. A carbon paste electrode containing an internal permanent magnet was prepared to attach the magnetic laccase-core-shell (Fe_3O_4-SiO_2) nanoparticles for rapid detection of hydroquinone in compost extracts [67]. This sensor is easily fabricated and regenerated due to magnetic force fixing. Another very interesting application is that a paramagnetic relaxation based sensor for selective dopamine detection according to its influence on transverse relaxation time of water protons in NMR [68]. Anyhow, magnetism is a special tool that can have a field day in sensing strategies and bring surprises.

Moreover, a kind of nanoparticle, quantum dots (QDs), as important fluorescent probes for biosensing also has received considerable attention recently. QDs are ordinarily some species of metal nanoparticles of IIB-VIA or IIIA-VA compound semiconductors e.g. CdSe, ZnSe, CdTe, InP, etc., as well as some non-toxic nanoparticles such as carbon dots (CDs). Compared to commonly organic dyes and fluorescent proteins, QDs possess particularly optical and electronic properties including size-tunable light emission, resistance to photobleaching, superior signal

brightness and simultaneous excitation of multiple fluorescence colors. Owing to that the luminescence performances of QDs are liable to be adjusted though surface modification with some certain materials to make their electrons and holes combination efficiency changes, it is flexible to design QDs into various sensing strategies for gas, e.g. NO_2, NH_3 [69]. Additionally, graphene oxide QD (GOQD) was also used for photoluminescent detection of trace lead [70]. As a result, QDs labeled DNA [71], protein [72] and immunity substance [73] were used to track and detect analyte(s) in simple, rapid and sensitive biosensors. According to the trend of the photosignal, the sensing strategies based on QDs can be divided into two categories:

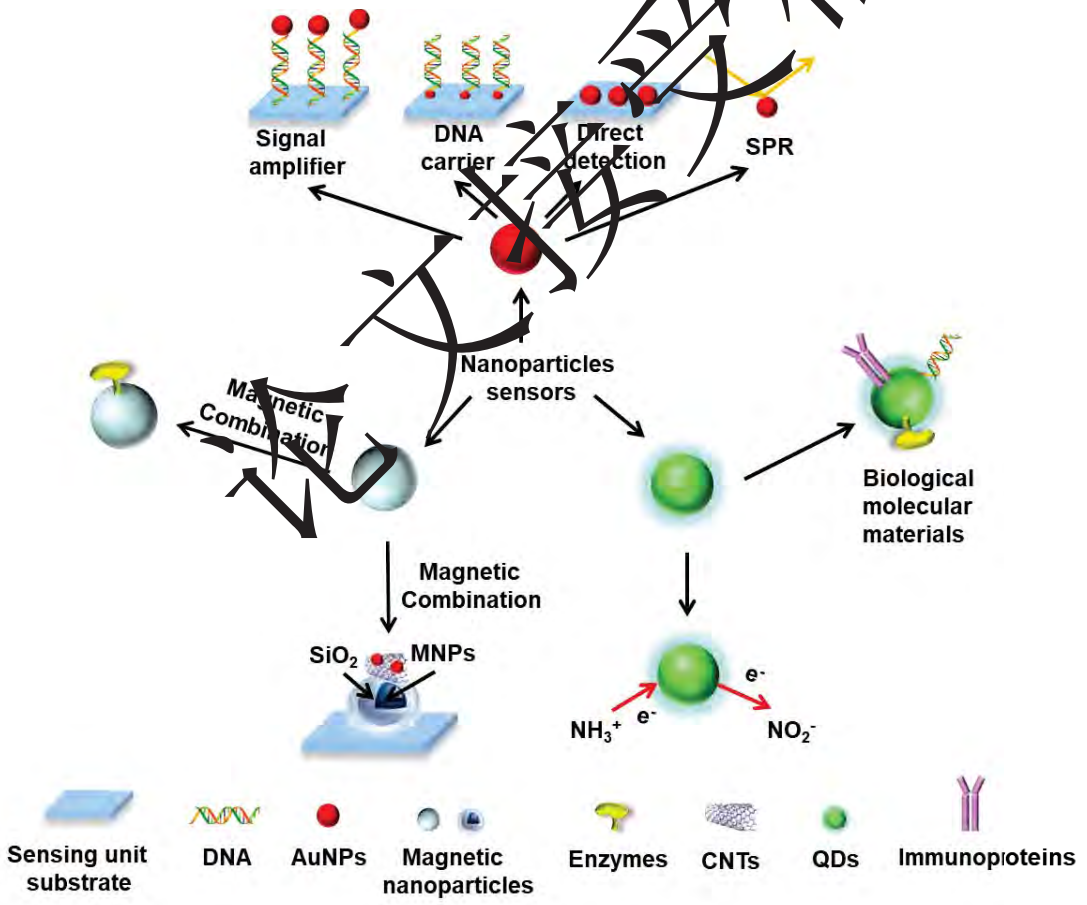


Figure 2. Various sensing strategies based on nanoparticles involving AuNPs, QDs and magnetic nanoparticles as signal amplifier, biological molecular materials carrier, substrate of sensing unit.

switching “turn-on” and “turn-off”. Indeed, CdSe-ZnS core-shell particles always are popular QDs. They were used to respectively construct a switching “turn-on” strategy [74] and a switching “turn-off” strategy [75] due to the corresponding configuration change of sensing system for Hg^{2+} detection. The sensing strategies are reliable and flexible,but there is still a misgiving to many researchers due to the possible toxicity from QDs. Non-toxic CDs, nevertheless, dispel the misgiving and have more and more fans of late. CDs combined with GO were also employed to detect Hg^{2+} [76]. It is foreseeable that CDs would be a dazzling light to illuminate the sensing field in the near future. The above research works are summarized in Figure 2.

2.1.3 Conductive polymer materials

Conductive film forming molecules materials, e.g. polythiophene (PTh), PPy and PANI etc., are electrically conductive organic polymers, and have been extensively utilized in sensing strategies due to their processability, inherent electronic, optical, and mechanical transduction nanometer-scale conducting polymer materials for sensitivity enhancement, and other advantageous features including their small dimensions, high surface to volume ratio, and signal amplification for sensing strategies.

The most notable feature of conducting polymer materials to sensing strategies is the optimization capabilities of electron-conductivity of sensing units. Owing to the advantages of high surface to volume ratio and rapid electron transfer, multidimensional FeOOH nanoneedle-decorated hybrid PPy was used in a nerve gas agent detection to enhance sensitivity (0.1 ppb) [77]. Furthermore, conductive polymer materials possess superior catalytic capability, e.g. iron oxide-reduced GO

incorporating PANI nanofiber was modified onto GCE surface to detect hydroquinone with a detection limit of 3.0×10^{-8} M [78]. In addition, PANI also is the excellent material that can get along well with biomoluculers and enhance electronic signals. In an indirectly bleomycin (BLM) SPR biosensor, the electrical signal response changes reflected the existence of BLM by the induced PANI, taking advantages of the excellent electrical properties and enhancing electrical signals of PANI [79]. Moreover, cationic water-soluble PTh can form interpolyelectrolyte complexes by adopting different conformations DNA, e.g. ssDNA, dsDNA and other conformations. Given that on an optical strategy based on specific ssDNA functionalized PTh for Pb^{2+} detection with solution color changing from red to yellow, the micromolar

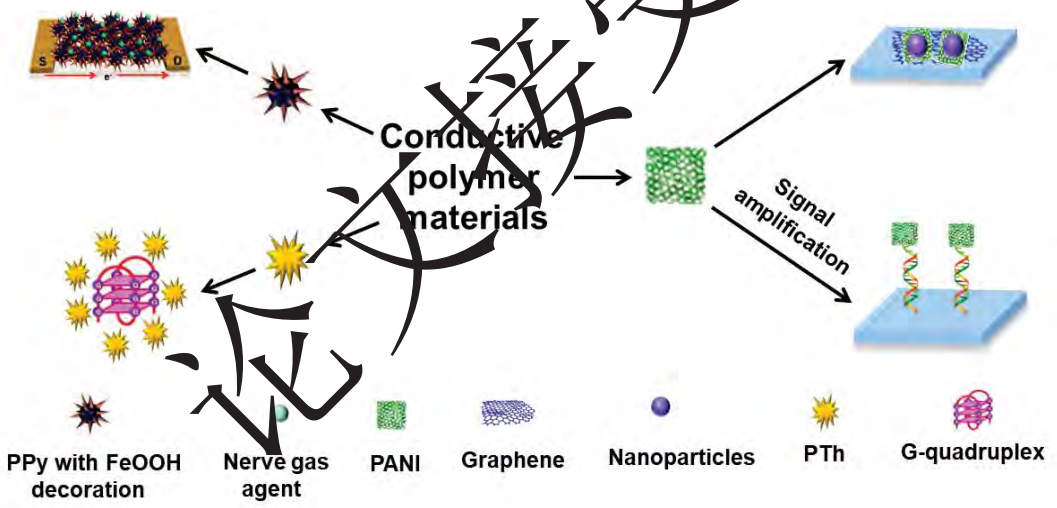


Figure 3. Applications of conductive polymer materials, e.g. PPy, PANI and PTh in sensing strategies. Electrode modified with PPy-COOH for nerve gas detection (Aadapted from ref. 77, copyright (2013) American Chemical Society); electrode was sequentially modified with grapheme, PANI and nanoparticles; PANI as signal indicator immobilized on DNAs; PTh immobilized on G-quardruplex could form interpolyelectrolyte complexes; Thereinto, strategy of different DNA comformotions functionalization with PTh.

concentrations Pb^{2+} were identified in 5 min even with the naked eye [80]. The above research works are summarized in Figure 3.

2.1.4 Mesoporous materials

Mesoporous material is defined as a material containing pores with diameters between 2 and 50 nm. Mesoporous materials fabricated from a template route have received worldwide interests due to their pore sizes and ordered porous structures, which endues the material some unique properties and bring some delightful results with nano-size effect or quantum size effect. The materials possess high surface areas, tunable pore sizes, special optical features, and vast framework compositions. Those properties are beneficial not only to implement the functionalization of various chemical groups on the materials surface, but also to absorb macromolecules, chemical molecules, and assemble nanoscale guest materials in their uniform and interpenetrating tunnels. Owing to the above advantages, ordered mesoporous materials have been one of the most popular materials in sensing.

Mesoporous carbon is widely used, especially in electrochemical sensing strategies owing to the high specific surface area and electrical conductivity (Figure 4). The 3D structure of mesoporous carbon was utilized to enhance the electrochemical response by improving the structure of the modified electrodes and facilitating charge transfer processes on the surface of modified electrode for a metolcarb sensor [81]. Furthermore, considering combination of properties, composite materials are attractive. Mesoporous carbon nitride (MCN) is one of favored composite materials because of its biocompatibility and conductivity. A catechol and

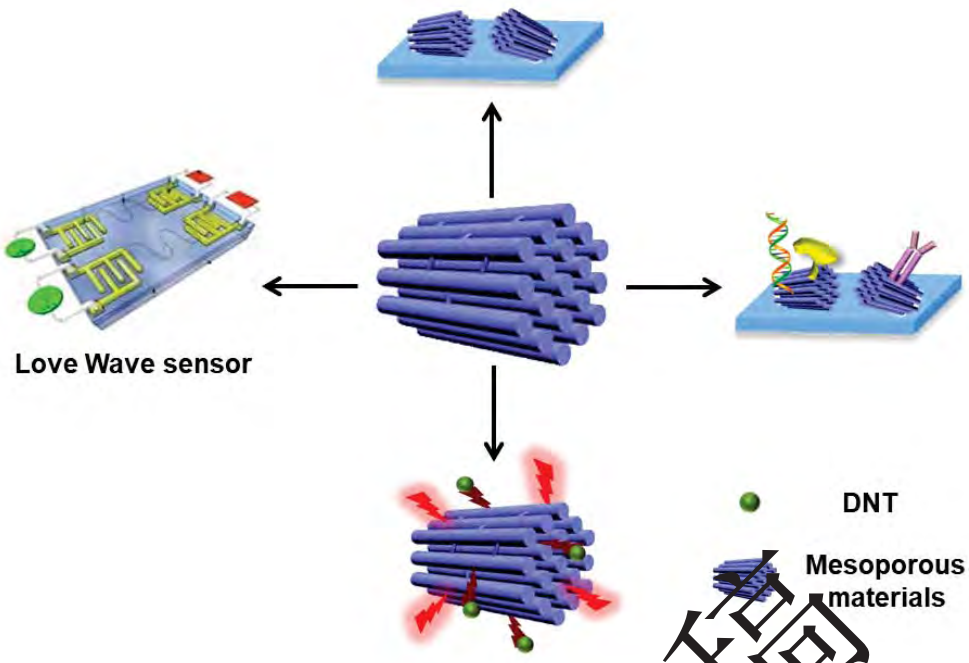


Figure 4. Mesoporous materials can be modified on the substrate for detection, biological molecular materials (e.g. DNAs, enzymes and immunoproteins) and fluorophores can combine on mesoporous materials for sensitive and specific detections, and TiO_2 mesoporous-coated Love Wave sensor (Adapted from ref. 85, copyright (2014) Elsevier). Water samples flow into the pipes and go through the biofilm, mesoporous TiO_2 and SiO_2 composite layer.

phenol sensor based on a tyrosinase-absorbed-MCN modified electrode could selectively and sensitively detect with the detection limit of 10.24 nM and 15.00 nM, respectively [82]. A DNA sensor fabricated using MCN as a substrate for manganese peroxidase genes detection with a detection limit of 8.0×10^{-18} M [83]. While, mesoporous materials are ideal carriers to small organic compounds owing to excellent chemical, thermal and mechanical stability. Vu *et al* [84] designed fluorescent films consisted of surfactant-templated mesoporous silica and a phenyl-substituted pyrene fluorophore to detect 2, 4-dinitrotoluene (DNT). Additionally, in

an acoustic sensing strategy based on Love wave for cadmium detection. Mesoporous TiO_2 coated on the SiO_2 could protect and decrease corrosion and improve the stability and lifetime of biofilm in the love wave microtubes, the polyelectrolyte smoothly go through the pores of mesoporous TiO_2 [85].

2.2 Highly efficient and stable detection strategy in environmental sensors

Detection process and signal expression are the two principal factors to detection strategy. From feasibility and accuracy point of view, an efficient and stable detection strategy is a guarantee of the fabrication of sensing system and the implementation of detecting process to avoid false positive response, as well as an effective way to enhance sensitivity and accuracy of sensing system. Despite the fact that the enormous sensing strategies are sound considering their construction foundations of a certain specific reactions, a few interesting and representative works are introduced herein.

2.2.1 Novel detection strategies

The analytes are quantitatively detected via the response signal changes originated from the sensing units and samples in sensing systems. No matter electrochemical, fluorescence, colorimetric, or other sensing strategies, they generally can be classified into two types: “turn-on” and “turn-off” modes according to the response signal changes, which attributed to the strategy of sensing construction in sensing unit and reaction system. The signal response intensity that is positive correlation to analyte is a “turn-on” mode, which is carried out in most sensing strategies, e.g. the classical glucose sensor. Contrarily, it is a “turn-off” mode, which usually exists in the

suppression sensing strategies or competitive sensing strategies, e.g. a competitive immunosensor or an enzyme sensor to inhibitors. Indeed, no matter "turn-on" or "turn-off" mode, the purpose is to obtain a high sensitivity and reliable sensing strategy. Therefore, to bring some inspiration, several representative and attractive strategies were enumerated here (Figure 5).

Currently, unless the introduction of some new and interesting design, a strategy

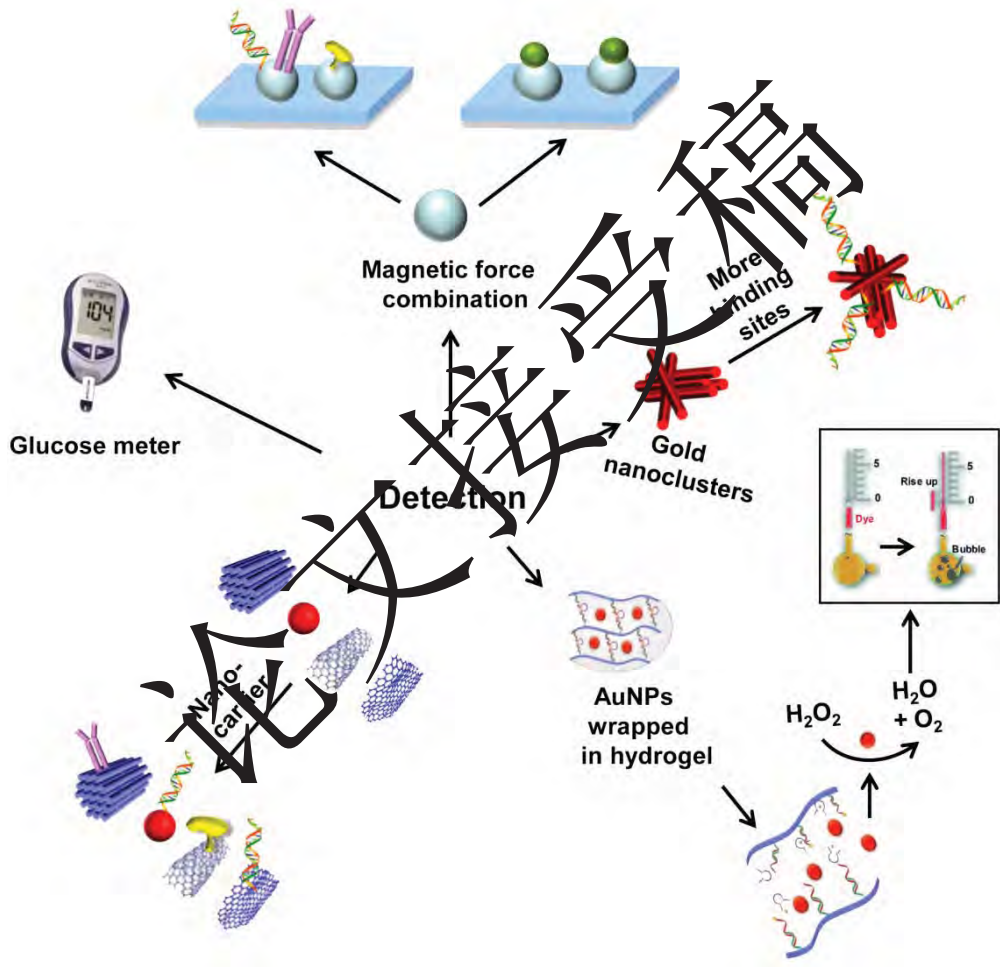


Figure 5. Different detection strategies for sensors, included strategy of magnetic force combination, expanding response area by gold nanoclusters, AuNPs wrapped in hydrogel, nanomaterials nanocarriers for biomolecular materials loadinge, and application strategy of glucose meter in pollutant detection. Adapted from ref. 93, copyright (2016) Wiley.

That a biomolecule e.g. enzyme, immunoglobulin and DNA etc. or a functional chemical substance is modified on a sensing unit with the help of nanomaterials or other materials to improve the sensitivity for a specific detection has been turned into a routine way. Undoubtedly, magnetism, as mentioned above, is an interesting property, which can make an easier assembly of a sensor by virtue of the paramagnetic materials, and reduce the energy barrier producing from too many modifiers, such as L-cysteine, nafion, chitosan and ferrocene, etc. The paramagnetic nanomaterials loading laccase could directly coat on carbon paste electrode via magnetic force for hydroquinone detection [67]. Similarly, a remarkable three-dimensional nano-configuration also could spark an amazing result owing to providing a spatial reaction field to enhance the reaction efficiency, because it provided more binding sites in electrode surface microenvironment than other dimensions, and directly promoted sensing sensitivity, e.g. 3D gold nanoclusters were electrodeposited on electrode to assemble mercury-specific oligonucleotides for trace mercury detection [86]. In addition, a triboelectric nanogeneratorsensor based on the different triboelectric polarity of AuNPs covered by polydimethylsiloxane and 3-mercaptopropionic acid was fabricated for Hg^{2+} detection [87]. As for colorimetric strategies, the working principle based on the color difference of different distribution of AuNPs or other colorimetric indicators is frequently used at present. It is a simple and intuitive qualitative detection method but limited to semi-quantitation. However, in recent years, the visual distance-based detection technology based on volumetric bar chart chip (V-Chip) is expected to solve the problem of quantitative detection by

translating the target recognition to visual length signal. Au@PtNPs or AuNPs wrapped in a hydrogel would be released in the presence of specific targets, e.g. Pb^{2+}, UO_2^{2+}, and cocaine etc. for catalyzing H_2O_2 to generate O_2, which pushed the ink bar moving in the V-Chip. The moving distance of ink bar visually quantified the target concentration [88-90]. Moreover, carrier nanomaterials e.g. CNTs, AuNPs loaded a large number of signal molecules such as enzyme, electrical activity indicator are applied in the conventional sensing strategies to significantly strengthen the expression of the response signal, which would further introduce in the following section.

Besides that, some nanomaterial-independent strategies have been reported, such as a strategy based on aldehyde functionalization universally rapid captured amino group-containing substance in environment sample via Schiff base reaction, followed by a specific identification of target pollutant using its antibody labeled a signal indicator [91]. Additionally, the simple strategy for heavy metal recognition based on the change of DNA conformation between ssDNA and dsDNA is attractive. The current response of Hg^{2+} reflected the structure changes between ssDNA and dsDNA, and the corresponding distance between ferrocene anchored on T-rich ssDNAs and electrode surface [92]. Nevertheless, it is bright to put new applications into old methods. When a conventional glucose meter for blood glucose testing is linked to the detection of other substances with a general method, it becomes an ingenious transform and a direct use of more than 30 years of scientific research and engineering to

glucose meter. The functional DNAs for heavy metal or organic compound were modified with an invertase. In the presence of the targets, the DNA fragment containing invertase would separate from the primary DNAs system to hydrolyze starch into glucose for quantitative glucose meter analysis [93-96]. The multifarious strategies are constantly evolving based on the previous works and emerging new technologies and ideas to match a higher detection standard. However, complexity of environmental samples, cost-effectiveness, practicability, and so on still need to concern and to find a smooth road to be commercialized and widely used.

2.2.2 Signal indicator and amplification

The choice of signal indicator and the related amplification strategy not only shows the sensor type, but also affects the response signals. The signal indicator can be generally divided into two categories: optical and electrochemical indicator. The former usually contains fluorescent indicator such as fluorescein isothiocyanate (FITC) [97], quantum dots [98] etc. or colorimetric indicator such as AuNP solution [99], a prussian blue colored starch-iodine solution [100] etc. And the latter involves some enzymes e.g. glucose oxidase (GOD) [101], HRP [83], acetylcholinesterase (AChE) [102], laccase [67] etc. and electroactive species, e.g. ferrocene [103], potassium ferricyanide [104], methylene blue (MB) [31], gentian violet [105], thionine [106] and toluidine blue [107] etc (Figure 6). Signal amplification strategy can improve the detection sensitivity to a certain extend. It is reported *ca.* 30% detection efficiency was improved with the signal amplification by comparing the electrochemical sensing

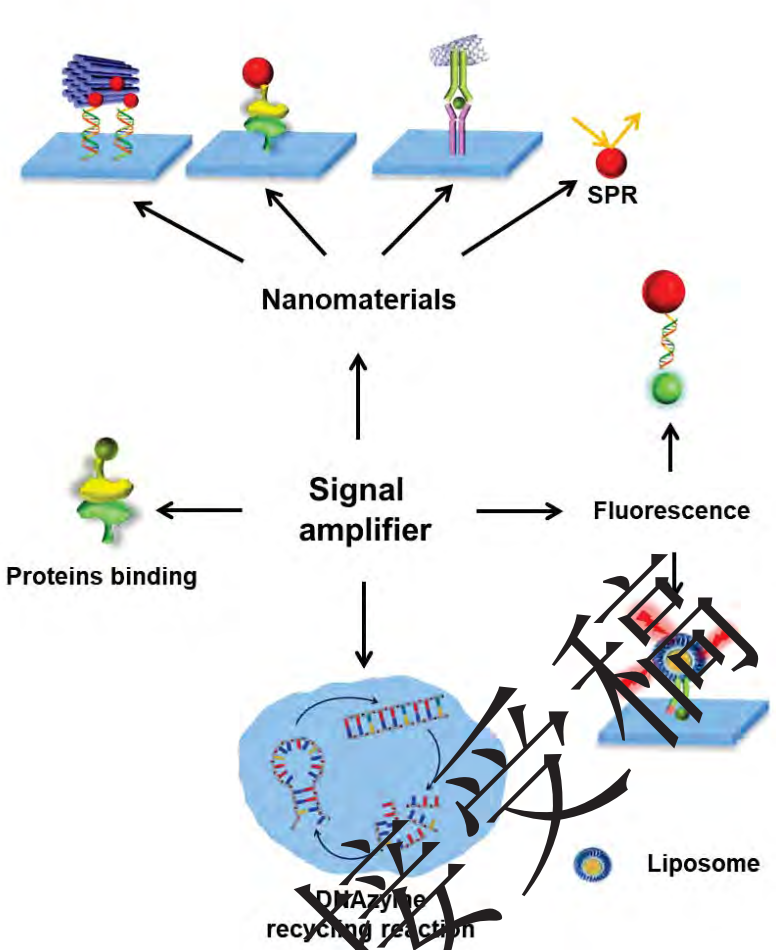


Figure 6. Various signal amplifier strategies involving different actions of nanomaterials, fluorescence enhancement (QD enhancement, liposome amplification), DNA recycling reaction, and proteins binding (various activities and antibodies).

strategy strategies with/without signal amplification using four kinds of functional electrodes [108]. Using nano-carrier is a vital strategy of signal amplification in sensors. A kind of excellent signal molecule carrier, nano-carbon carriers e.g. the aforementioned CNTs carriers [51,52] and ordered mesoporous carbon [109] emerged in some sensing design with significant enhancement in detection accuracy by strengthening the signal response. Another efficient carrier, AuNPs, not only load

more signal labelled QDs [110], DNAs [111] and MB labelled ssDNA [31], but also have their own signal enhancement capability. Besides, biomolecules such as liposome, DNAzyme etc. were also took advantage in the relevant fields. Zhang *et al* [112] embedded FITC in picloram-antibody labeled liposomes to detect the chlorinated herbicide in wastewater samples with the detection performance improved by several orders of magnitude. Xu *et al* [113] utilized the Pb^{2+} triggered exonuclease aided DNA recycling system to amplify the fluorescence signal. Moreover, DNAzymes were designed in a molecular beacon as a signal amplifier of Pb^{2+} fluorescence sensor [114]. Additionally, the ascorbate peroxidase 2/antibody binding domain fusion protein possessing both peroxidase activity and antibody binding capability was utilized to a tyramide signal amplification assay [115].

2.3 The application of specific biological molecules in environmental sensors

Biomolecular materials also have been applied as sensing unit in lots of sensing strategies according to their inherent properties e.g. specificity, rapid response. Specific biomolecules (e.g. enzyme [116], immunoglobulin [117] and DNA [118] etc.) are a vital part of biosensing systems for specific recognition and selectivity improving of pollutant detection. The specific responses between the biomolecules and the targets are sensitive, efficient and stable, which are the powerful tool for a bio-sensing strategy construction (Figure 7). Because of the redox, some common enzymes are designed in various sensing strategies for rapid and easy detection due to the direct and reflect the target concentration. Currently, aptamer is a piece of DNA or

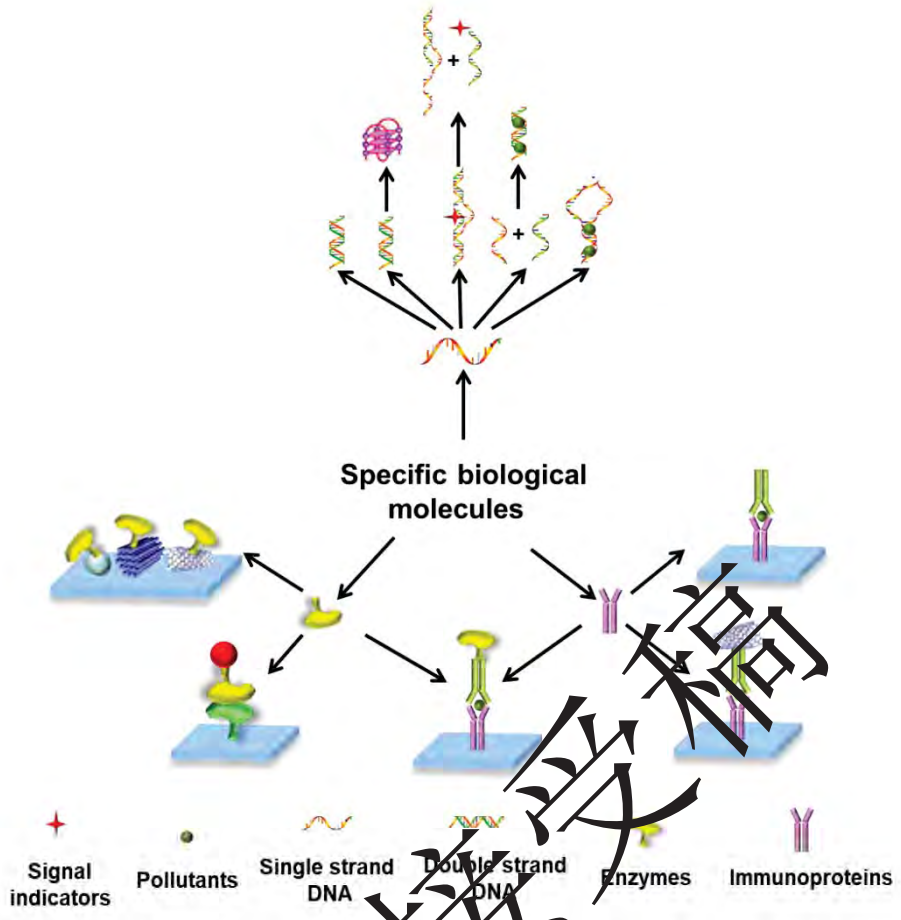


Figure 7. Sensors based on different specific biological molecules including DNA (double helix, G-quadruplex, double strand breaking at special nucleotide sites, mispairing double helix, and loops), enzyme, and immunoglobulin (reaction between antigen and antibody, or signal amplifying of immunoglobulins combined with nanomaterials and proteins).

RNA sequence that binds to a specific target molecule, screening through exponential enrichment systematic evolution of ligands technology (systematic evolution of reaction between the enzymes and the targets e.g. GOD to glucose [119], AChE to organic phosphorus pesticide [120,121], HRP to hydrogen peroxide [122] or phenylhydrazine [123], laccase to phenols or anilines [67], etc. Due to the specific immune reaction between antigen and antibody, a variety of immunoglobulins were

cultured and used in the immunosensors [99,124,125]. To DNA, the completely complementary DNA probe with the certain conserved sequence was used to detect the conserved sequence of biological target ligands by exponcntial enrichment, SELEX) from a nucleic acid molecule library, and is attracting more and more attentions. The aptamers e.g. containing the sequences that are capable of forming T-Hg^{2+}-T mispairing, or Pb^{2+}-induced allosteric G-quadruplex, or other specific chemical binding structures for sensing detection of heavy metal ions (Hg^{2+}, Pb^{2+}, UO_2^{2+}, As^{3+}, etc.) or POPs and other organic compounds (polychlorinated biphenyls [126], estradiol [127] and ethynylestradiol [128], cocaine [129], etc.) that are difficult/cumbersome to be detected by the conventional means. For instance, T-Hg^{2+}-T mispairing aptamer-target identification was designed in sensing strategies for Hg^{2+} detection, and the detection limit reached attomolar concentration[31], even zeptomolar concentration [130]. 8-17 DNAzyme was designed in a DNA sensor to have a specific catalytic hydrolysis for Pb^{2+} detection [109], and 39E DNAzyme was applied in UO_2^{2+} detection [131]. The specific G-quadruplex combining a microfluidic chip was developed for arsenic detection [132]. Additionally, the biomolecular materials e.g. chitosan [133], avidin-biotin [134], protein [135], DNA [136] etc. as carrier or medium are extended to other sensing strategies. Owing to the film-forming ability, chitosan is used to wrap or immobilize other functional materials for the fabrication of the sensing units. Avidin-biotin is a common binding system which is capable of assisting the sensing strategies, especially in immune-sensing, enzyme labelling system. Similarly, more and more reports of macromolecular protein or DNA served

as a carrier to load other molecules for further sensing response have appeared. It is not hard to image that biomolecular materials are capable of making the sensors becoming a super tool with a full considering the efficient biochemical reaction capability and without a worry about the life of biological activity or spontaneous regeneration.

3. Simplification of sensors for environmental pollutions detection

It is an obviously easy choice between simple and cumbersome and complex strategies, especially at a better/similar detection level. The evolving sensing strategies have tended to be a simpler and more automatic pattern. Great efforts have been paid to ripen the available techniques for utility. Take, for example, electrochemical detection systems are longoingly improving along with the development of miniaturization, operation and detecting strategies simplification, and are becoming a potential alternative for environmental monitoring attributing to portable enabling on-site analysis and providing convenient, real-time feedback information in the presence of pollutants [137-139]. Obviously, these devices offer superior tunability, portability and ability to directly transduce binding events without tedious and expensive labelling procedures.

3.1 Simple device

Simpler device brings sensing systems more accessible to a wider audience. So far, the portable sensor is of a most popular style owing to facility, accuracy and easy operation for non-professionals in *in vitro* and on-site detection, e.g. the pocket-sized

personal glucose meter, a commercialized sensing device has been widely accepted for measuring blood sugar. And the device has been further used for detections of uranium [94], melamine [140], cocaine [141], etc. The sensing strategy was based on the target-induced release of invertase from a functional-DNA-invertase conjugate. This strategy makes full use the proven performance of glucose meter to avoid changing the design and manufacturing process of detecting device, and also can be extended to other hazardous substances by the substitution of different ligands for environmental monitoring. Certainly, other novel devices were explored as well. As the aforementioned visual microfluidic sensing device based on a W-Chip and a uranyl ion responsive hydrogel was simple and portable for UO_2^{2+} detection [94]. As another example mentioned above, the small wave sensor was developed for simultaneous metal ions, pH, conductivity, color, turbidity and free and total chlorine detections in-piped water quality continuous monitor [85]. In addition, with the integration of the sensing concept, microbial fuel cells (MFC) also can become a sensing device for environmental monitoring. Modin *et al* [142] developed a MFC strategy for simple and convenient monitoring of biochemical oxygen demand (BOD). Similarly, a sensing strategy on the basis of the microbial desalination cell was developed for volatile fatty acid monitoring [143]. Furthermore, a small ordered mersopous tungsten oxides-coated sensing device was used in H_2S detection with excellent response at low concentration (0.25 ppm) and reversibility with fast response (2 s) and recovery (38 s) [144]. Additionally, with the development of chip technology, the smaller and portable devices are developed in sensing strategies,

which will be further described later. Pursuing the small portable detection devices, nevertheless, often has to sacrifice a certain sensitivity, whereby the balance of these two is an important future focus. Even so, there is still a long way to go before implementing a comprehensive application, which rests with breakthrough technologies of the device simplification.

3.2 Simpler operation and process

Simple operation and process is another welcome means that is facilitated to get a stable detecting strategy and improve the detection efficiency. Colorimetry is a convenient and intuitive visual method in detecting strategies for pollutants estimation. For example a colorimetric strategy of H_2S, alkaline bismuth hydroxide $Bi(OH)_3$ or its derivatives were coated on a wet Amplitude Prozorb, and quickly reacted with H_2S in nitrogen gas to form water and colored sulfide with Bi (III) [145]. Impersonally, there is a certain restriction to apply colorimetry since its semiquantitative analysis. At present, however, translating target recognition to visual length signal e.g. V-Chip provided an option for the quantitative analysis of colorimetry [89,90].

In other detecting system, many attempts have been used to simplify the detection process due to costs cutting and the general behavior. Zhang *et al* [86] adopted an anionic intercalator, disodium-anthraquinone-2,6-disulfonate, as the electrochemical indicator in a mercuric sensor to simplify detection operation. Electrostatic adsorption can be effectively avoided between DNA and the anionic intercalator, therefore, it is possible to reduce the experimental steps (washing, adjusting ion concentrations etc.) and the false positive signal

response to be taken into account using cationic intercalators. Similarly, in another sensing strategy [146], DNA adsorbent and fluorescence quencher were acted by GO in the initial state. When meeting Hg^{2+}, the adsorbed DNAs were released from GO by the triggered hybridization chain reactions and the detectable fluorescence was recovered. Despite the progress, these strategies need to further simplify and improve to meet the application in future.

3.3 High automation

The applications of automatic devices have been found in diverse areas, such as manufacture, food and textile industry, which can cut down the excessive human labor and restrict the exposure of employees to hazardous conditions. With incorporating of the automatic devices for environment pollutants monitoring, sensing strategies become more efficient, owing to saving the costs and labors, and decreasing the error of manual operation. Certainly, it is necessary to use automatic devices in some operations, especially involving in a toxic work environment. In short, automation makes detection easier.

As an attempt, the automatic sensing device based on a robotics-assisted mass spectrometry was constructed. The device involved the custom-written programs in C language, a robotic arm for delivering sample vials to the laboratory, and some auxiliary devices e.g. multi-relay board, photo-interrupters, gyroscopes, infrared sensors, force sensors, etc. which promoted and protected the analysis process to automate the determination [147]. The automatic devices also can be incorporated in some sensing systems to enhance working efficiency for water quality monitoring. A

syringe pump incorporated a miniature porous aluminum oxide chip to construct a bacterial cell sensor for the online monitoring of water quality [148]. With the help of the syringe pump, the water samples controllably flowed through the chip at all times, and realized the detection. For the same purpose, a cell phone connected with a paper sensing for water quality test, which was proposed and the results could transmit to website and somewhere else [149]. While, as another way to boost the automatic sensing, an optical barcode system based on the photoluminescence (PL) of nanoporous anodic alumina (NAA) in the UV-visible range was used in a smart enzymatic sensor. The NAA geometry (i.e., the pore length and its diameter) by virtue of its PL spectrum contributed to the identifiability of the barcode, which opened a new window toward automatic, accurate and fast measurements of enzyme levels, and could extend to environmental monitoring [150]. Additionally, to reduce labor and improve efficiency, an automatic sensing system combining wireless technique was developed for soil monitoring involving soil moisture, temperature, humidity, pressure, molecular analysis for better crop growth, and tracking of monitoring fields in daily life [151]. Although the current level of automation is not very high, predictably, with the unceasing improvement of automation technology, more and more new highly automated sensing strategies will continue to be developed in future.

4. Practicability of sensors for environmental pollutants detection

The ultimate aim of the development of the sensing strategies is to achieve a convenient detection of real samples. In case the sensing devices can replace the traditional detection methods involving expensive and sophisticated

instrumentations and/or complicated sample preparation processes, such as flame atomic absorption spectrum (AAS), spectrophotometer and chromatography etc. would save the economic and labor costs largely. Nowadays, continual progresses have been made in the miniaturization, time-effectiveness, simplification operation, strong anti-interference performance, low costs, and in-site detecting etc. of the sensing strategies, which lead them closer to the final destination.

4.1 Miniaturization

The miniaturized sensing device would greatly facilitate the application of the sensors, and achieve a rapid detection with accuracy, which is promising for on-site detection. Microelectrode, as a branch of the miniaturization of the sensor, has developed for many years (Figure 8). Microelectrodes based on carbon nanomaterials have exhibited amazing detection performance, e.g., a microelectrode array based on carbon nanomaterial for glucose detection [152]. The still developing microelectrode array, predictably, is capable of detecting in site complicated real water samples. Similarly, microelectrode arrays were also in positive to detect indoor air pollutants [153]. A self-oriented synthesized MWCNTs network presented good performance in formaldehyde, ammonia, and toluene vapors detection [154]. Besides, TiO_2, gold, silver, platinum, and so on nanomaterials can be utilized in microelectrodes fabrication as well, e.g. the microelectrode arrays based on TiO_2 were obtained Another kind of microelectrode such as the interdigitated through photolithography and photocatalytic deposition [155]. MoS_2, as the typical 2D transition-metal

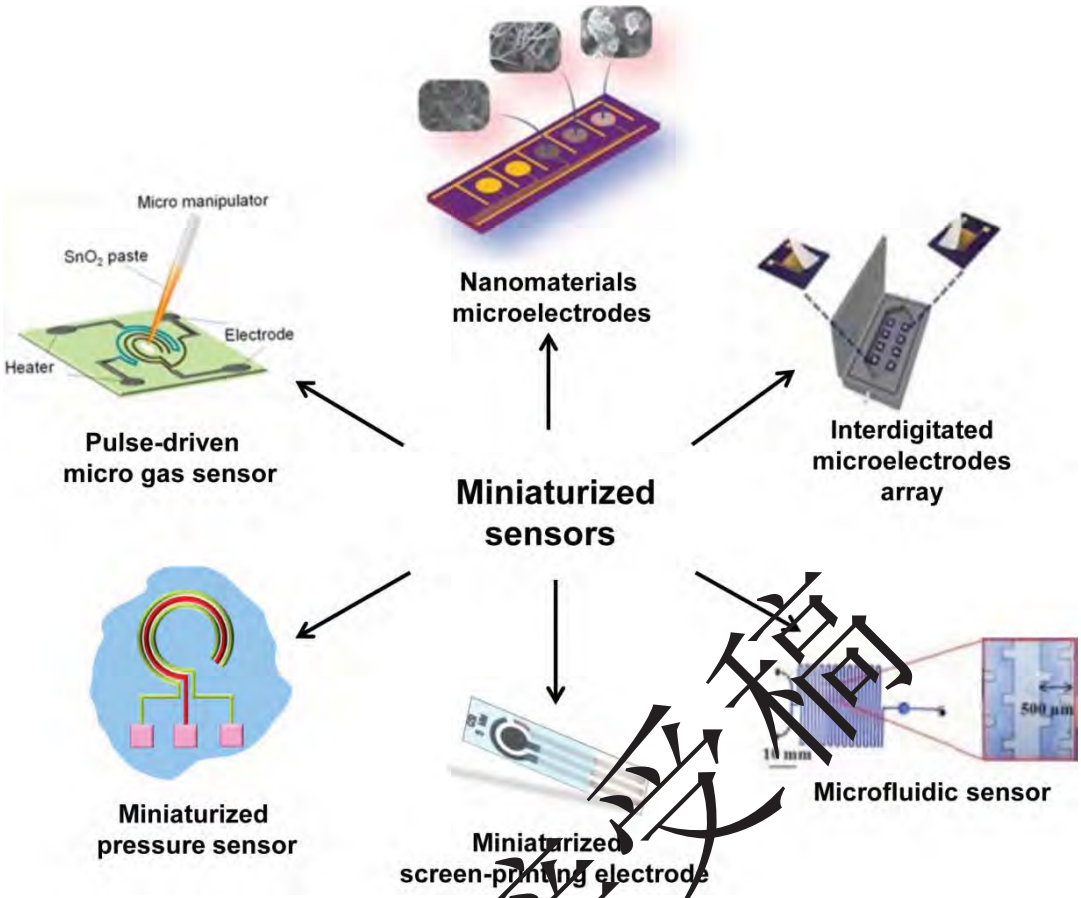


Figure 8. Different miniaturization sensors. Adapted from ref. 152, 157, copyright (2014) American Chemical Society; adapted from ref. 164, copyright (2015) American Chemical Society; adapted from ref. 166, copyright (2014) Elsevier.

dichalcogenides, has been widely used for gas sensors [156]. microelectrode array modified with MoS_2 film and different conjugated thiolated ligands for establishing a definitive library of VOCs [157]. The small device is potable and suitable for indoor detection of various VOCs. Similarly, a interdigitated microelectrode arrays by modifying with high-aspect ratio 3D carbon pillars was constructed for electrochemical detection [158]. Additionally, screen-print microelectrode also attracts more and more concern. In order to improve the sensitivity of screen-print

diamond microelectrode, the polyester resin binder/boron-doped diamond powder ratios were adjusted [159].

Likewise, with the development of micro-fabrication technology, the improvements of other devices promote the development of sensing miniaturization. A micro gas sensing device with diameter of 9 mm consisted of a micro heater modified with Pd/SnO_2 mesoporous film (area: □ 150 μm) for VOCs detection. With the heating of the micro heater, VOCs molecules could deeply diffuse into the mesoporous film and produce the detectable response signals [160]. The potable micro-sensing device is promising for gas monitoring. The same to detect VOCs, a small liquid sensor was fabricated by a polymer-covered graphene micro-tube piping structure with a cross-linked and interconnected channel network [161]. The sensor presented excellent detectability owing to the strain sensitive property of the resistivity of the 3D hollow micro-tubing. Naturally the miniaturized sensing devices were applied in other substances detecting such as pH and protein [162]. In addition, due to the amenability to miniaturization, the introducing of microfluidic contributed to less sample volumes with high sensitivity for pollutant detection [70]. Tahirbegi *et al* [163] manufactured a glass microfluidic device for indirect pesticide detection via the metabolism/photosynthesis of algae under the action of pesticides. The small device could monitor the dynamical concentration of various pesticides rapidly. The microfluidic device was employed with a solid-phase extraction chamber and a peristaltic pneumatic micropump to preconcentrate Pb^{2+} in samples for sensitive detection [70]. Similarly, a microfluidic platform was developed via a competitive

magneto-enzyme immunoassay on the boron-doped diamond electrodes modified with platinum nanoparticles (PtNPs) to detect pesticide [164]. Obviously, although is still subject to certain technical restrictions at present, the miniaturized sensing device is improving the comprehensive performance of the sensors. It is believed that it would bring a wider application of the sensing devices with the developments of various miniaturization strategies.

4.2 Fast preparation and maintaining bioactivity

Reducing the time and labor costs in sensor preparation is another path to improve the practicability of sensing strategies. Simplifying the assembly process of a sensor, particularly with regard to one involving biocomponent such as the immobilization steps of biomolecules on electrodes, the binding between thiol and gold is convenient. As above mentioned that the thiol-modified DNA direct assembled on the Au electrode or AuNPs modified electrodes keeping the bioactivity, and then performed the relatively specific detections combining the different detection modes such as electrochemisty [109,165], colorimetry [166,167], fluorescence [168,169], surface-enhanced Raman scattering (SERS) etc [170,171] Another chemical crosslinking by Schiff base reaction, which is based on the reaction of amine with ketone or aldehyde, or other chemicals containing carboxyl group also is a feasible route for fast and easy binding of chemical or biological substance onto the sensing unit. For uranyl cations analysis, Schiff base reaction between o-methoxyphenyl methyl ketone and 2-aminothiophenol was utilized [172]. Likewise, according to Schiff base reaction between aldehydes and thiosemicarbazone, thiosemicarbazone was adopted in a

fluorescence sensing strategy for Hg^{2+} detection [173]. Roy *et al* [174] also took advantage of the reaction to immobilize the amino modified DNA on the carboxyl-polyethylene glycol functionalized glass platform for rapid detection. Furthermore, it is easy to perceive that carbon materials (e.g. CNTs, graphene and mesoporous carbon) are popular with the sensors especially the biosensors in recent years, because they are readily available and functionalized, which are conducive to fast preparation of sensors. Meanwhile, as an inert material, they exhibit good biological affinity and maintain the bioactivity of biomolecules. Accordingly, DNA directly coated on the surface of carboxyl group functionalized SWCNTs or GOs rich in hydroxyl and carboxyl groups to save preparation time and maintain the bioactivity of DNA [146,175]. Similarly to enzymes, via the chemical groups on the nitrogen-doped carbon spheres (N-HMCS), also were immobilized easily on the N-HMCS modified GCE [176]. Certainly, some modifications or immobilizations use electronic effect such as conjugated effect, electrostatic interaction, etc. Conjugate assembly is an effective strategy in sensing fabrication, including π-π conjucate, Au-S etc (Figure 9). For example, conjugated polymers were modified on the surface of sensing units to further assemble other chemical or biological molecules based on conjugated effect. And enzymes/immunoglobulins to GOs/CNTs, thiol modified DNA to AuNPs also belong to this category [177-179]. In order to improve sensing fabrication and stability, it is taken full advantage of between the fixed target components in sensing strategies. Sukumaran *et al* [180] successively modified nitrogen doped graphene,

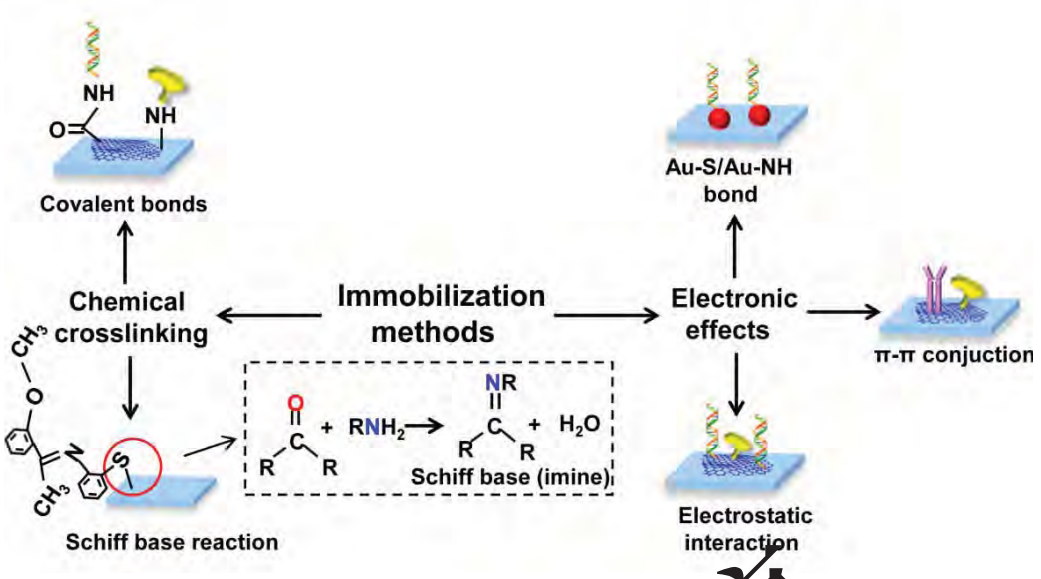


Figure 9. Fast preparation and maintaining bioactivity via chemical crosslinking and electronic effects in sensor fabrications

ionic liquid and DNA via identically electrostatic adsorption onto the electrode surface. They are able to complete the quick assembly of sensing units and especially do not affect the activity of biocomponents. Besides, due to the natural advantage in biocompatibility, the above mentioned biomolecular materials e.g. DNA [165,181], protein [182,183] etc. as a medium, were used to maintain the good performance for a biosensing system. Taking into account the strong specificity and catalytic ability of the biochemical effects, once the bottleneck of life of biological activity or spontaneous regeneration is broken, biosensing strategies would rapidly grow up in the environment, medical, food security and other fields owning to their efficiency and accuracy detection.

4.3 Efficient detection process

The efficiency of detection process involves two aspects: response speed and reliability of detection process. For detection purposes, a rapid response is of a

crucial indicator belonging to a category of practicability, which can increase detecting efficiency and reduces the possibility of extra signal interference (Figure 10). An extremely simple biological colorimetric strategy for H_2S detection is impressive [184]. AuNPs was introduced into the Tris buffer solution contanning Tween 80 and H_2S for reaction of 1 min at room temperature, followed by stabilized with the additional NaCl for 7 min. The mixture maintained red in the present of H_2S, otherwise, aggregated and turned into blue. Whilst the rapidly biological sensors are also invented. For instance, pesticide analysis is usually complicated by high-performance liquid chromatography (HPLC), gas chromatograph (GC) and gas chromatography-mass spectrometer (GC-MS) etc., even the efficiency is improved by enzyme-linked immunosorbent assay (ELISA), immunosensor, but it's still a little time-consuming in term of immune reaction process. The enzymatic

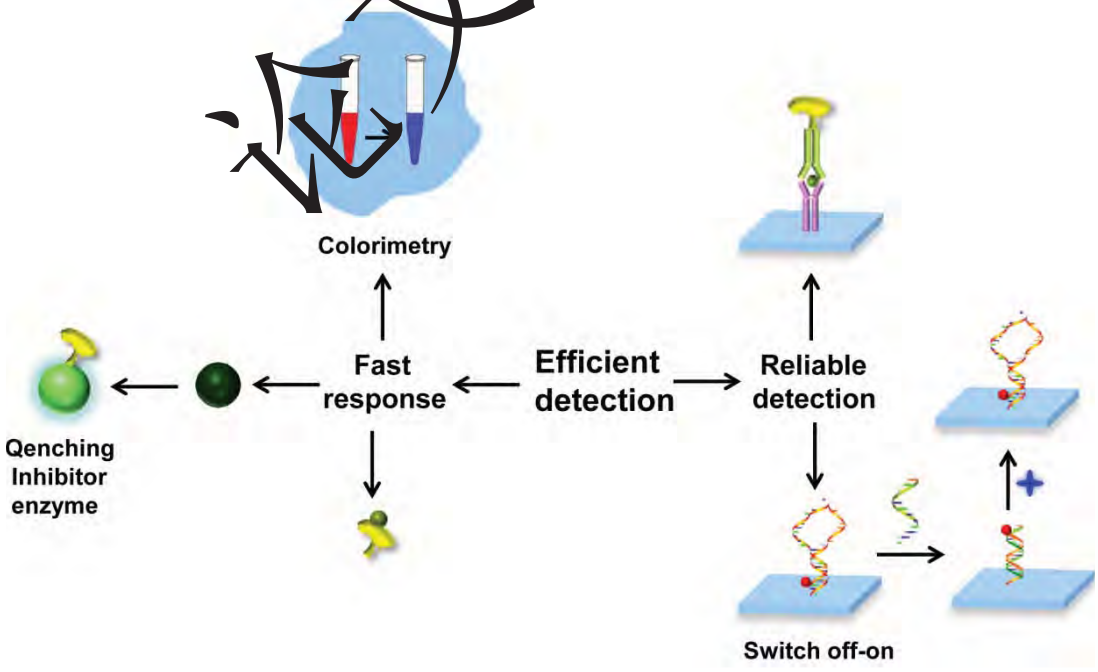


Figure 10. Efficient detection involving fast responses and reliable detection

sensor, however, can further shorten the time-cost [69,82]. Alternatively, a simple enzymatic sensor was developed to rapidly detect fenoxycarb pesticide in river water [185]. The fluorescence of nitrogen doped graphene QDs was quenched when mixed with AChE and its substrate for 5 min, nevertheless, would restore in the presence of fenoxycarb, the inhibitor of AChE, after 15 min reaction. From this it appears that the efficiency for pesticide analysis becomes more acceptable due to the time needed greatly reduced, not to mention the enzyme sensors for phenols and other compounds detection within 1 minutes [67,82,186]. Similarly, a rational detection process is of a reliable guarantee to obtain an accurate response, which can help promoting the application of sensing strategies. An accurate, high signal-to-noise ratio immunosensor was fabricated based on the specific immune response and ingenious designed tyrosinase(Tyr)-responsive nonenzymatic redox cycling [187]. In the nonenzymatic redox cycling, NADH could reduce highly electroactive catechol coming from the transformation of poorly electroactive phenol by Tyr, for response amplification. The mentioned above strategies devoted reliable detection to the sensor. In addition, line DNA probe array is another effective detection strategy for accuracy and specificity chasing. The nanostructured microelectrode was decorated with DNA clutch probes for detection based on signal “switch off-on” strategy [188]. The disparate DNAs could hybridize with their respective complementary DNAs, and precisely separated and detected. Because the changing of electrochemical signal quantitatively reflects the detecting targets, the signal “switch off-on” strategy sparks

an amazing interest in sensing development. Interestingly, a “switch off-on” strategy attracted our attention.

4.4 Anti-interference performance

The components of environmental samples are of complexity and uncertainty, therefore, the anti-interference ability, i.e. environmental suitability of a detecting method reflects its applicability, which is an important indicator. A significant feature of sensing strategies is that they possess a certain ability of anti-interference. Selectivity can be considered as a reflection of anti-interference. Sensors, especially biosensors have high selectivity against interfering substances in samples. A stable electrochemical sensor was constructed with specific DNA-based conductive carbon hybridized TiO_2 nanotube arrays for Pb^{2+} detection. The sensor has excellent stability, wide pH adaption from 4 to 8, and selectivity in several divalent metal ions solution such as Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Co^{2+}, Ba^{2+} and Hg^{2+} [189]. An aptamer-based fluorescence biosensor showed an outstanding anti-interference performance toward 17β-estradiol based on that the aptamer high affinity and specificity for the target with much lower signal for other endocrine disrupting compounds and chemicals [190]. As shown in a Pb^{2+} sensing strategy [191], DNAzyme also presented good selectivity and flexibility. Certainly, the pH condition of samples is an essential factor for detection and analysis. The adaptive pH range of a lable-free FET biosensor based on MoS_2 was 3 to 9 [162]. Similarly, a mercuric sensor based on 3D Au nano-cluster and anionic intercalator presented an attractive resistance to pH changes, especially, the current responses were basically same and

reached maximum in the pH range 6.0 to 7.8, which just fitted to common river water (pH=6.0 to 6.9) and municipal wastewater (pH=6.5 to 7.5) [86]. Certainly, the feasibility of the sensing strategies with a certain environmental suitability will be obviously enhanced.

4.5 Low cost

Not only the aforementioned points, there also is a very practical factor, i.e. cost should be considered in the application of sensing strategies. In a sense, low cost is of an important prerequisite to promote their applications. In general, inexpensive materials taken in fabrication sensing can cut down the cost inevitably. The carbon materialsare relatively inexpensive, and have been widely used for sensing fabrication. A sensor developed with cross-reactive array of polycyclic aromatic hydrocarbons (PAHs) and SWCNT bilayers could detect polar and nonpolar VOCs with economical cost and effective accuracy [192]. Likewise, SiO_2 also is a cheap material and inspires more sensing constructions. For example, low-cost silole-infiltrated SiO_2 inverse opal photonic crystal was synthesized and immersed in miscellaneous organic vapors for detection [193]. Moreover, cutting down the consumption of reagents is another effective method for reducing cost. As an attempt, a microfluidic sensor was designed for the manipulation in small volumes and less reagent required [194]. Additionally, from the cost point of view, extending lifetime of sensor is a reliable way as well. In an impressive case, a synthesized stable polymer, poly(m-phenylenediamine-co-2-hydroxy-5-sulfonic aniline), modified electrode could use for Pb^{2+} detection with a long lifetime of up to 5 months [195]. Another way to extend sensor lifetime is

providing effective regeneration. For instance, Nöll *et al* [196] fabricated a reusable fluorescence sensing strategy based on molecular beacons. To regenerate the sensor after each detection process, heating treatment at 90°C or rinsing with urea solution and water could recover the initial form of molecular beacons for next utilization. To a large degree, reusable sensing strategies can cut the cost down deeply.

4.6 In-situ detection

Compared with the traditional detection methods e.g. HPLC, GC/GC-MS, AAS, etc. for pollutant analysis, sensing strategies have a significant advantage, which are suitable for in situ detection due to their portability and easy operation. A sensing strategy combining a portable pressure meter was applied to in situ detection [197]. Likewise, the aforementioned sensing strategies combining glucose meter [94] also take advantage and extend the function of such commercial portable devices. In addition, other portable sensing strategies have also been developed for in situ detection, e.g. thermotolerant (faecal) coliforms was adopted constructing a portable tryptophan-liked fluorescence sensing for in situ monitoring faecal pollutants in drinking water [198]. For in situ detection of sensing strategies, there is another trend in term of sensing construction for worldwide water monitoring involving no reagents and rapidly instantaneous readouts. This feature was reflected in an autonomous underwater spectrophotometric sensor for in situ detection of dissolved inorganic carbon in seawater [199]. In addition, miniaturized sensing devices can be served to detect or possess the potential for on-site detection. The miniature organic electrochemical transistor sensor based on PtNPs binding on TiO_2 nanotube arrays

modified electrode was fabricated for on-site detection of chemical oxygen demand (COD) [200]. The sensor is suitable for the working in slightly polluted water, such as ground water and underground water. Similarly, to detect microsystins in river water, an optical microsensor arrays based on specific monoclonal antibody were fabricated on compact discs and read out the discernible response signal by a DVD drive [201]. It is of an interesting idea to guide building the applicably miniature, portable and easy-to-use sensing strategy for environmental detection.

Furthermore, a comparision of typical pollutants detections with different sensors types, sensor units, detection ranges, limitations and times in environmental samples is exhibited in Table 1 and Table 2.

Table 1. Typical inorganic pollutants detections with different types of sensor, sensor unit, detection range, limitation and time in environmental samples

Target	Sensor type	Sensor unit	Environmental sample	Detection range	Detection limit	Detection time	Ref.
Hg^{2+}	Electrochemical (SWV, Methylene blue)	aptamer/electrodeposited graphene-Au + nanoAu carrier signal amplification	tap water, river water, landfill leachate	1.0 aM -100 nM	0.001 aM	~ 1 h	[49]
	Localized SPR	AuNPs	air	1 - 825 μg/m^3	1 pg/m^3	—	[86]
	Triboelectric nanogenerator sensor	AuNPs	—	0.1 - 5 μM	30 nM	60 min	[87]
	ECL	ferrocene-grapheme/aptamer/	river water, sea water	0.05 - 100	18 pM	35 min	[112]

		AuNPs/$Ru(bpy)_3^{2+}$		nM			
	Fluorescent	aptamer/Mn-doping CdS/ZnS core/shell QDs + aptamer/AuNPs	tap water	1 - 10 nM	0.49 nM	18 min	[128]
	Field-effect transistor	Pb^{2+}/rGO-AuNPs-GSH	drinking water	10 nM - 10 μM	10 nM	2 s	[39]
	Fluorescent	aptamer/GOOD	drinking water, tap water, lake water	1 - 1000 nM	0.64 nM	2 s	[92]
Pb^{2+}	Colorimetric (red to yellow)	aptamer/PMNT/TAPB	tap water	0 - 120 nM	6 nM	5 min	[99]
	V-chip	aptamer hydrogel/Au@PtNPs	waste water	0.08 - 42 nM	0.04 nM	~ 40 min	[108]
	Electrochemical (DPV)	aptamer/MCN- electrodeposited Au + MCN-nanoAu carrier signal	tap water, spring water, river water	10^{-3} - 10^{-14} M	1.02×10^{-15} M	30 min	[129]

		amplification					
UO_2^{2+}	Personal glucose meters	aptamer + sucrose	drinking water, table dust	—	5.0 nM	85 min	[105]
	V-chip	aptamer hydrogel/AuNPs	lake water	0 - 300 nM	20 nM	2 h	[110]
As^{3+}	Electrochemical (SWASV)	different shapes of AuNPs	—	100 - 1000 ppb	0.0157, 0.4787, 0.1816 μA/ppb·cm^2	—	[131]
	Luminescence	aptamer/iridium(III) complex	natural water	50 - 300 nM	7.6 nM	20 min	[150]
Nitrite	Colorimetric (red to colourless)	the Griess reagents	—	4.0 - 85.0 mg/L	0.52 mg/L	15 min	[185]
	Electrochemical (DPV)	Fe_3O_4-RGO nanocomposite	tap water, rain water, river water	10 - 2882 μM	0.1 μM	—	[103]

H_2S	Heat conduction	ordered mesoporous WO_3	air	0.25 - 200 ppm	50 ppm	2 s	[162]
	Colorimetric (red to blue)	aptamer/AuNPs	air	0.1 - 0.5 ppm	0.08 ppm	2 s	[102]
NH_3	Fluorescent	graphene/MoS_2 QDs		2 - 10 ppm	35.5 ppb	1 s	[90]

Table 2. Typical organic pollutants detections with different types of sensor, sensor unit, detection range, limitation and time in environmental samples

Target	Sensor type	Sensor unit	Environmental sample	Detection range	Detection limit	Detection time	Ref.
Hydroquinone	Electrochemical (I-t)	laccase/magnetic core-shell (Fe_3O_4-SiO_2) nanoparticles	compost extracts	10 - 137.5 μM	0.15 nM	60 s	[88]
Malathion and acephate	Electrochemical (DPV)	AChE	grape, apple, mango, orange, banana, tomato, rice, wheat	0.07 - 1.3 ppm, 0.1 - 0.85 ppm	0.194 ppm, 0.147 ppm	4 min	[141]
Phenylhydrazine	MBFCs	anode: GOx/polyTBA-AuNPs cathode: polyTPHyd-	—	10.0 μM - 5.0 mM	2.5 ± 0.2 μM	—	[144]

		AuNP					
Polychlorinated biphenyl	SERS	aptamer/Ag nano-crown array	—	10 mM - 0.1 nM	0.1 nM	1 min	[147]
17b-estradiol	Fluorescent	aptamer/AuNPs	spiked water samples	0.48 - 200 nM	0.48 nM	10 min	[146]
Ethynylestradiol	Polyacrylamide gel electrophoresis	dimethyl sulphate/ aptamer	tap water, lake water	0.5 - 1.0 μM	0.13μM	15 min	[147]
Cocaine	Fluorescent	aptamer/SiNPs-aptamer/ AuNPs	serum	0 - 40 nM	209 pM	40 min	[148]
Atrazine	Electrochemical (CA)	anti-atrazine antibodies-magnetic beads/ atrazine-HRP/PtNPs	orange juice	0.9 - 4.5 nM	3.5 pM	20 min	[164]

Fenoxycarb	Fluorescent	AChE/N-doped GQDs	river water	6 - 70 μM	3.15 μM	15 min	[185]

5. High throughout detection for environmental pollutants detection

High throughput detection, with the ability to simultaneously detect a variety of samples, is of a trend of future monitoring, which shows a great advantage to improve detection efficiency. The sensing strategies are evolving towards this direction such as multichannel detection and chips, which make the sensing strategies more accessible to multi-target, multi-functional detection. Moreover, soft sensing, a method of combining sensor with software, can process the multiple data analysis, which also belongs to the category of high-throughput in a sense. Such sensing strategies are more conducive to the foreseeable transformation into commercial development for application in future.

5.1 Multichannel detection and chips

The biggest advantage of multichannel sensors and chips is that they can perform simultaneous detection of multiple pollutants for monitoring assessment. As far as the detection efficiency is concerned, it is of great significance. Especially chips on the basis of multi-specific response system integration are a more sophisticated technology, which can rapidly provide more qualitative and quantitative information by detecting wide range of chemical species and biomolecules [202-204] (Figure 11).

In an interesting multichannel detection case, a fluorescence platform using a QD array functionalized with calixarene, cyclodextrin, -OH and -OMe was built to differentiate five explosives in wastewater, i.e. DNT, TNT, tetryl (2,4,6-trinitrophenylmethyl nitramine), RDX, and trinitramine [205]. The explosives could be detected in a rapid single fluorometric test, which relied on the characteristic

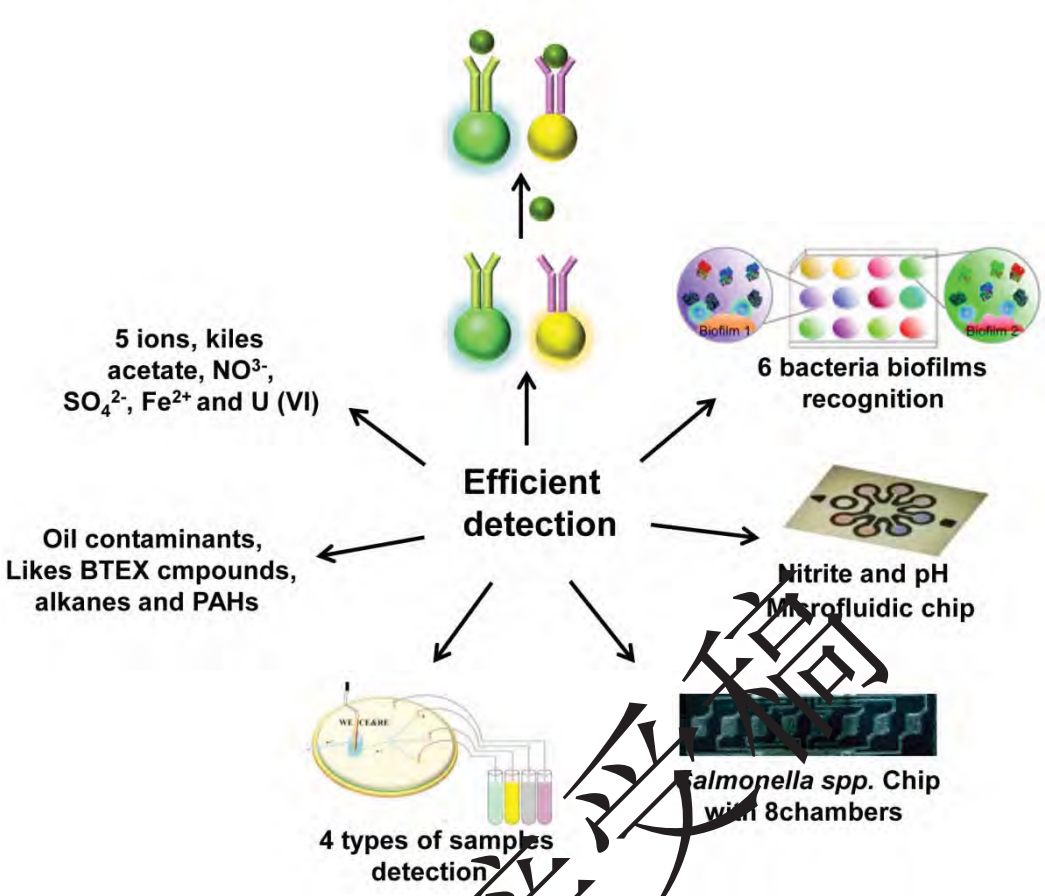


Figure 11. Different multichannel sensors strategies for pollutants detections. Adapted from ref. 207 and 208, Copyright (2014) American Chemical Society; Adapted from ref. 209, copyright (2015) The Royal Society of Chemistry; Adapted from ref. 210, copyright (2017) Elsevier.

fluorescence changes by binding differences between the cross-reactive functional surfaces of QD array and the explosives. Moreover, six bacteria biofilms could be identified by a multichannel nanosensor based on the fluorescence changes of AuNP-fluorescent protein conjugates, which were destroyed by the competitive interactions between the bacterial species and the cationic AuNPs, and produced instantaneously characteristic fluorescence changes [206]. This targeting strategy was applicable to clinical visual and

camera-based diagnosis. In addition, a typical multichannel detection form, microfluidic strategy often appears in many sensing systems. For example, the nitrite and pH of water samples were simultaneously detected on a paper based microfluidic device with an Android smartphone [207]. Furthermore, multichannel lab-on-a-chip is one of the most recent trends in chemical and biological analysis [208]. Eight food samples containing *Salmonella spp.* were simultaneously rapidly detected by an eight-chamber lab-on-a-chip system with integrated magnetic bead-based sample preparation and loop-mediated isothermal amplification [209]. The sensing system was able to effectively detect *Salmonella spp.* on site within 40 min, much shorter than a few hours to days cost via conventional bacterial identification or molecular-based methods detection. Likewise, a microchannel chip with 3 cm in diameter was constructed for four kinds of samples simultaneous detection [210]. There were four independent micropump connected with four inlets, where could pipe samples into microchambers in the chip to electrochemically identify the target molecules. The multichannel device and chips have been developed and made great progress in recent years and possess the advantages, such as speediness, accuration, effectivity, timesaving potability, etc. Hazen *et al* [211] utilized γ-Proteobacteria 16S rRNA genes to rapidly detect various oil contaminants in deep sea, such as BTEX cmpounds, alkanes and PAHs, which provide timely and quick analysis information to assess the bioremediation for coping with the unexpected Deepwater Horizon blowout. Likewise seven genes modules were

applied for acetate, NO^{3-}, SO_4^{2-}, Fe^{2+} and U (VI) monitoring in response to emulsified vegetable oil amendment [212]. However, microscale analysis and sophisticated manipulation may be obstacles in production and popularization in a large scale, especially it is unignorable that a portion of devices are complex and expensive in fabrication, maintenance or operation. In any case, with technology simplifying and cost reduction, the outlook of multichannel and chips sensing is promising, indubitably.

5.2 Soft sensing and systems coordination

Soft sensing, briefly the combination of sensor and algorithm-based software, can handle and provide more data and information with the help of computers, i.e. sensors provide instantaneous on-site data and software makes a data analysis by the simulation and prediction model of the running computer programs. It is useful in data fusion, where measurements of different characteristics and dynamics are covered. Environmental information is also complex giving ample scope for soft sensing abilities. The electrochemical response signals corresponding to the concentration of hydroquinone in compost extracts were detected by a laccase sensor, and then were nonlinearly analyzed using backpropagation-artificial neural network model. Compared with the linear analysis by the biosensor, the proposed nonlinear analysis method exhibited a more robust detection capability for on line analysis, because ANN could easily simulate, analyze and solve the nonlinear, overlap and uncertain problems in complex systems [213]. Magnetic tube recovery ratio was measured by fuzzy system and neural network techniques instead of real-time control the index in

mineral processing [214]. The data would form fuzzy system which the modeling error between the real data and the fuzzy system will be compensated by a neural network. Group genetic case-based reasoning soft-sensing method consisting of genetic algorithms and group decision-making was carried out for the dissolved oxygen (DO) concentration monitoring in wastewater treatment process [215]. Obviously, continuous and evolutionary adaptation and optimization algorithm can further coordinate and improve the cooperation of each component in the systems, which are going to make them more intelligent and suitable for environmental detection and analysis. In addition, according to the concept, soft sensing and chemometrics have some degree of similarities in a sense. Chemometrics is a discipline that establishes a connection between the measured values of a chemical system and the state of the system by means of statistical or mathematical methods. Indeed there is a certain intersection between them. Chemometric techniques such as partial least squares, locally weighted regression and multilinear partial least squares regression were utilized for regression modeling prediction of biomass and substrate concentrations in *Streptomyces coelicolor* cultivation monitoring, and could predict the process variables on-line [216]. The soft sensing based on 2D fluorescence spectroscopy coupled with partial least squares regression was exploited for optical density, time of culture, glucose and 2-PE concentrations monitoring on line [217]. Moreover, chemometrics could be used in solid-state fermentation (SSF) monitoring, especially the enzyme activities in SSF were challenges [218]. In general, soft sensing experts at complex, large capacity of data processing and simulation, and facilitates

the integration of integrated monitoring platform for multiple data analysis. Moreover, with the development of artificial intelligence and algorithm, the auxiliary software and computer technology would further promote detect media to coordinate and optimize the detection system, which can contribute to the more powerful detection to meet technical requirements and future trends.

6. FUTURE OUTLOOK

At present, the sensing method is still mainly in the laboratory stage, however it has shown great potential in environmental pollutants detection, due to its inherent nature such as high sensitivity and selectivity, low cost, flexibility, and portability etc. Meanwhile, in order to push forward its practicality, numerous researchers have racked their brains for the breakthrough bottlenecks in application by the inspiration in nanomaterials, biology, electronics, micro-nano processing and so on. In sum, the sensing strategies will further evolve to approach the practicality in future.

Accuacy. Although many types of sensing strategies have been developed, according to sensing principle, most of them are focused on the accuracy (sensitivity and selectivity). In term of sensitivity, improving sensing units is a currently principal way, and strengthening the signal response system is another effective way as well. Herein, the fast-developing material science becomes the basic driving force for the above two major ways. The novel materials (e.g. two dimensional dirac material represented by graphene, safe and cheap carbon materials, easily functionalized porous materials, and some of outstanding metal nanomaterials, organic polymer materials) will continue to play a pivotal role for sensing method in future. Certainly,

materials like carbon materials with superior properties and abundant resources are more recommended. Additionally, the reliability of detection process is conducive to accuracy, which is mainly through the adoption of specific reaction system such as chemical/biochemical systems, and the introduction of the appropriate strategy to eliminate/reduce the possibility of false positive response for the selectivity. Among all kinds of sensors, electrochemical sensors have shown advantages in sensitivity, which are easier to meet the needs of identification and safety warning of low/trace-concentration pollutants in the environment. However, blindly pursuing accuracy, it is inevitable to cause over-reliance and piling materials, complex construction and detection process, etc. issues. Alternatively, a rational approach is carried out to develop more efficient strategies taking into account accuracy and practicability for meeting the challenge of environmental monitoring.

Environmental monitoring requirements. The unpredictability and complexity are the intrinsic characteristics of environmental samples, which is a stumbling block of environmental monitoring. Therefore, to promote the application of sensing method in environmental monitoring, the following several aspects can be carried out.

Strengthening the selectivity and environmental adaptability. The more specific chemical/biochemical reaction system, or size effect and the structural characteristics of some materials should be used to enhance the target specific identification in complex environment; and make full use of the characteristics of the system itself to construct a sensing strategy with some auxiliary means

for enhancement of environmental resistance to reduce the impact of environmental factors on the detection.

Strengthening sensor regeneration. Most of the sensing strategies currently cannot reach the standard of practical application in the regeneration. Obviously, the practical progress also is a big step forward for the sensing method application in the regeneration. The sensing detection is mainly based on the contact response and the capture effect. The regeneration of the sensors based on specific contact catalysis (such as enzyme sensors and some chemical sensors) usually is fulfilled by the normal operating i.e. separation and cleaning. while, it is more complex for the sensors based on the capture effect (e.g. immunosensor, aptasensor) due to various types of capture with different known and unknown action mechanisms. Clear mechanisms are in great favors of the efficient regeneration, but on the whole the related mechanism research is not thorough enough, which is an urgent problem to be solved for the application of sensing method in environmental monitoring. At present, the design of disposable sensor or sensor for quick-replacement sensitive units is a substitute strategy to alleviate this problem.

Practicability. The present greatest challenge for sensing method in application is its practicability. It can be easily related to cost, manufacturing, operability, portability etc., which are the direct transition points to apply sensing technology to production. In fact the mentioned difficulties have been trying to overcome by the global researchers. It is of a crucial target to develop more

practical sensors like a personal glucose meter, for environmental monitoring having the attributes such as cost-effectiveness, simple production and operability, fast response, small (micro) size, and real-time in situ detection. In terms of simplifying sensor construction, perhaps the photoelectric sensor will receive great attention for a period of time, because of its own response signal properties. In addition, the use and integration of some current commercial portable devices and technologies, such as personal glucose meter and mobile phone, to develop new sensors is also a fast and effective method.

Biosensing strategy. For biosensing strategy, there is an unavoidable problem i.e. the activity cycle of biological molecules, and the factors affecting biological activity. To facilitate the adoption of biosensing strategy in actual detection, the unremitting efforts of how to eliminate/reduce the influence on biological activity for long-term and repeated use have been making. Adding a nano-protective cover to bioactive molecules against the interference of various environmental factors to enhance their service life may be a way out. Once the bottleneck can be broken, it will rapidly open up new avenues for the wide application of biosensing strategy owing to the high specificity and reaction efficiency of biological (molecular) system, which will be more consistent in the development of environmental monitoring.

Intergration trends. The above aspects are mainly around the technical level of the current sensing method itself according to the sensing principle, which involve the technical parts to be desired from laboratory to practical application stage. Looking

ahead, it is developing towards the standardized, intelligent, integrated multi-target fast sensing mode and new sensing technology. Undoubtedly, building uniform specification and technical standards are inevitable trend and is for the sake of the general public, which facilitates to maximize interoperability, compatibility, repeatability, etc. In other respects, some sensing strategies were developed combining with the mathematical model and algorithm, and supplementing automated design and device, had exhibited a certain degree of intelligence, online analysis potential. Moreover, chip, multi-channel, high-throughput modes are also used in multi-target detection analysis for advanced and sophisticated sensing method. In addition, with the birth and evolution of new technology, and with the discovery and breakthrough of new principles and mechanism, will appear more and more miraculous sensing detection technology to achieve integration of detection-imaging.

Declaration of Competing Interest

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

Acknowledgements

The study is financially supported by the Program for the National Natural Science Foundation of China (51979102, 51521006, 51508175, 52000065), Science and Technology Plan Project of Hunan Province, China (2015SK2001), China Postdoctoral Science Foundation (2016M600490, 2017T100462).

References

[1] D. Chen, H. Feng, J. Li, Graphene oxide: preparation, functionalization, and electrochemical applications, *Chem. Rev.* 112(2012) 6027-6053.

[2] Y. Liu, X. Dong, P. Chen, Biological and chemical sensors based on graphene materials, *Chem. Soc. Rev.* 41(2012) 2283-2307.

[3] M. M. Barsan, M. E. Ghica, C. M. Brett, Electrochemical sensors and biosensors based on redox polymer/carbon nanotube modified electrodes: a review, *Anal. Chim. Acta* 881(2015) 1-23.

[4] S. Kruss, A. J. Hilmer, J. Zhang, N. F. Reuel, B. Mu, M. S. Strano, Carbon nanotubes as optical biomedical sensors, *Adv. Drug. Deliv. Rev.* 65(2013) 1933-1950.

[5] X. Fang, B. Y. Zong, S. Mao, Metal-organic framework-based sensors for environmental contaminant sensing, *Nano-Micro Lett.* 10(2018) 64.

[6] K. Saha, S. S. Agasti, C. Kim, X. Li, V. M. Rotello, Gold nanoparticles in chemical and biological sensing, *Chem. Rev.* 112(2012) 2739-2779.

[7] H. Pang, L. Xu, D. X. Yan, Z. M. Li, Conductive polymer composites with segregated structures, *Prog. Polym. Sci.* 39(2014) 1908-1933.

[8] J. Wei, D. Yang, H. Chen, Y. Gao, H. Li, Stripping voltammetric determination of mercury(II) based on SWCNT-PhSH modified gold electrode, *Sens. Actuator B-Chem.* 190(2014) 968-974.

[9] G. Yang, C. Zhu, D. Du, J. Zhu, Y. Lin, Graphene-like two-dimensional layered nanomaterials: applications in biosensors and nanomedicine, *Nanoscale* 7(2015) 14217-14231.

[10] F. Perreault, A. Fonseca de Faria, M. Elimelech, Environmental applications of graphene-based nanomaterials, *Chem. Soc. Rev.* 44(2015) 5861-5896.

[11] S. K. Vashist, D. Zheng, K. Al-Rubeaan, J. H. Luong, F. S. Sheu, Advances in carbon nanotube based electrochemical sensors for bioanalytical applications, *Biotechnol. Adv.* 29(2011) 169-188.

[12] S. B. Yang, B. S. Kong, D. H. Jung, Y. K. Baek, C. S. Han, S. K. Oh，H. T. Jung, Recent advances in hybrids of carbon nanotube network films and nanomaterials for their potential applications as transparent conducting films *Nanoscale* 3(2011) 1361-1373.

[13] M. Majdoub, Z. Anfar, A. Amedlous, Emerging chemical functionalization of g-C_3N_4: covalent/noncovalent modifications and applications, *ACS nano* DOI: 10.1021/acsnano.0c06116.

[14] J. Liu, H. Q. Wang, M. Antonietti, Graphitic carbon nitride “reloaded”: emerging applications beyond (photo)catalysis, *Chem. Soc. Rew.* 45(2016) 2308-2326.

[15] R. Liu, H. H. Liu, Z. Ji, C. H. Chang, T. Xia, A. E. Nel, Cohen, Y. Evaluation of toxicity ranking for metal oxide nanoparticles via an in vitro dosimetry model, *ACS Nano* 9(2015) 9303-9313.

[16] A. Merkoci, Nanoparticles-based strategies for DNA, protein and cell sensors, *Biosens. Bioelectron*. 26(2010) 1164-1177.

[17] S. Nambiar, J. T. Yeow, Conductive polymer-based sensors for biomedical applications, *Biosens. Bioelectron.* 26(2011) 1825-1832.

[18] R. Balint, N. J. Cassidy, S. H. Cartmell, Conductive polymers: towards a smart biomaterial for tissue engineering, *Acta Biomater.* 10(2014) 2341-2353.

[19] A. Walcarius, Mesoporous materials and electrochemistry, *Chem. Soc. Rev.* 42(2013) 4098-4140.

[20] A. Trifonov, K. Herkendell, R. Tel-Vered, O. Yehezkeli, M. Woerner, I. Willner, Enzyme-capped relay-functionalized mesoporous carbon nanoparticles: effective bioelectrocatalytic matrices for sensing and biofuel cell applications, *ACS Nano* 7(2013) 11358-11368.

[21] C. B. Liu, X. Y. Chen, B. Y. Zong, S. Mao, Recent advances in sensitive and rapid mercury determination with graphene-based sensors, *J. Mater. Chem. A* 7(2019) 6616-6630.

[22] J. Ping, Y. Wang, J. Wu, Y. Ying, Development of an electrochemically reduced graphene oxide modified disposable bismuth film electrode and its application for stripping analysis of heavy metals in milk, *Food Chem.* 151(2014) 65-71.

[23] P. K. Sahoo, B. Panigrahy, S. Sahoo, A. K. Satpati, D. M. Li, D. Bahadur, In situ synthesis and properties of reduced graphene oxide/Bi nanocomposites: as an electroactive material for analysis of heavy metals, *Biosens. Bioelectron.* 43(2013) 293-296.

[24] H. Huang, T. Chen, X. Liu, H. Ma, Ultrasensitive and simultaneous detection of heavy metal ions based on three-dimensional graphene-carbon nanotubes hybrid electrode materials, *Anal. Chim. Acta* 852(2014) 45-54.

[25] M. Yu, J. Chen, J. Liu, S. Li, Y. Ma, J. Zhang, J. An, Mesoporous $NiCo_2O_4$ nanoneedles grown on 3D graphene-nickel foam for supercapacitor and methanol electro-oxidation, *Electrochim. Acta* 151(2015) 99-108.

[26] Z. Q. Zhao, X. Chen, Q. Yang, J. H. Liu, X. J. Huang, Selective adsorption toward toxic metal ions results in selective response: electrochemical studies on a polypyrrole/reduced graphene oxide nanocomposite, *Chem. Commun.* 48(2012) 2180-2182.

[27] X. M. Feng, R. M. Li, Y. W. Ma, R. F. Chen, N. E. Shi, Q. L. Fan, W. Huang, One-Step Electrochemical synthesis of graphene/polyaniline composite film and its applications, *Adv. Funct. Mater.* 21(2011) 2989-2996.

[28] N. Promphet, P. Rattanarat, R. Rangkupan, O. Chailapakul, N. Rodthongkum, An electrochemical sensor based on graphene/polyaniline/polystyrene nanoporous fibers modified electrode for simultaneous determination of lead and cadmium, Sens. *Actuator B-Chem.* 207(2015) 526-534.

[29] X. Gong, Y. Bi, Y. Zhao, C. Liu, W. Y. Teoh, Graphene oxide-based electrochemical sensor: a platform for ultrasensitive detection of heavy metal ions, *RSC Adv.* 4(2014) 24653.

[30] L. Chen, Y.Tang, K. Wang, C. Liu, S. Luo, Direct electrodeposition of reduced graphene oxide on glassy carbon electrode and its electrochemical application, *Electrochem. Comm.* 13(2011) 133-137.

[31] Y. Zhang, G. M. Zeng, L. Tang, J. Chen, Y. Zhu, X. X. He, Y. B. He, Electrochemical sensor based on electrodeposited graphene-Au modified electrode and nanoAu carrier

amplified signal strategy for attomolar mercury detection, *Anal. Chem.* 87(2015) 989-996.

[32] V. Georgakilas, J. A. Perman, J. Tucek, R. Zboril, Broad family of carbon nanoallotropes: classification, chemistry, and applications of fullerenes, carbon dots, nanotubes, graphene, nanodiamonds, and combined superstructures, *Chem. Rev.* 115(2015) 4744-4822.

[33] H. J. Peng, J. Q. Huang, M. Q. Zhao, Q. Zhang, X. B. Cheng, X. Y. Liu, W. Z. Qian, F. Wei, Nanoarchitectured graphene/CNT@porous carbon with extraordinary electrical conductivity and interconnected micro/mesopores for lithium-sulfur batteries, *Adv. Funct. Mater.* 24(2014) 2772-2781.

[34] N. J. Kybert, M. B. Lerner, J. S. Yodh, G. Preti, A. T. C. Johnson, Differentiation of complex vapor mixtures using versatile DNA-carbon nanotube chemical sensor arrays, *ACS Nano* 7(2013) 2800-2807.

[35] X. Y. Chen, G. H. Zhou, S. Mao, J. H. Chen, Rapid detection of nutrients with electronic sensors: a review, Environ. Sci. Nano. 5(2018) 837-862.

[36] Q. Liu, J. He, T. Yao, Z. Sun, W. Cheng, S. He, Y. Xie, Y. Peng, H. Cheng, Y. Sun, Y. Jiang, F. Hu, Z. Xie, W. Yan, Z. Pan, Z. Wu, S. Wei, Aligned Fe_2TiO_5-containing nanotube arrays with low onset potential for visible-light water oxidation, *Nat. Comm.* 5(2014) 5122.

[37] S. Yao, J. Yuan, H. A. Mehedi, E. Gheeraert, A. Sylvestre, Carbon nanotube forest based electrostatic capacitor with excellent dielectric performances, *Carbon* 116(2017) 648-654.

[38] H. Yin, Y. Zhou, J. Xu, S. Ai, L. Cui. L. Zhu, Amperometric biosensor based on tyrosinase immobilized onto multiwalled carbon nanotubes-cobalt phthalocyanine-silk fibroin film and its application to determine bisphenol A, *Anal. Chim. Acta* 659, (2010) 144-150.

[39] O. G. Apul, T. Karanfil, Adsorption of synthetic organic contaminants by carbon nanotubes: a critical review, *Water Res*. 68(2015) 34-55.

[40] Z. Syrgiannis, A. Bonasera, E. Tenori, V. La Parola, C. Hadad, M. Gruttadauria, F. Giacalone, M. Prato, Chemical modification of carbon nanomaterials (SWCNTs, DWCNTs, MWCNTs and SWCNHs) with diphenyl dihalogenides, *Nanoscale* 7(2015) 6007-6013.

[41] J. L. Gong, B. Wang, G. M. Zeng, C. P. Yang, C. G. Niu, Q. Y. Niu, W. J. Zhou, Y. Liang, Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent, *J. Hazard. Mater*. 164(2009) 1517-1522.

[42] H. Zhao, B. Rizal, C. McMahon, H. Wang, P. Dhakal, T. Kirkpatrick, Z. Ren, T. C. Chiles, M. J. Naughton, D. Cai, Ultrasensitive chemical detection using a nanocoax sensor, *ACS Nano* 6(2012) 3171-3178.

[43] S. Kabiri, D. N. H. Tran, T. Altalhi, D. Losic, Outstanding adsorption performance of grapheme-carbon nanotube aerogels for continuous oil removal, *Carbon* 80(2014) 523-533.

[44] J. Lin, Z. Wei, H. Zhang, M. Shao, Sensitive immunosensor for the label-free determination of tumor marker based on carbon nanotubes/mesoporous silica and graphene modified electrode. *Biosens. Bioelectron.* 41(2013) 342-347.

[45] S. A. Miners, G. A. Rance, A. N. Khlobystov, Chemical reactions confined within carbon nanotubes, *Chem. Soc. Rev.* 45(2016) 4727-4746.

[46] Y. Zhu, G. M. Zeng, Y. Zhang, L. Tang, J. Chen, M. Cheng, L. H. Zhang, L. He, Y. Guo, X. X. He, M. Y. Lai, Y. B. He, Sensitive electrochemical sensor using a MWCNTs/GNPs-modified electrode for lead (II) detection based on Pb(2+)-induced G-rich DNA conformation, *Analyst*139(2014) 5014-5020.

[47] Y. Zhang, G. M. Zeng, L. Tang, Y. P. Li, L. J. Chen, Y. Pang, Z. Li, C. L. Feng, G. H. Huang, An electrochemical DNA sensor based on a layers-film construction modified electrode, *Analyst* 136(2011) 4204-4210.

[48] K. Wang, S. Luo, Y. Wu, X. He, F. Zhao, J. Wang, F. Jiang, S. Fan, Super-aligned carbon nanotube films as current collectors for lightweight and flexible Lithium ion batteries, *Adv. Funct. Mater.* 23(2013) 846-853.

[49] K. Lee, A. Mazare, P. Schmuki, One-dimensional titanium dioxide nanomaterials: nanotubes, *Chem. Rev.* 114(2014), 9385-9454.

[50] K. Komori, T. Terse-Thakoor, A. Mulchandani, Bioelectrochemistry of heme peptide at seamless three-dimensional carbon nanotubes/graphene hybrid films for highly sensitive electrochemical biosensing, *ACS Appl. Mater. Interfaces* 7(2015) 3647-3654.

[51] F. Yang, J. Han, Y. Zhuo, Z. Yang, Y. Chai, R. Yuan, Highly sensitive impedimetric immunosensor based on single-walled carbon nanohorns as labels and bienzyme

biocatalyzed precipitation as enhancer for cancer biomarker detection, *Biosens. Bioelectron.* 55(2014) 360-365.

[52] Y. Cao, R. Yuan, Y. Chai, L. Mao, H. Liu, H. Liu, Y. Zhuo, Ultrasensitive luminol electrochemiluminescence for protein detection based on in situ generated hydrogen peroxide as coreactant with glucose oxidase anchored AuNPs@MWCNTs labeling, *Biosens. Bioelectron.* 31(2012) 305-309.

[53] L. Zhang, T. Li, B. Li, J. Li, E. Wang, Carbon nanotube-DNA hybrid fluorescent sensor for sensitive and selective detection of mercury(II) ion, *Chem. Commun.* 46(2010) 1476-1478.

[54] J. L. Jun, Z. W. Zhu, J. W. Di, Y. M. Long, W. F. Li, Y. F. Tu, A sensitive sensor for trace Hg^{2+} determination based on ultrathin g-C_3N_4 modified glassy carbon electrode, *Electrochim. Acta* 186(2015) 192-200.

[55] T. Y. Ma, Y. H. Tang, S. Dai, S. Z. Qiao, Proton-functionalized two-dimensional graphitic carbon nitride nanosheet: an excellent metal-/label-free biosensing platform, *Small* 12(2014) 2382-2389.

[56] Z. X. Zhou, Y. Y. Zhang, Y. F. Shen, S. Q. Liu, Y. J. Zhang, Molecular engineering of polymeric carbon nitride: advancing applications from photocatalysis to biosensing and more, *Chem. Soc. Rev.* 47(2018)2298-2321.

[57] G. h. Dong, K. Zhao, L. Z. Zhang, Carbon self-doping induced high electronic conductivity and photoreactivity of g-C_3N_4, *Chem. Commun.* 48(2012) 6178-6180.

[58] F. Li, H. S. Yin, Y. Chen, S. Y. Wang, J. Y. Li, Y. M. Zhang, C. X. Li, S. Y. Ai, Preparation of P-g-C_3N_4-WS2 nanocomposite and its application in

photoelectrochemical detection of 5-formylcytosine, *J. Colloid. Interface. Sci.* 56(2020) 348-357.

[59] A. Mohammad, M. E. Kan, M. H. Cho, Sulfur-doped-graphitic-carbon nitride (S-g-C_3N_4) for low cost electrochemical sensing of hydrazine, *J. Alloy. Compd.* 816(2020) 152522-152531.

[60] L. C. Chen, X. T. Zeng, P. Si, Y. M. Chen, Y. W. Chi, D. H. Kim, G. N. Chen, Gold nanoparticle-graphite-Like C_3N_4 nanosheet nanohybrids used for electrochemiluminescent immunosensor, *Anal. Chem*. 86(2014) 4188-4195.

[61] C. J. Sui, H. W. Wan, H. S. Yin, S. R. Zhang, G. L. N. Watenhouse, J. Wang, L. S. Zhu, S. Y. Ai, Photoelectrochemical biosensor for 5-mC detection based on the photocurrent inhibition effect of ZnO on MoS_2/C_3N_4 heterojunction, *Biosens. Bioelectron.* 142(2019) 111516-111522.

[62] S. Mao, J. B. Chang, G. H. Zhou, J. H. Chen, Nanomaterial-enabled rapid detection of water contaminants, *Small* 11(2015) 5336-5359.

[63] D. D. Han, S. S. Li, Z. Guo, X. Chen, J. H. Liu, X. J. Huang, Shape dependent stripping behavior of Au nanoparticles toward arsenic detection: evidence of enhanced sensitivity on the Au (III) facet, *RSC Adv.* 6(2016) 30337-30344.

[64] J. Z. James, D. Lucas, C. P. Koshland, Gold nanoparticle films as sensitive and reusable elemental mercury sensors, *Environ, Sci. Technol.* 46(2012) 9557-9562.

[65] X. J. Hu, J. S. Wang, Y. G. Liu, X. Li, G. M. Zeng, Z. L. Bao, X. X. Zeng, A. W. Chen, F. Long, Adsorption of chromium (VI) by ethylenediamine-modified cross-

linked magnetic chitosan resin: Isotherms, kinetics and thermodynamics, *J. Hazard. Mater.* 185(2011) 306-314.

[66] P. Miao, Y. G. Tang, L. Wang, DNA Modified Fe_3O_4@Au magnetic nanoparticles as selective probes for simultaneous detection of heavy metal ions, *ACS Appl. Mater. Interfaces* 9(2017) 3940-3947.

[67] Y. Zhang, G. M. Zeng, L. Tang, D. L. Huang, X. Y. Jiang, Y. N. Chen, A hydroquinone biosensor using modified core-shell magnetic nanoparticles supported on carbon paste electrode, *Biosens. Bioelectron.* 22(2007) 2121-2126.

[68] T. O. Ahmadov, P. Joshi, J. Zhang, K. Nahan, J. A. Caruso, H. Zhang, Paramagnetic relaxation based biosensor for selective dopamine detection, *Chem. Comm.* 51(2015) 11425-11428.

[69] Y. Niu, W. Jiao, R. Wang, G. Ding, Y. Huang, Hybrid nanostructures combining graphene-MoS_2 quantum dots for gas sensing, *J. Mater. Chem. A* 4(2016) 8198-8203.

[70] M. Park, H. D. Ha, Y. T. Kim, J. H. Jung, S. H. Kim, D H. Kim, T. S. Seo, Combination of a Sample Pretreatment Microfluidic Device with a Photoluminescent Graphene Oxide Quantum Dot Sensor for Trace Lead Detection, *Anal. Chem.* 87, (2015) 10969-10975.

[71] L. Zhang, X. Z. Cheng, L. Kuang, A. Z. Xu, R. P. Liang, J. D. Qiu, Simple and highly selective detection of arsenite based on the assembly-induced fluorescence enhancement of DNA quantum dots, *Biosens. Bioelectron.* 94(2017) 701-706.

[72] S. Liu, F. Shi, L. Chen, X. Su, Bovine serum albumin coated $CuInS_2$ quantum dots as a near-infrared fluorescence probe for 2,4,6-trinitrophenol detection, *Talanta* 116(2013) 870-875.

[73] C. Zhang, Y. Han, L. Lin, N. Deng, B. Chen, Y. Liu, Development of quantum dots-labeled antibody fluorescence immunoassays for the detection of morphine, J. Agri. *Food Chem.* 65(2017) 1290-1295.

[74] D. W. Huang, C. G. Niu, X. Y. Wang, X X. Lv, G. M. Zeng, "Turn-on" fluorescent sensor for Hg^{2+} based on single-stranded DNA functionalized Mn:CdS/ZnS quantum dots and gold nanoparticles by time-gated mode, *Anal. Chem.* 85(2013) 1164-1170.

[75] R. Freeman, T. Finder, I. Willner, Multiplexed analysis of Hg^{2+} and Ag^{+} ions by nucleic acid functionalized CdSe/ZnS quantum dots and their use for logic gate operations, *Angew. Chem.* 121(2009) 7958-7961.

[76] X. Cui, L. Zhu, J. Wu, Y. Hou, P. Wang, Z. Wang, M.Yang, A fluorescent biosensor based on carbon dots-labeled oligodeoxyribonucleotide and graphene oxide for mercury(II) detection, *Biosens. Bioelectron.* 63(2015) 506-512.

[77] J. S. Lee, D. H. Shin, J. Jun, J. Jang, Multidimensional polypyrrole/iron oxyhydroxide hybrid nanoparticles for chemical nerve gas agent sensing application, *ACS Nano* 7(2013) 10139-10147.

[78] S. Radhakrishnan, K. Krishnamoorthy, C. Sekar, J. Wilson, S. J. Kim, A promising electrochemical sensing platform based on ternary composite of polyaniline-Fe_2O_3-reduced graphene oxide for sensitive hydroquinone determination,*Chem. Engineer. J.* 259(2015) 594-602.

[79] H. Li, J. Chang, T. Hou, F. Li, HRP-mimicking DNAzyme-catalyzed in situ generation of polyaniline to assist signal amplification for ultrasensitive surface plasmon resonance biosensing, *Anal Chem.* 89(2017) 673-680.

[80] Y. Lu, Y. Li, G. Wang, W. Tang, A highly sensitive and selective optical sensor for Pb^{2+} by using conjugated polymers and label-free oligonucleotides, *Biosens. Bioelectron.* 39(2013) 231-235.

[81] Y. Yang, Y. Cao, X. Wang, G. Fang, S. Wang, Prussian blue mediated amplification combined with signal enhancement of ordered mesoporous carbon for ultrasensitive and specific quantification of metolcarb by a three-dimensional molecularly imprinted electrochemical sensor, *Biosens. Bioelectron.* 64(2015) 247-254.

[82] Y. Zhou, L. Tang, G. M. Zeng, J. Chen, Y. Cai, Y. Zhang, G. D. Yang, Y. Liu, C. Zhang, W. Tang, Mesoporous carbon nitride based biosensor for highly sensitive and selective analysis of phenol and catechol in compost bioremediation, *Biosens. Bioelectron.* 61(2014) 519-525.

[83] Y. Zhou, L. Tang, G. M. Zeng, J. Chen, J. J. Wang, C. Fan, G. D. Yang, Y. Zhang, X. Xie, Amplified and selective detection of manganese peroxidase genes based on enzyme-scaffolded-gold nanoclusters and mesoporous carbon nitride, *Biosens Bioelectron.* 65(2015) 382-389.

[84] A. Vu, J. Phillips, P. Bühlmann, A. Stein, Quenching performance of surfactant-containing and surfactant-free fluorophore-doped mesoporous silica films for nitroaromatic compound detection, *Chem. Mater.* 25(2013) 711-722.

[85] I. Gammoudi, L. Blanc, F. Morote, C. Grauby-Heywang, C. Boissiere, R. Kalfat, D. Rebiere, T. Cohen-Bouhacina, C. Dejous, High sensitive mesoporous TiO_2-coated love wave device for heavy metal detection, *Biosens. Bioelectron.* 57(2014) 162-170.

[86] Y. Zhang, G. M. Zeng, L. Tang, Y. P. Li, Z. M. Chen, G. H. Huang, Quantitative detection of trace mercury in environmental media using a three-dimensional electrochemical sensor with an anionic intercalator., *RSC Adv.* 4(2014) 18485.

[87] Z. H. Lin, G. Zhu, Y. S. Zhou, Y. Yang, P. Bai, J. Chen, Z. L. Wang, A self-powered triboelectric nanosensor for mercury ion detection, A*ngew. Chem. Int. Edit.* 52(2013) 5065-5069.

[88] Z. Zhu, Z. Guan, S. Jia, Z. Lei, S. Lin, H. Zhang, Y. Ma, Z. Q. Tian, C. J. Yang, Au@Pt nanoparticle encapsulated target-responsive hydrogel with volumetric bar-chart chip readout for quantitative point-of-care testing, *Angew. Chem.-Int. Edit.* 53(2014) 12503-12507.

[89] Y. Huang, Y. Ma, Y. Chen, X. Wu, L. Fang, Z. Zhu, C. J. Yang, Target-responsive DNAzyme cross-linked hydrogel for visual quantitative detection of lead, *Anal. Chem.* 86(2014) 11434-11439.

[90] Y. Huang, L. Fang, Z. Zhu, Y. Ma, L. Zhou, X. Chen, D. Xu, C. Yang, Design and synthesis of target-responsive hydrogel for portable visual quantitative detection of uranium with a microfluidic distance-based readout device, *Biosens. Bioelectron.* 85(2016) 496-502.

[91] Q. Sun, Q., Chen, Q., Blackstock, D., Chen, W. Post-Translational Modification of Bionanoparticles as a Modular Platform for Biosensor Assembly. *ACS Nano* **2015**, 9(2015) 8554-8561.

[92] B. Zhuo, Y. Li, A. Zhang, F. Lu, Y. Chen, W. Gao, An electrochemiluminescence biosensor for sensitive and selective detection of Hg^{2+} based on π-π interaction between nucleotides and ferrocene-graphene nanosheets, *J. Mater. Chem. B* 2(20154) 3263.

[93] J. Zhang, Y. Xiang, M. Wang, A. Basu, Y. Lu, Dose-dependent response of personal glucose meters to nicotinamide coenzymes: applications in point-of-care diagnostics of many non-glucose targets in a single step, *Angew. Chem.-Int. Edit.* 55(2016) 732-736.

[94] Y. Xiang, Y. Lu, Using personal glucose meters and functional DNA sensors to quantify a variety of analytical targets, *Nat. Chem.* 3(2011) 697-703.

[95] Q. Wang, H. Wang, X. Yang, K. Wang, R. Liu, Q. Li, J., Ou, A sensitive one-step method for quantitative detection of alpha-amylase in serum and urine using a personal glucose meter, *Analyst* 140(2015) 1161-1165.

[96] X. Liang, L. Wang, D. Wang, L. Zeng, Z. Fang, Portable and quantitative monitoring of mercury ions using DNA-gated mesoporous silica nanoparticles using a glucometer readout, *Chem. Comm.* 52(2016) 2192-2194.

[97] J. Han, K. Burgess, Fluorescent indicators for intracellular pH, *Chem. Rev.* 110(2010) 2709-2728.

[98] S. Silvi, A. Credi, Luminescent sensors based on quantum dot-molecule conjugates, *Chem. Soc. Rev.* 44(2015) 4275-4289.

[99] K. Saha, S. S. Agasti, C. Kim, X. Li, V. M. Rotello, Gold nanoparticles in chemical and biological sensing, *Chem. Rev.* 112(2012) 2739-2779.

[100] S. Dutta, N. Mandal, D. Bandyopadhyay, Paper-based alpha-amylase detector for point-of-care diagnostics, *Biosens. Bioelectron.* 78(2016) 447-453.

[101] D. Liu, J. Yang, H. F. Wang, Z. Wang, X. Huang, Z. Wang, G. Niu, A. R. Hight Walker, X. Chen, Glucose oxidase-catalyzed growth of gold nanoparticles enables quantitative detection of attomolar cancer biomarkers, *Anal. Chem.* 86(2014) 5800-5806.

[102] D. Chen, J. Wang, Y. Xu, D. Li, L. Zhang, Z. Li, Highly sensitive detection of organophosphorus pesticides by acetylcholinesterase-coated thin film bulk acoustic resonator mass-loading sensor, *Biosens. Bioelectron.* 41(2013) 163-167.

[103] Z. Xu, Y. Dong, J. Li, R. Yuan, A ferrocene-switched electrochemiluminescence "off-on" strategy for the sensitive detection of cardiac troponin I based on target transduction and a DNA walking machine, *Chem. Comm.* 51(2015) 14369-14372.

[104] H. Abdolmohammad-Zadeh, E. Rahimpour, A novel chemosensor based on graphitic carbon nitride quantum dots and potassium ferricyanide chemiluminescence system for Hg(II) ion detection. *Sens. Actuator B-Chem.* 225(2016) 258-266.

[105] Y. Wu, S. Zhan, H. Xing, L. He, L. Xu, P. *Zhou*, Nanoparticles assembled by aptamers and crystal violet for arsenic(III) detection in aqueous solution based on a resonance Rayleigh scattering spectral assay, *Nanoscale* 4(2012) 6841-6849.

[106] Y. Lin, Q. Zhou, Y. Lin, D. Tang, R. Niessner, D. Knopp, Enzymatic hydrolysate-induced displacement reaction with multifunctional silica beads doped with horseradish peroxidase-thionine conjugate for ultrasensitive electrochemical immunoassay, *Anal. Chem.* 87(2015) 8531-8540.

[107] Y. He, Y. Wang, X. Yang, S. Xie, R. Yuan, Y. Chai, Metal organic frameworks combining $CoFe_2O_4$ magnetic nanoparticles as highly efficient SERS sensing platform for ultrasensitive detection of N-terminal pro-brain natriuretic peptide, *ACS Appl. Mater. Interfaces* 8(2016) 7683-7690.

[108] Y. Zhang, C. Qian, G. M. Zeng, L. Tang, C. Zhang, Y. Zhu, G. L. Feng, Y. Y. Liu, Effects of functionalized electrodes and gold nanoparticle carrier signal amplification on an electrochemical DNA sensing strategy, *ChemElectroChem* (2016) 1868-1874.

[109] G. M. Zeng, Y. Zhu, Y. Zhang, C. Zhang, L. Tang, P. C. Guo, L. H. Zhang, Y. J. Yuan, M. Cheng, C. Yang, Electrochemical DNA sensing strategy based on strengthening electronic conduction and a signal amplifier carrier of nanoAu/MCN composited nanomaterials for sensitive lead detection, *Environ.-Sci. Nano* 3(2016) 1504-1509.

[110] D. W. Huang, C. G. Niu, M. Ruan, X. Wang, G. M. Zeng, C. Deng, Highly sensitive strategy for Hg^{2+} detection in environmental water samples using long lifetime fluorescence quantum dots and gold nanoparticles, *Environ. Sci. Technol.* 47(2013) 4392-4398.

[111] X. Yang, J. Xu, X. Tang, H. Liu, D. Tian, A novel electrochemical DNAzyme sensor for the amplified detection of Pb^{2+} ions, *Chem. Commun.* 46(2010) 3107-3109.

[112] Y. Zhang, G. M. Zeng, L. Tang, C. G. Niu, Y. Pang, J. Chen, C. L. Feng, G. H. Huang, Highly sensitive fluorescence quantification of picloram using immunorecognition liposome, *Talanta* 83(2010) 210-215.

[113] H. Xu, P. Xu, S. Gao, S. Zhang, X. Zhao, C. Fan, X. Zuo, Highly sensitive recognition of Pb(2+) using Pb(2+) triggered exonuclease aided DNA recycling, *Biosens. Bioelectron*. 47(2013) 520-523.

[114] X. B. Zhang, Z. Wang, H. Xing, Y. Xiang, Y. Lu, Catalytic and molecular beacons for amplified detection of metal ions and organic molecules with high sensitivity, *Anal. Chem*. 82(2010) 5005-5011.

[115] J. Lee, E. K. Song, Y. Bae, J. Min, H. W. Rhee, T. J. Park, M. Kim, S. Kang, An enhanced ascorbate peroxidase 2/antibody-binding domain fusion protein (APEX2-ABD) as a recombinant target-specific signal amplifier, *Chem. Commun*. 51(2015) 10945-10948.

[116] Y. Cheng, H. He, C. Yang, G. Zeng, X. Li, H. Chen, G. Yu, Challenges and solutions for biofiltration of hydrophobic volatile organic compounds, *Biotechnol. Adv.* 34(2016) 1091-1102.

[117] L. Tang, G. M. Zeng, G. L. Shen, Y. P. Li, Y. Zhang, D. L. Huang, Rapid detection of picloram in agricultural field samples using a disposable immunomembrane-based electrochemical sensor, *Environ. Sci. Technol.* 42(2008) 1207-1212.

[118] D. L. Huang, G. M. Zeng, C. L. Feng, S. Hu, X. Y. Jiang, L. Tang, F. F. Su, Y. Zhang, W. Zeng, H. L. Liu, Degradation of lead-contaminated lignocellulosic waste

by phanerochaete chrysosporium and the reduction of lead toxicity, *Environ. Sci. Technol.* 42(2008) 4946-4951.

[119] C. Liu, Y. Sheng, Y. Sun, J. Feng, S. Wang, J. Zhang, J. Xu, D. Jiang, A glucose oxidase-coupled DNAzyme sensor for glucose detection in tears and saliva, Biosens Bioelectron. 70(2015) 455-461.

[120] P. Raghu, T. Madhusudana Reddy, K. Reddaiah, B. E. Kumara Swamy, M. Sreedhar, Acetylcholinesterase based biosensor for monitoring of Malathion and Acephate in food samples: a voltammetric study, *Food Chem.* 142(2014) 188-196.

[121] G. M. Zeng, M. Chen, Z. T. Zeng, Risks of neonicotinoid pesticides, *Science* 340(2013) 1403.

[122] Y. Liu, X. Liu, Z. Guo, Z. Hu, Z. Xu, X. Lu, Horseradish peroxidase supported on porous graphene as a novel sensing platform for detection of hydrogen peroxide in living cells sensitively, *Biosens. Bioelectron.* 87(2017) 101-107.

[123] H. B. Noh, Y. B. Shim, Catalytic activity of polymerized self-assembled artificial enzyme nanoparticles: applications to microfluidic channel-glucose biofuel cells and sensors, *J. Mater. Chem. A* 4(2016) 2720-2728.

[124] A. B. Chinen, C. M. Guan, J. R. Ferrer, S. N. Barnaby, T. J. Merkel, C. A. Mirkin, Nanoparticle probes for the detection of cancer biomarkers, cells, and tissues by fluorescence, *Chem. Rev.* 115(2015) 10530-10574.

[125] R. Li, K. Wu, C. Liu, Y. Huang, Y. Wang, H. Fang, H. Zhang, C. Li, 4-Amino-1-(3-mercapto-propyl)-pyridine hexafluorophosphate ionic liquid functionalized gold

nanoparticles for IgG immunosensing enhancement, *Anal. Chem.* 86 (2014) 5300-5307.

[126] C. Fu, Y. Wang, G. Chen, L. Yang, S. Xu, W. Xu, Aptamer-based surface-enhanced Raman scattering-microfluidic sensor for sensitive and selective polychlorinated biphenyls detection, *Anal. Chem.* 87(2015) 9555-9558.

[127] X. Ni, B. Xia, L. Wang, J. Ye, G. Du, H. Feng, X. Zhou, T. Zhang, W. Wang, Fluorescent aptasensor for 17beta-estradiol determination based on gold nanoparticles quenching the fluorescence of Rhodamine B, *Anal. Biochem.* 523(2017) 17-23.

[128] S. U. Akki, C. J. Werth, S. K. Silverman, Selective aptamers for detection of estradiol and ethynylestradiol in natural waters, *Environ. Sci. Technol.* 49(2015) 9905-9913.

[129] A. S. Emrani, N. M. Danesh, M. Lamezani, S. M. Taghdisi, K. A. Abnous, Novel fluorescent aptasensor based on hairpin structure of complementary strand of aptamer and nanoparticles as a signal amplification approach for ultrasensitive detection of cocaine, *Biosens. Bioelectron.* 79(2016) 288-293.

[130]S. Amiri, A. Navaee, A. Salimi, R. Ahmadi, Zeptomolar detection of Hg^{2+} based on label-free electrochemical aptasensor: One step closer to the dream of single atom detection, *Electrochem, Comm.* 78(2017) 21-25.

[131] Y. Xiang, Y. Lu, An invasive DNA approach toward a general method for portable quantification of metal ions using a personal glucose meter, *Chem. Commun.* 49(2013) 585-587.

[132] S. Lin, W. Wang, C. Hu, G. Yang, C. N. Ko, K. Ren, C. H. Leung, D. L. Ma, The application of a G-quadruplex based assay with an iridium(III) complex to arsenic ion detection and its utilization in a microfluidic chip, *J. Mater. Chem. B* 5(2017) 479-484.

[133] I. M. El-Sherbiny, A. Hefnawy, E. Salih, New core-shell hyperbranched chitosan-based nanoparticles as optical sensor for ammonia detection, *Int. J. Biol. Macromol.* 86(2016) 782-788.

[134] Y. C. Yang, W. L.Tseng, 1,4-benzenediboronic-acid-induced aggregation of gold nanoparticles: application to hydrogen peroxide detection and biotin-avidin-mediated immunoassay with naked-eye detection, *Anal. Chem.* 88(2016) 5355-5362.

[135] F. Hasebe, K. Matsuda, T. Shiraishi, T. Futamura, T. Nakano, T. Tomita, K. Ishigami, H. Taka, R. Mineki, T. Fujimura, H. Osada, T. Kuzuyama, M. Nishiyama, Amino-group carrier-protein-mediated secondary metabolite biosynthesis in Streptomyces, *Nat. Chem. Biol.* 12(2016) 967-972.

[136] Y. R. Wang, Y. Zhu, Y. Hu, C. M. Zeng, Y. Zhang, C. Zhang, C. L. Feng, How to construct DNA hydrogels for environmental applications: Advanced water treatment and environmental analysis, *Small* 14(2018) 1703305.

[137] D. Yuan, A. H. Anthis, M. Ghahraman Afshar, N. Pankratova, N. Cuartero, G. A. Crespo, E. Bakker, All-solid-state potentiometric sensors with a multiwalled carbon nanotube inner transducing layer for anion detection in environmental samples, *Anal. Chem.* 87(2015) 8640-8645.

[138] M. Havlik, M. Marchetti-Deschmann, G. Friedbacher, W. Winkler, P. Messner, L. Perez-Burgos, C. Tauer, G. Allmaier, Comprehensive size-determination of whole

virus vaccine particles using gas-phase electrophoretic mobility macromolecular analyzer, atomic force microscopy, and transmission electron microscopy, *Anal Chem*. 87(2015) 8657-8664.

[139] J. S. Gois, T. S. Almeida, J. C. Alves, R. G. Araujo, D. L. Borges, Assessment of the halogen content of brazilian inhalable particulate matter (PM10) using high resolution molecular absorption spectrometry and electrothermal vaporization inductively coupled plasma mass spectrometry, with direct solid sample analysis, *Environ. Sci. Technol.* 50(2015) 3031-3038.

[140] C. Gu, T. Lan, H. Shi, Y. Lu, Portable Detection of Melamine in milk using a personal glucose meter based on an in vitro selected structure-switching aptamer, *Anal Chem.* 87(2016) 7676-7682.

[141] X. Wei, T. Tian, S. Jia, Z. Zhu, Y. Ma, J. Sun, Z. Lin, C. J. Yang, Target-responsive DNA hydrogel mediated "stop-flow" microfluidic paper-based analytic device for rapid, portable and visual detection of multiple targets, *Anal. Chem.* 87(2015) 4275-4282.

[142] O. Modin, B. M. Wilen, A novel bioelectrochemical BOD sensor operating with voltage input, *Water Res.* 46, (2012) 6113-6120.

[143] X. Jin, I. Angelidaki, Y. Zhang, Microbial electrochemical monitoring of volatile fatty acids during anaerobic digestion, *Environ. Sci. Technol*. 50(2016) 4422-4429.

[144] Y. Li, W. Luo, N. Qin, J. Dong, J. Wei, W. Li, S. Feng, J. Chen, J. Xu, A. A. Elzatahry, M. H. Es-Saheb, Y. Deng, D. Zhao, Highly ordered mesoporous tungsten

oxides with a large pore size and crystalline framework for H_2S sensing, *Angew. Chem.-Int. Edit.* 53(2014) 9035-9040.

[145] S. M. Rosolina, T. S. Carpenter, Z. L. Xue, Bismuth-based, disposable sensor for the detection of hydrogen sulfide gas, *Anal Chem.* 88(2016) 1553-1558.

[146] J. Huang, X. Gao, J.Jia, J. K. Kim, Z. Li, Graphene oxide-based amplified fluorescent biosensor for Hg(2+) detection through hybridization chain reactions, *Anal Chem*. 86(2014) 3209-3215.

[147] S. H. Chiu, P. L. Urban, Robotics-assisted mass spectrometry assay platform enabled by open-source electronics, *Biosens. Bioelectron.* 64(2015) 260-268.

[148] S. Yagur-Kroll, E. Schreuder, C. J. Ingham, R. Heideman, R. Rosen, S. Belkin, A miniature porous aluminum oxide-based flow-cell for online water quality monitoring using bacterial sensor cells, *Biosens. Bioelectron.* 64(2015) 625-632.

[149] C. Sicard, C. Glen, B. Aubie, D. Wallace, S. Jahanshahi-Anbuhi, K. Pennings, G. T. Daigger, R. Pelton, J. D. Brennan, C. D. Filipe, Tools for water quality monitoring and mapping using paper-based sensors and cell phones, *Water Res.* 70(2015) 360-369.

[150] A. Santos, G. Macias, J. Ferre-Borrull, J. Pallares, L. F. Marsal, Photoluminescent enzymatic sensor based on nanoporous anodic alumina, *ACS Appl. Mater. Interfaces* 4(2012) 3584-3588.

[151] A. H. Hade, D. M. K. Sengupta, Automatic control of drip Irrigation system&monitoring of soil by wireless, *IOSR J. Agri. Vet. Sci.* 7(2014) 57-61.

[152] I. Taurino, A. Magrez, F. Matteini, A. Cavallini, L. Forro, G. D. Micheli, S. Carrara, High-performance multipanel biosensors based on a selective integration of nanographite petals, *Nano Lett.* 14(2014) 3180-3184.

[153] G. M. Zeng, M. Chen, Z. T. Zeng, Shale gas: surface water also at risk, *Nature* 499 (2013) 154.

[154] F. L. Meng, L. Zhang, Y. Jia, J. Y. Liu, Y. F. Sun, T. Luo, M. Q. Li, J. H. Liu, X. J. Huang, Electronic chip based on self-oriented carbon nanotube microelectrode array to enhance the sensitivity of indoor air pollutants capacitive detection, *Sens. Actuator B-Chem*. 153(2011) 103-109.

[155] X. Li, Y. Tian, P. Xia, Y. Luo, Q. Rui, Fabrication of TiO_2 and metal nanoparticle-microelectrode arrays by photolithography and site-selective photocatalytic deposition, *Anal. chem*. 81(2009) 8249-8255.

[156] X. Y. Chen, C. B. Liu, S. Mao, Environmental analysis with 2D transition-metal dichalcogenide-based field-effect transistors, *Nano-Micro Lett*. 12(2020) 95.

[157] J. S. Kim, H. W. Yoo, H. O. Choi, H. T. Jung, Tunable volatile organic compounds sensor by using thiolated ligand conjugation on MoS_2, *Nano Lett.* 14(2014) 5941-5947.

[158] L. Amato, A. Heiskanen, R. Hansen, L. Gammelgaard, T. Rindzevicius, M. Tenje, J. Emnéus, S. S. Keller, Dense high-aspect ratio 3D carbon pillars on interdigitated microelectrode arrays, *Carbon* 94(2015) 792-803.

[159] T. Kondo, I. Udagawa, T. Aikawa, H. Sakamoto, I. Shitanda, Y. Hoshi, M. Itagaki, M. Yuasa, Enhanced sensitivity for electrochemical detection using screen-printed

diamond electrodes via the random microelectrode array effect, *Anal. Chem*. 88(2016) 1753-1759.

[160] K. Suematsu, Y. Shin, N. Ma, T. Oyama, M. Sasaki, M. Yuasa, T. Kida, Shimanoe, K. Pulse-driven micro gas sensor fitted with clustered Pd/SnO_2 nanoparticles, *Anal. Chem*. 87, (2015) 8407-8415.

[161] T. Yang, H. Zhang, Y. Wang, X. Li, K. Wang, J. Wei, D. Wu, Z. Li, H. Zhu, Interconnected graphene/polymer micro-tube piping composites for liquid sensing, *Nano Res.* 7(2014) 869-876.

[162] D. Sarkar, W. Liu, X. J. Xie, A. C. Anselmo, S. Mitragotri, K. Banerjee, MoS_2 Field-Effect Transistor for next-generation label-free biosensors, *ACS Nano* 8(2017) 3992-4003.

[163] I.B. Tahirbegi, J. Ehgartner, P. Sulzer, S. Zieger, A. Kasjanow, M. Paradiso, M. Strobl, D. Bouwes, T. Mayr, Fast pesticide detection inside microfluidic device with integrated optical pH, oxygen sensors and algal fluorescence, *Biosens. Bioelectron.* 88(2017) 188-195.

[164] M. Medina-Sanchez, C. Mayorga-Martinez, T. Watanabe, T. Ivandini, Y. Honda, F. Pino, K. Nakata, A. Fujishima, Y. Einaga, A. Merkoci, Microfluidic platform for environmental contaminants sensing and degradation based on boron-doped diamond electrodes, *Biosens. Bioelectron*. 75(2016) 365-374.

[165] G. M. Zeng, C. Zhang, D. L. Huang, C. Lai, L. Tang, Y. Y. Zhou, P. Xu, H. Wang, L. Qin, M. Cheng, Practical and regenerable electrochemical aptasensor based on

nanoporous gold and thymine-Hg^{2+}-thymine base pairs for Hg^{2+} detection, *Biosens. Bioelectron.* 90(2017) 542-548.

[166] J. Chen, J. Wen, L. Zhuang, S. Zhou, An enzyme-free catalytic DNA circuit for amplified detection of aflatoxin B1 using gold nanoparticles as colorimetric indicators, *Nanoscale* 8(2016) 9791-9797.

[167] X. Wei, Z. Chen, L. Tan, T. Lou, Y. Zhao, DNA-catalytically active gold nanoparticle conjugates-based colorimetric multidimensional sensor array for protein discrimination, *Anal. Chem.* 89(2017) 556-559.

[168] P. Vilela, A. Heuer-Jungemann, A. El-Sagheer, T. Brown, O. L. Muskens, N. R. Smyth, A. G. Kanaras, Sensing of vimentin mRNA in 2D and 3D models of wounded skin using DNA−coated gold nanoparticles, *Small.* 14(2018) 1703489.

[169] R. X. Bian, X. T. Wu, F. Chai, L. Li, L. Y. Zhang, T. T. Wang, C. G. Wang, Z. M. Su, Facile preparation of fluorescent Au nanoclusters-based test papers for recyclable detection of Hg^{2+} and Pb^{2+}, *Sens. Actuator B-Chem.* 241(2017) 592-600.

[170] P. Zheng, M. Li, R. Jurevic, S. K. Cushing, Y. Liu, N. Wu, A gold nanohole array based surface-enhanced Raman scattering biosensor for detection of silver(I) and mercury(II) in human saliva, *Nanoscale* 7(2015) 11005-11012.

[171] E. Chung, R. Gao, J. Ko, N. Choi, D. W. Lim, E. K. Lee, S. I. Chang, J. Choo, Trace analysis of mercury(II) ions using aptamer-modified Au/Ag core-shell nanoparticles and SERS spectroscopy in a microdroplet channel, *Lab on a chip* 13(2013) 260-266.

[172] M. Motaghedifard, M. Behpour, S. M. Ghoreishi, Self-assembling monolayer of Schiff's base formed between o-methoxyphenyl methyl ketone and 2-aminothiophenol

at the surface of gold electrode for electrochemical impedimetric sensing of uranyl cations, *Sens. Actuator B-Chem*. **2**203(2014) 802-811.

[173] L. Feng, W. Shi, J. Ma, Y. Chen, F. Kui, Y. Hui, Z. Xie, A novel thiosemicarbazone Schiff base derivative with aggregation-induced emission enhancement characteristics and its application in Hg^{2+} detection, *Sens. Actuator B-Chem*. 237(2016) 563-569.

[174] S. Roy, J. H. Soh, J. Y. Ying, A microarray platform for detecting disease-specific circulating miRNA in human serum, B*iosens. Bioelectron*. 75(2016) 238-246.

[175] X. Ouyang, R. Yu, J. Jin, J. Li, R. Yang, W. Tan, J. Yuan, New strategy for label-free and time-resolved luminescent assay of protein: conjugate Eu^{3+} complex and aptamer-wrapped carbon nanotubes, *Anal. Chem*. 83(2011) 782-789.

[176] M. Zhang, G. Y. Zhou, Y. Feng, T. R. Xiong, H. C. Hou, Q. H. Guo, Flexible 3D nitrogen-doped carbon nanotubes nanostructure: A good matrix for enzyme immobilization and biosensing, *Biosens. Bioelectron.* 22(2016) 829-838.

[177] J. N. Tiwari, V. Vij, K. C. Kemp, K. S. Kim, Engineered carbon-nanomaterial-based electrochemical sensors for biomolecules, *ACS Nano* 10(2016) 46-80.

[178] J. Liu, Z. Liu, C. J. Barrow, W. Yang, Molecularly engineered graphene surfaces for sensing applications: A review, *Anal. Chim. Ac*ta 859(2015) 1-19.

[179] V. Biju, Chemical modifications and bioconjugate reactions of nanomaterials for sensing, imaging, drug delivery and therapy, *Chem. Soc. Rev*. 43(2014)744-764.

[180] P. Sukumaran, V. Thazhe Veettil, S. Rajappa, C. Z. Li, Alwarappan, S. Ionic liquid modified N-doped graphene as a potential platform for the electrochemical discrimination of DNA sequences, *Sens. Actuator B-Chem.* 247(2017) 556-563.

[181] X. Wang, C. Yang, S. Zhu, M. Yan, S. Ge, J. Yu, 3D origami electrochemical device for sensitive Pb^{2+} testing based on DNA functionalized iron-porphyrinic metal-organic framework, *Biosens.Bioelectron.* 87(2017) 108-115.

[182] S. J. Kim, S. J. Choi, J. S. Jang, N. K. Kim, H. Hakim, H. L. Tuller, I. D. Kim, Mesoporous WO_3 nanofibers with protein-templated nanoscale catalysts for detection of trace biomarkers in exhaled breath, *ACS Nano* 10(2016) 5891-5899.

[183] P. Gai, C. Gu, T. Hou, F. Li, Ultrasensitive self-powered aptasensor based on enzyme biofuel cell and DNA bioconjugate: A facile and powerful tool for antibiotic residue detection, *Anal. Chem.* 89(2017) 2163-2169.

[184] Z. Zhang, Z. Chen, S. Wang, C. Qu, L. Chen, On-site visual detection of hydrogen sulfide in air based on enhancing the stability of gold nanoparticles, *ACS Appl. Mater. Interfaces* 6(2014) 6300-6307.

[185] E. Caballero-Diaz, S. Benitez-Martinez, M. Valcarcel, Rapid and simple nanosensor by combination of graphene quantum dots and enzymatic inhibition mechanisms, *Sens. Actuator B-Chem.* 240(2017) 90-99.

[186] Y. V. Gerasimova, D. M. Kolpashchikov, Enzyme-assisted target recycling (EATR) for nucleic acid detection, *Chem. Soc. Rev.* 43(2014) 6405-6438.

[187] M. R. Akanda, H. Ju, A tyrosinase-responsive nonenzymatic redox cycling for amplified electrochemical immunosensing of protein, *Anal. Chem.* 88(2016) 9856-9861.

[188] Y. Li, Y. Tian, Y. Tong, W. Po, a Jusheng, L. A sensitive photoelectrochemical aptasensor for oxytetracycline based on a signal “switch off-on” strategy, *Sens. Actuator B-Chem.* 240(2017) 785-792.

[189] M. Liu, G. Zhao, Y. Tang, Z. Yu, Y. Lei, M. Li, Y. Zhang, D. Li, A simple, stable and picomole level lead sensor fabricated on DNA-based carbon hybridized TiO_2 nanotube arrays, *Environ. Sci. Technol.* 44(2010) 4241-4246.

[190] N. Yildirim, F. Long, C. Gao, M. He, H. C. Shi, A. Z. Gu, Aptamer-based optical biosensor for rapid and sensitive detection of 17beta-estradiol in water samples, *Environ. Sci. Technol.* 46(2012) 3288-3294.

[191] H. Li, Q. Zhang, Y. Cai, D. M. Kong, H. X. Shen, Single-stranded DNAzyme-based Pb^{2+} fluorescent sensor that can work well over a wide temperature range, *Biosens. Bioelectron*. 34(2012) 159-164.

[192] Y. Zilberman, R. Ionescu, X. Feng, K. Muellen, H. Haick, Nanoarray of polycyclic aromatic hydrocarbons and carbon nanotubes for accurate and predictive detection in real-world environmental humidity, *ACS Nano* 5(20171) 6743-6753.

[193] Y. Zhang, J. Qiu, M. Gao, P. Li, L. Gao, L. Heng, B. Z. Tang, L. Jiang, A visual film sensor based on silole-infiltrated SiO_2 inverse opal photonic crystal for detecting organic vapors, *J. Mater. Chem. C* 2(2014) 8865-8872.

[194] M. A. Ali, K. Mondal, Y. Wang, H. Jiang, N. K. Mahal, M. J. Castellano, A. Sharma, L. Dong, In situ integration of graphene foam-titanium nitride based bio-scaffolds and microfluidic structures for soil nutrient sensors, *Lab on a chip* 17(2017) 274-285.

[195] M. R. Huang, Y. B. Ding, X. G. Li, Y. Liu, K. Xi, C. L. Gao, R. V. Kumar, Synthesis of semiconducting polymer microparticles as solid ionophore with abundant complexing sites for long-life Pb(II) sensors, *ACS Appl. Mater. Interfaces* 6(2014) 22096-22107.

[196] G. Nöll, Q. Su, B. Heidel, Y. Yu, A reusable sensor for the label-free detection of specific oligonucleotides by surface plasmon fluorescence spectroscopy, *Adv. Healthc. Mater.* 3(2014) 42-46.

[197] Z. Zhu, Z. Guan, D. Liu, S. Jia, J. Li, Z. Lei, S. Lin, T. Ji, Z. Tian, C. J. Yang, Translating molecular recognition into a pressure signal to enable rapid, sensitive, and portable biomedical analysis, *Angew. Chem.-Int. Edit.* 54(2015) 10448-10453.

[198] S. J. Sorensen, D. J. Lapworth, B. P. Marchant, D. C. Nkhuwa, S. Pedley, M. E. Stuart, R. A. Bell, M. Chirwa, J. Kabika, M. Liemisa, M. Chibesa, In-situ tryptophan-like fluorescence: A real-time indicator of faecal contamination in drinking water supplies, *Water Res.* 81(2015) 38-46.

[199] X. Liu, R. H. Byrne, L. Adornato, K. K. Yates, E. Kaltenbacher, X. Ding, B. Yang, In situ spectrophotometric measurement of dissolved inorganic carbon in seawater, *Environ. Sci. Technol.* 47(2013) 11106-11114.

[200] J. Liao, S. Lin, M. Zeng, Y. Yang, A miniature photoelectrochemical sensor based on organic electrochemical transistor for sensitive determination of chemical oxygen demand in wastewaters, Water Res. 94(2016) 296-304.

[201] S. Morais, J. Tamarit-Lopez, R. Puchades, A. Maquieira, Determination of microcystins in river waters using micirosensor arrays on disk, *Environ. Sci. Technol.* 44(2010) 9024-9029.

[202] G. Zhao, M. Pumera, Marangoni self-propelled capsules in a maze: pollutants 'sense and act' in complex channel environments, *Lab on a chip* 14(2014) 2818-2823.

[203] F. Lefevre, A. Chalifour, L. Yu, V. Chodavarapu, P. Juneau, R. Izquierdo, Algal fluorescence sensor integrated into a microfluidic chip for water pollutant detection, *Lab on a*

chip 12(2012) 787-793.

[204] H. Becker, All I want for Christmas, Lab on a chip 11(2011) 1571-1573.

[205] W. J. Peveler, A. Roldan, N. Hollingsworth, M. J. Porter, I. P. Parkin, Multichannel detection and differentiation of explosives with a quantum dot array, *ACS Nano* 10(2016) 1139-1146.

[206] X. Li, H. Kong, R. Mout, K. Saha, D. F. Moyano, S. M. Robinson, S. Rana, X. Zhang, M. A. Riley, V. M. Rotello, Rapid identification of bacterial biofilms and biofilm wound models using a multichannel nanosensor, *ACS Nano* 8(2014) 12014-12019.

[207] N. Lopez-Ruiz, F. V. Curto, M. M. Erenas, F. Benito-Lopez, D. Diamond, A. J. Palma, L. F. Capitan-vallvey, Smartphone-based simultaneous pH and nitrite colorimetric determination for paper microfluidic devices, *Anal. Chem.* 86(2014) 9554-9562.

[208] D. Mark, S. Haeberle, G. Roth, F. V. Stetten, R. Zengerle, Microfluidic lab-on-a-chip platforms: requirements, characteristics and applications, *Chem. Soc. Rev.* 39(2010) 1153-1182.

[209] Y. Sun, T. L. Quyen, T. C. Hung, W. H. Chin, A. Wolff, D. D. Bang, A lab-on-a-chip system with integrated sample preparation and loop-mediated isothermal amplification for rapid and quantitative detection of *Salmonella spp.* in food samples, *Lab on a chip* 15(2015) 1898-1904.

[210] J. Liu, Y. Zhang, M. Jiang, L. Tian, S. Sun, N. Zhao, F. Zhao, Y. Li, Electrochemical microfluidic chip based on molecular imprinting technique applied for therapeutic drug monitoring, *Biosens. Bioelectron.* 91(2017) 714-720.

[211] T. C. Hazen, E. A. Dubinsky, T. Z. DeSantis, G. L. Andersen, Y. M. Piceno, N. Singh, J. K. Jansson, A. Probst, S. E. Borglin, J. L. Fortney, W. T. Stringfellow, M. Bill, M. E. Conrad, L. M. Tom, K. L. Chavarria, T. R. Alusi, R. Lamendella, D. C. Joyner, C. Spier, J. Baelum, M. Auer, M. L. Zemla, R. Chakraborty, E. L. Sonnenthal, P. D'Haeseleer, H. Y. N. Holman, S. Osman, Z. Lu, J. D. Van Nostrand, Y. Deng, J. Zhou, O. U. Mason, Deep-sea oil plume enriches indigenous oil-degrading bacteria, *Science* 330(2010) 204-208.

[212] Y. Deng, P. Zhang, Y. Qin, Q. Tu, Y. Yang, Z. He, C. W. Schadt, J. Zhou, Network succession reveals the importance of competition in response to emulsified vegetable oil amendment for uranium bioremediation, *Environ. Microbiol.* 18(2016) 205-218.

[213] Y. Zhang, W. W. Li, G. M. Zeng, L. Tang, C. L. Feng, D. L. Huang, Y. P. Li, Novel neural network-based prediction model for quantifying hydroquinone in compost with biosensor Environ, *Engineer. Sci.* 26(2009) 1063-1070.

[214] F. Wu, T. Chai, Soft sensing method for magnetic tube recovery ratio via fuzzy systems and neural networks, *Neurocomputing* 73(2017) 2489-2497.

[215] A. Yan, H. Shao, P. Wang, A soft-sensing method of dissolved oxygen concentration by group genetic case-based reasoning with integrating group decision making, *Neurocomputing* 169(2015) 422-429.

[216] P. Odman, C. L. Johansen, L. Olsson, K. V. Gernaey, A. E. Lantz, Sensor combination and chemometric variable selection for online monitoring of Streptomyces coelicolor fed-batch cultivations, *Appl. Microbiol. Biotechnol*. 86(2010) 1745-1759.

[217] M. Zabadaj, K. Chreptowicz, J. Mierzejewska, P. Ciosek, wo-dimensional fluorescence as soft sensor in the monitoring of biotransformation performed by yeast, *Biotechnol. progr* 33(2017) 299-307.

[218] S. Ito, A. C. Barchi, B. Escaramboni, P. D. Oliva Neto, R. D. Herculano, F. Azevedo Borges, M. C. Romeiro Miranda, E. G. Fernández Núñez, UV/Vis spectroscopy combined with chemometrics for monitoring solid-state fermentation with *Rhizopus microsporus var. oligosporus*, *J. Chem. Technol. Biotechnol*. 92(2017) 2563–2572.

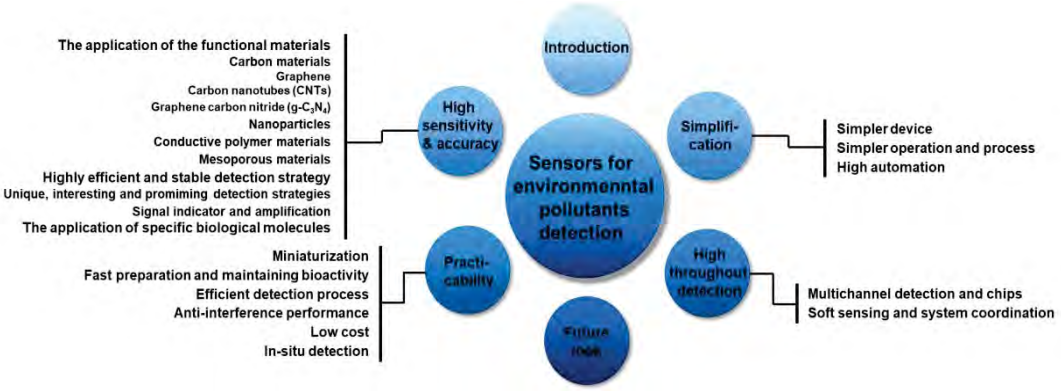


Figure 1. The structure of the review.

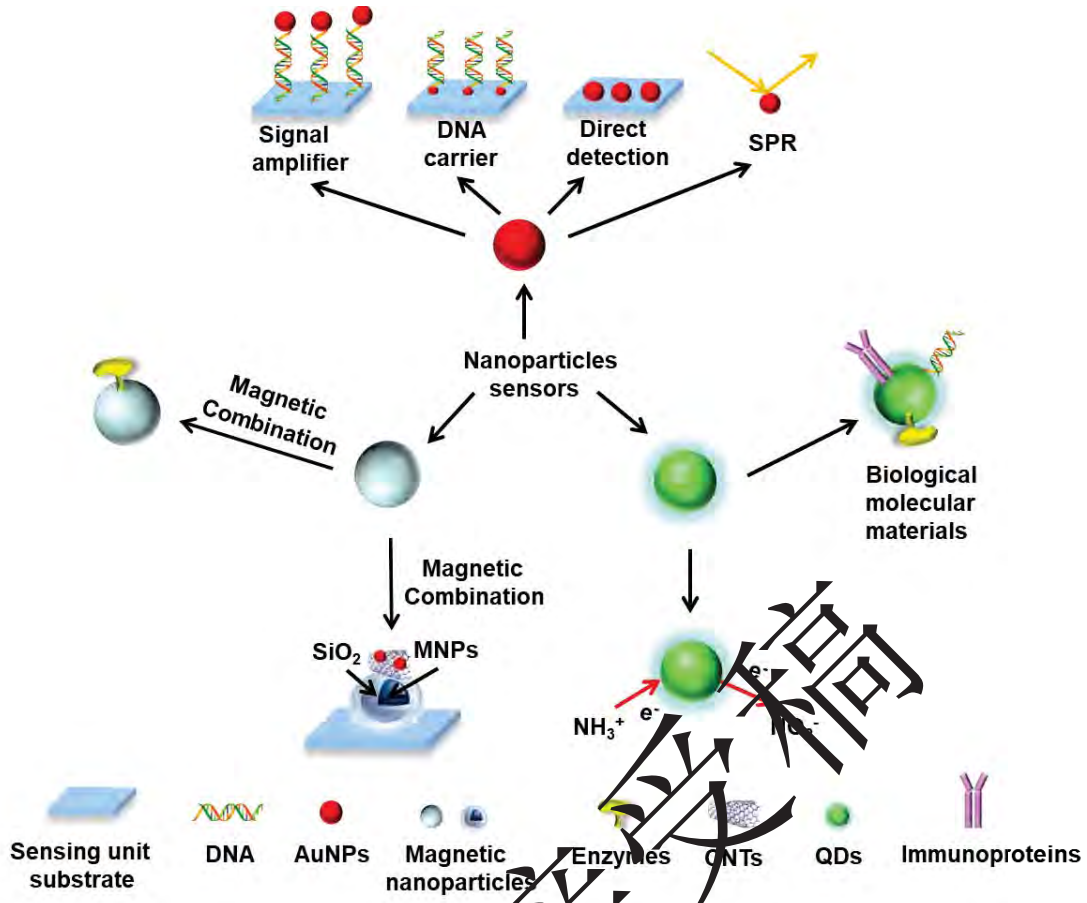


Figure 2. Various sensing strategies based on nanoparticles involving AuNPs, QDs and magnetic nanoparticles as signal amplifier, biological molecular materials carrier, substrate of sensing unit.

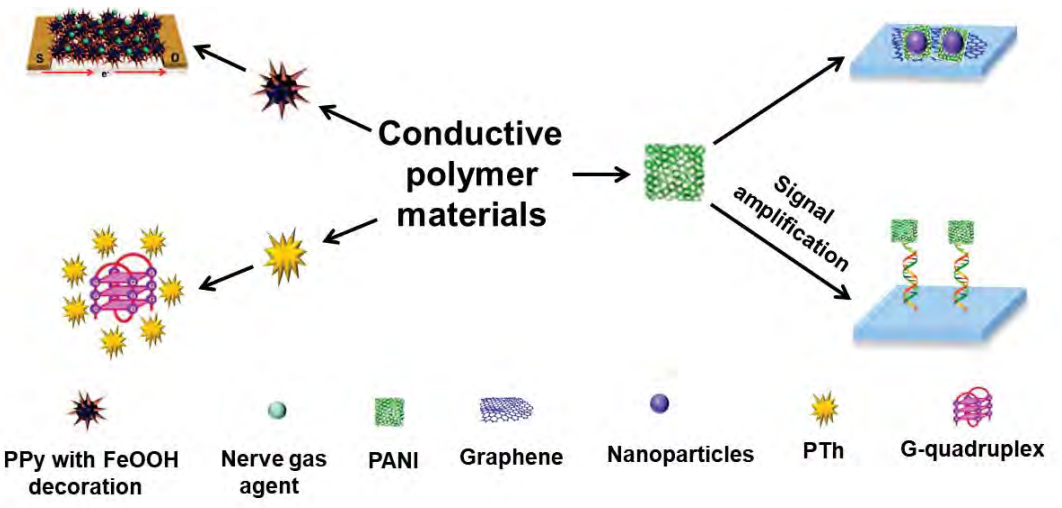


Figure 3. Applications of conductive polymer materials, e.g. PPy, PANI and PTh in sensing strategies. Electrode modified with PPy-COOH for nerve gas detection (Adapted from ref. 77, copyright (2013) American Chemical Society); electrode was sequentially modified with grapheme, PANI and nanoparticles; PANI as signal indicator immobilized on DNAs; PTh immobilized on G-quardruplex could form interpolyelectrolyte complexes; Thereinto, strategy of different DNA comformotions functionalization with PTh.

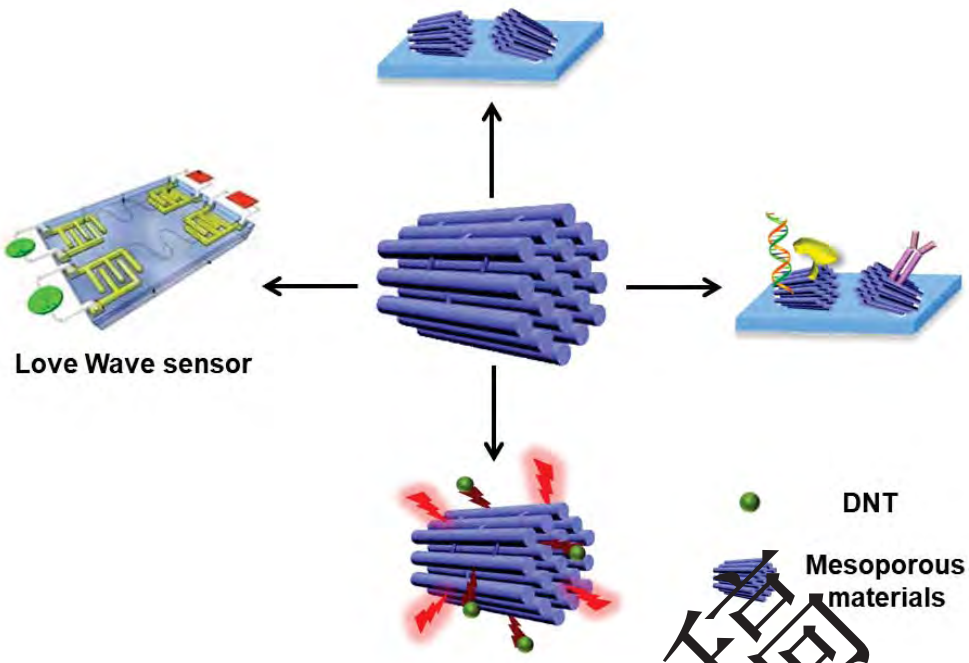


Figure 4. Mesoporous materials can be modified on the substrate for detection, biological molecular materials (e.g. DNAs, enzymes and immunoproteins) and fluorophores can combine on mesoporous materials for sensitive and specific detections, and TiO_2 mesoporous-coated Love Wave sensor (Adapted from ref. 85, copyright (2014, Elsevier). Water samples flow into the pipes and go through the biofilm, mesoporous TiO_2 and SiO_2 composite layer.

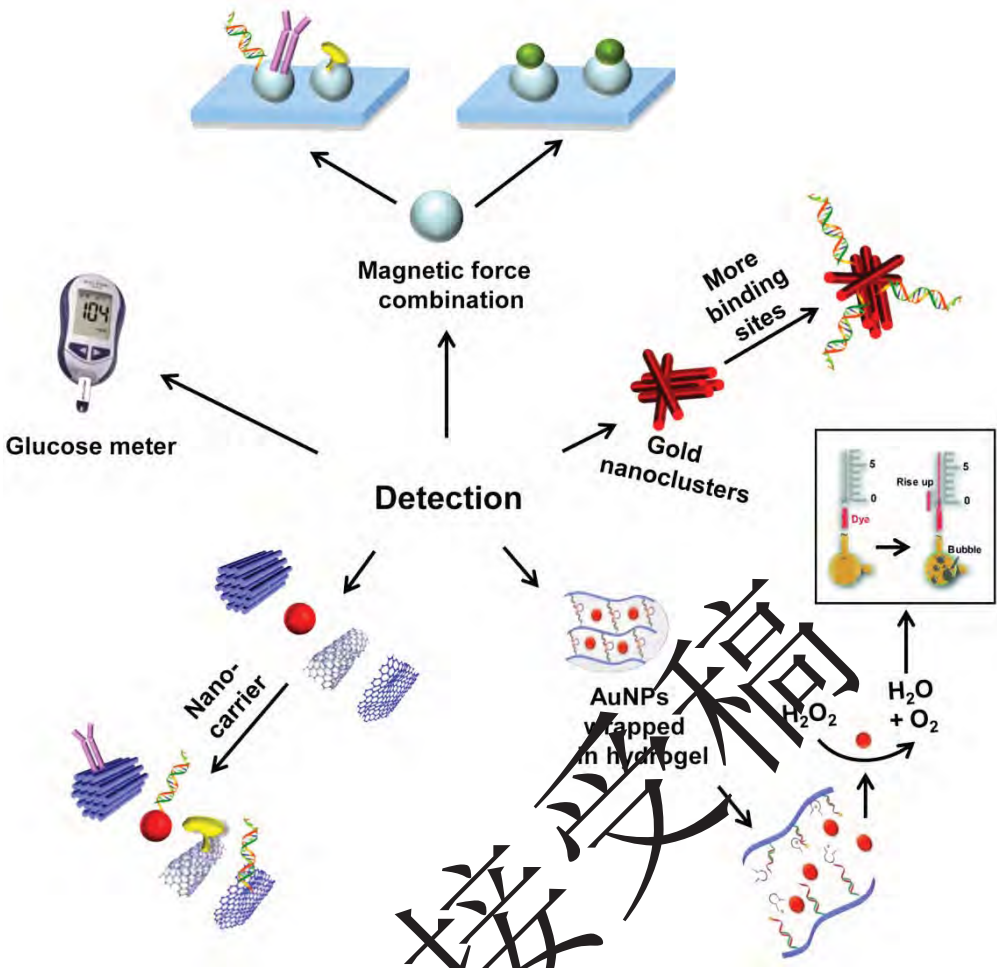


Figure 5. Different detection strategies for sensors, included strategy of magnetic force combination, expanding response area by gold nanoclusters, AuNPs wrapped in hydrogel, nanomaterials nanocarriers for biomolecular materials loadinge, and application strategy of glucose meter in pollutant detection. Adapted from ref. 93, copyright (2016) Wiley.

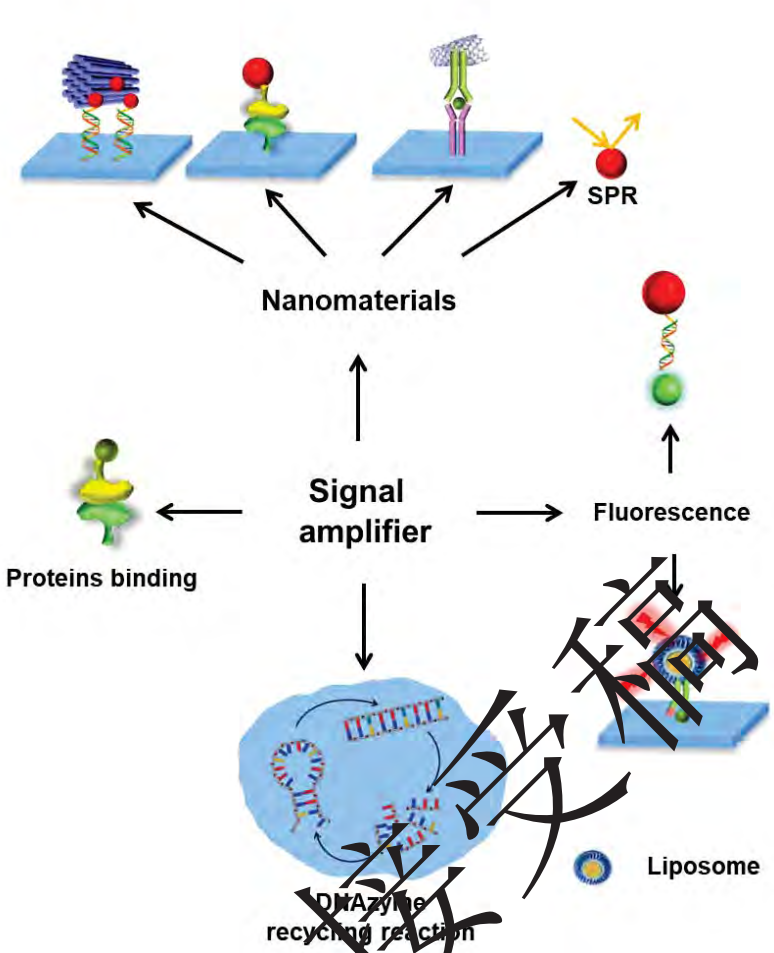


Figure 6. Various signal amplifier strategies involving different actions of nanomaterials, fluorescence enhancement (QD enhancement, liposome amplification), DNA recycling reaction, and proteins binding (various activities and antibodies).

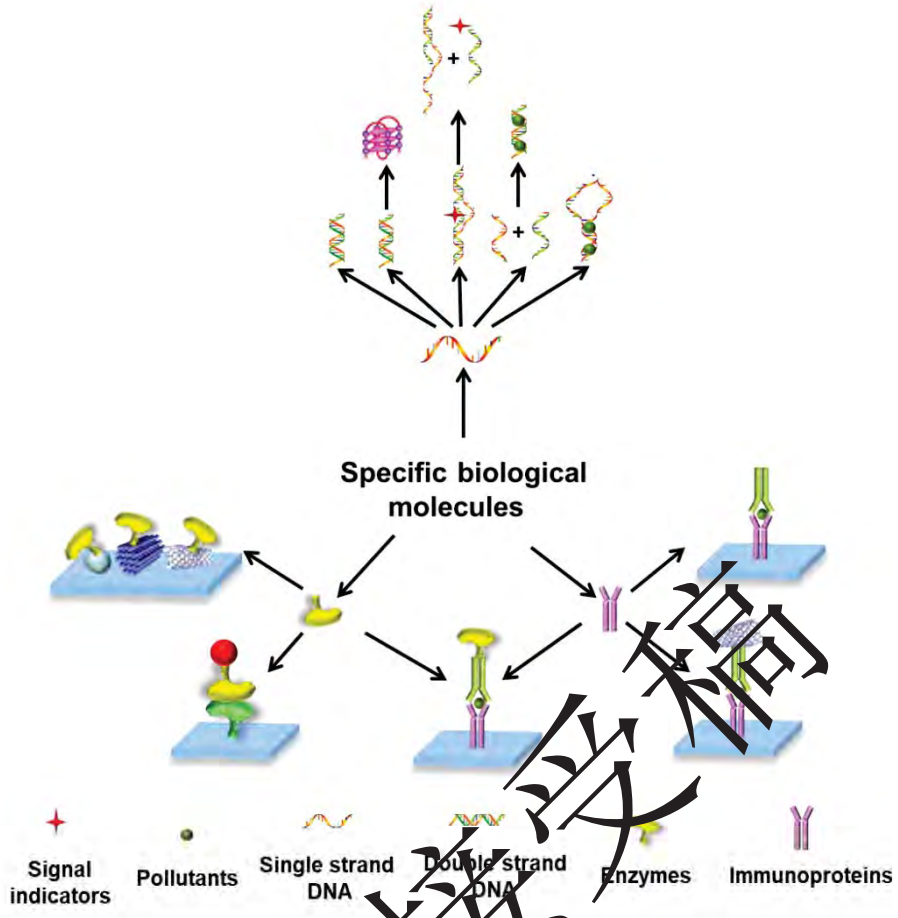


Figure 7. Sensors based on different specific biological molecules including DNA (double helix, G-quadruplex, double strand breaking at special nucleotide sites, mispairing double helix, and loops), enzyme, and immunoglobulin (reaction between antigen and antibody, or signal amplifying of immunoglobulins combined with nanomaterials and proteins).

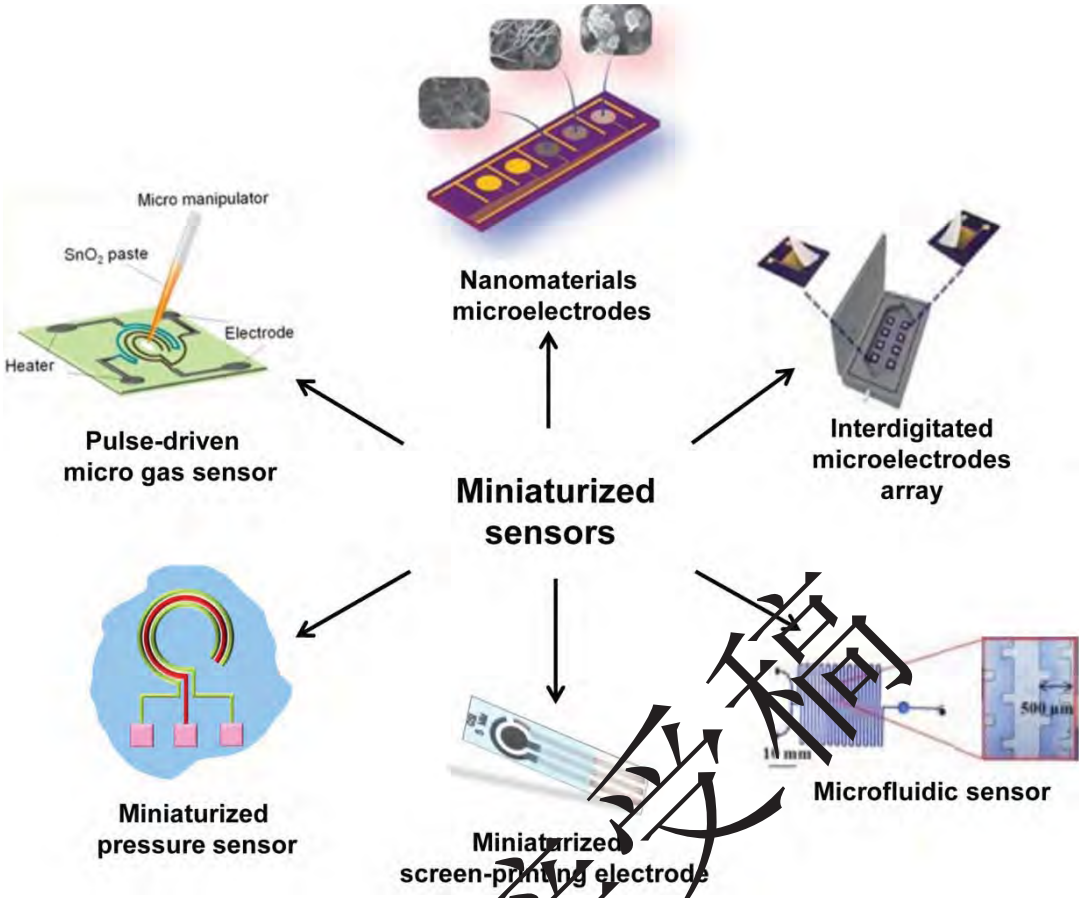


Figure 8. Different miniaturization sensors. Adapted from ref. 152, 157, copyright (2014) American Chemical Society; adapted from ref. 160, copyright (2015) American Chemical Society; adapted from ref. 166, copyright (2014) Elsevier.

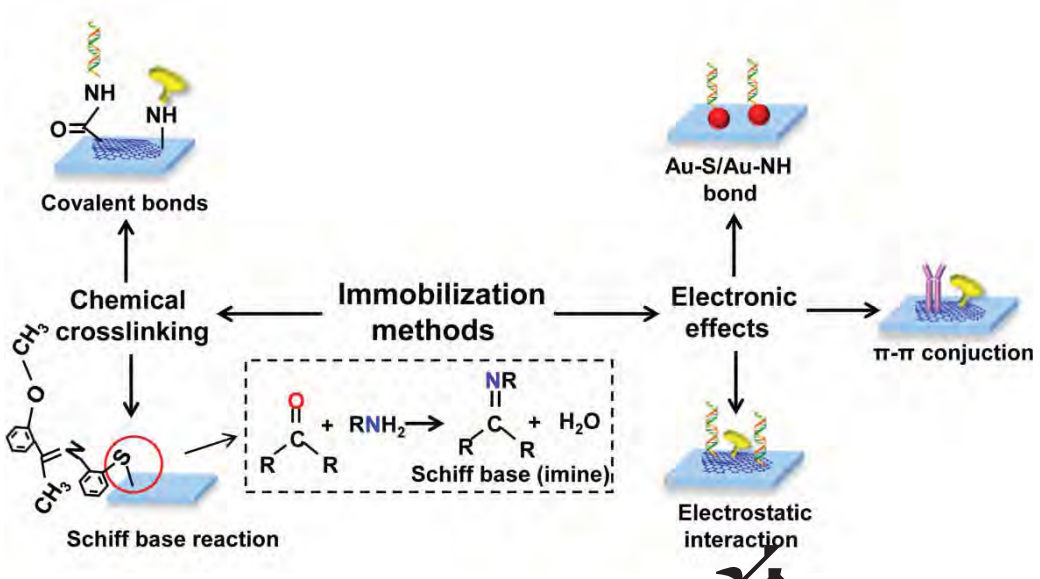


Figure 9. Fast preparation and maintaining bioactivity via chemical crosslinking and electronic effects in sensor fabrications

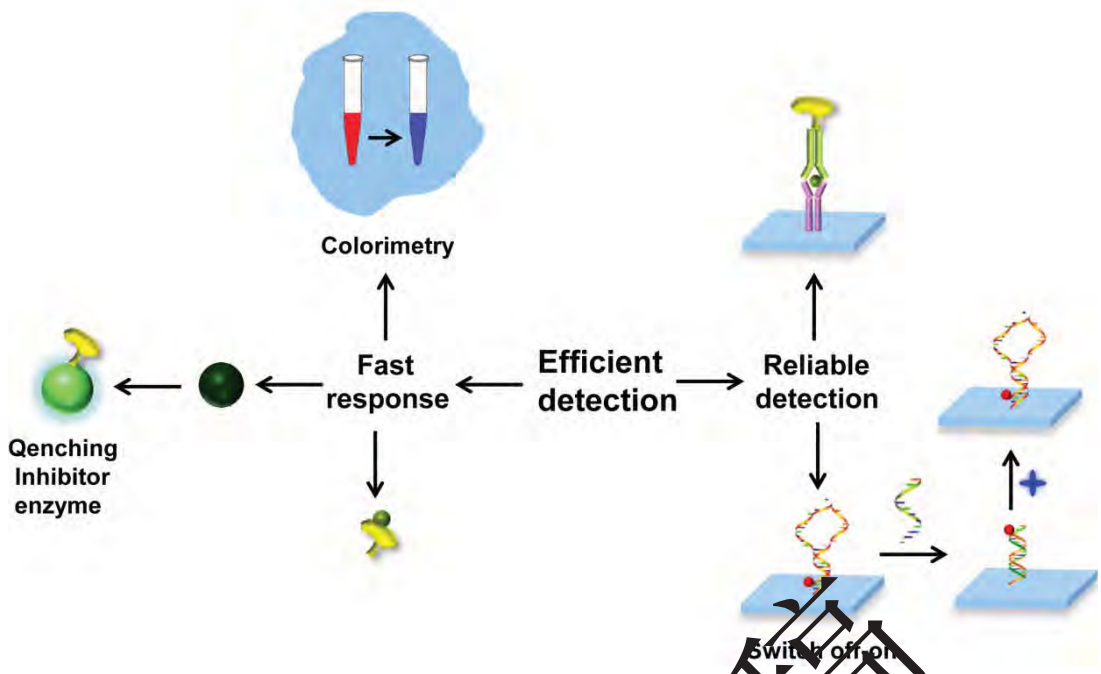


Figure 10. Efficient detection involving fast responses and reliable detection

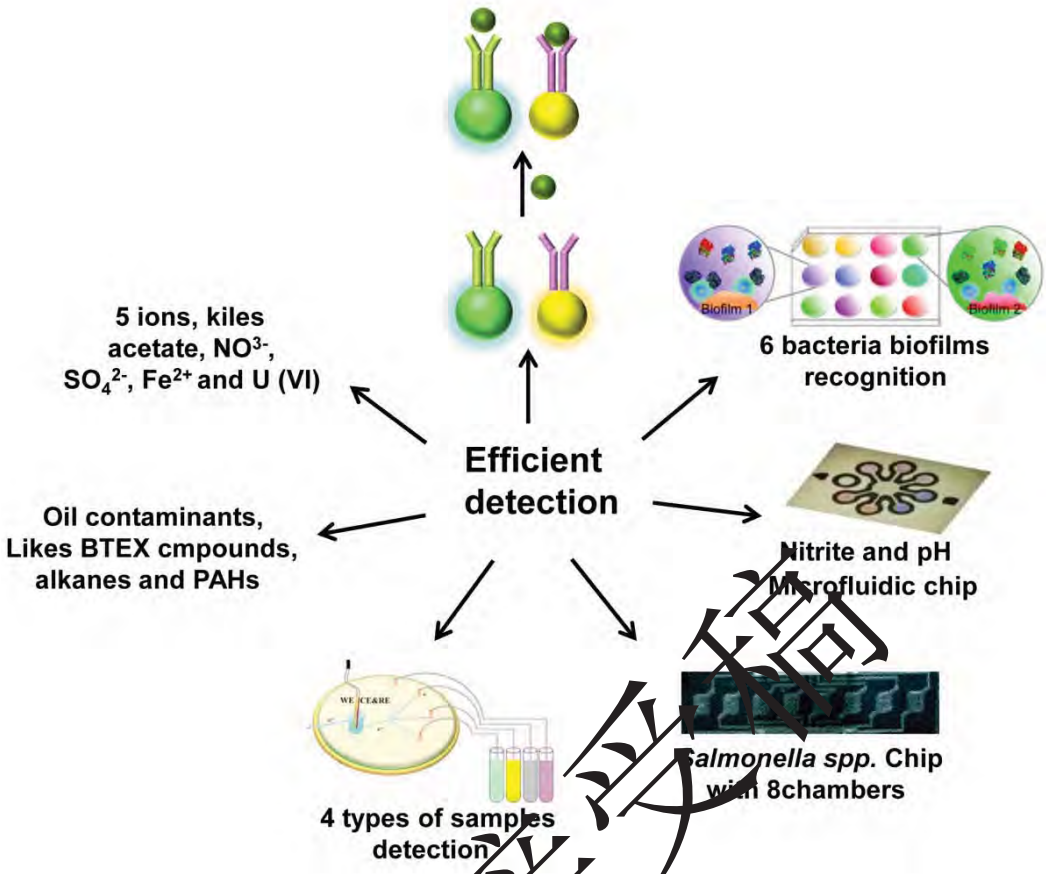


Figure 11. Different multichannel sensors strategies for pollutants detections. Adapted from ref. 207 and 208, Copyright (2014) American Chemical Society; Adapted from ref. 209, copyright (2015) The Royal Society of Chemistry; Adapted from ref. 210, copyright (2017) Elsevier.

Table 1. Typical inorganic pollutants detections with different types of sensor, sensor unit, detection range, limitation and time in environmental samples in the review

Target	Sensor type	Sensor unit	Environmental sample	Detection range	Detection limit	Detection time	Ref.
Hg^{2+}	Electrochemical (SWV, Methylene blue)	aptamer/electrodeposited graphene-Au + nanoAu carrier signal amplification	tap water, river water, landfill leachate	1.0 aM -100 nM	0.001 aM	~ 1 h	[49]
	Localized SPR	AuNPs	air	1 - 825 μg/m^3	1 pg/m^3	—	[86]
	Triboelectric nanogenerator sensor	AuNPs	—	0.1 - 5 μM	30 nM	60 min	[87]
	ECL	ferrocene-grapheme/aptamer/	river water, sea water	0.05 - 100	18 pM	35 min	[112]

		AuNPs/$Ru(bpy)_3^{2+}$		nM			
	Fluorescent	aptamer/Mn-doping CdS/ZnS core/shell QDs + aptamer/AuNPs	tap water	1 - 10 nM	0.49 nM	18 min	[128]
Pb^{2+}	Field-effect transistor	Pb^{2+}/rGO-AuNPs-GSH	drinking water	10 nM - 10 μM	10 nM	2 s	[39]
	Fluorescent	aptamer/GOOD	drinking water, tap water, lake water	1 - 1000 nM	0.64 nM	2 s	[92]
	Colorimetric (red to yellow)	aptamer/PMNT/TMBB	tap water	0 - 120 nM	6 nM	5 min	[99]
	V-chip	aptamer hydrogel/Au@PtNPs	waste water	0.08 - 42 nM	0.04 nM	~ 40 min	[108]
	Electrochemical (DPV)	aptamer/MCN- electrodeposited Au + MCN-nanoAu carrier signal	tap water, spring water, river water	10^{-3} - 10^{-14} M	1.02×10^{-15} M	30 min	[129]

		amplification					
UO_2^{2+}	Personal glucose meters	aptamer + sucrose	drinking water, table dust	—	5.0 nM	85 min	[105]
	V-chip	aptamer hydrogel/AuNPs	lake water	0 - 300 nM	20 nM	2 h	[110]
As^{3+}	Electrochemical (SWASV)	different shapes of AuNPs	—	100 - 1000 ppb	0.0157, 0.4787, 0.1816 μA/ppb·cm^2	—	[131]
	Luminescence	aptamer/iridium(III) complex	natural water	50 - 300 nM	7.6 nM	20 min	[150]
Nitrite	Colorimetric (red to colourless)	the Griess reagents	—	4.0 - 85.0 mg/L	0.52 mg/L	15 min	[185]

	Electrochemical (DPV)	Fe_3O_4-RGO nanocomposite	tap water, rain water, river water	10 - 2882 μM	0.1 μM	—	[103]
H_2S	Heat conduction	ordered mesoporous WO_3	air	0.25 - 200 ppm	50 ppm	2 s	[162]
	Colorimetric (red to blue)	aptamer/AuNPs	air	0.1 - 0.5 ppm	0.08 ppm	2 s	[102]
NH_3	Fluorescent	graphene/MoS_2 QDs	—	2 - 10 ppm	35.5 ppb	1 s	[90]

Table 1. Typical organic pollutants detections with different types of sensor, sensor unit, detection range, limitation and time in environmental samples in the review

Target	Sensor type	Sensor unit	Environmental sample	Detection range	Detection limit	Detection time	Ref.
Hydroquinone	Electrochemical (I-t)	laccase/magnetic core-shell (Fe_3O_4-SiO_2) nanoparticles	compost extracts	10 - 137.5 nM	0.15 nM	60 s	[88]
Malathion and acephate	Electrochemical (DPV)	AChE	grape, apple, mango, orange, banana, tomato, rice, wheat	0.07 - 1.3 ppm, 0.1 - 0.85 ppm	0.194 ppm, 0.147 ppm	4 min	[141]
Phenylhydrazine	MBFCs	anode: GOx/polyTBA/AuNPs	—	10.0 μM - 5.0 mM	2.5 ± 0.2 μM	—	[144]

		cathode: polyTPHyd-AuNP					
Polychlorinated biphenyl	SERS	aptamer/Ag nano-crown array	—	10 mM - 0.1 nM	0.1 nM	1 min	[147]
17b-estradiol	Fluorescent	aptamer/AuNPs	spiked water samples	0.48 - 200 nM	0.48 nM	10 min	[146]
Ethynylestradiol	Polyacrylamide gel electrophoresis	dimethyl sulphate/ aptamer	tap water, lake water	0.5 - 1.0 μM	0.13μM	15 min	[147]
Cocaine	Fluorescent	aptamer/SiNPs aptamer/ AuNPs	serum	0 - 40 nM	209 pM	40 min	[148]
Atrazine	Electrochemical (CA)	anti-atrazine antibodies-magnetic beads/ atrazine-	orange juice	0.9 - 4.5 nM	3.5 pM	20 min	[164]

		HRP/PtNPs					
Fenoxycarb	Fluorescent	AChE/N-doped GQDs	river water	6 - 70 μM	3.15 μM	15 min	[185]

Declaration of interests

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

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

No competing interests.

Author statement

This work is under the efforts of all authors. All authors read and contributed to the manuscript.

*Data in Brief*Co-submission Instructions

Article Title

Sensors for the environmental pollutant detection: are we already there?

Authors

Yi Zhang[‡, a, b, c], Yuan Zhu[‡, a, b], Zhuotong Zeng[‡, d], Guangming Zeng[*, a, b], Yingrong Wang[a, b], Yi Hu[a, b], Lin Tang[*, a, b], Chongling Feng[e]

Affiliations

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, China
[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, China
[c] Department of Chemistry, University of Science and Technology of China, Hefei, 230026, China
[d] Xiangya Medical College, South Central University, Changsha 410013, China
[e] Research Center of Environmental Science and Engineering, Center South University of Forestry and Technology, Changsha, 410004, China

Corresponding author(s)

Tel: +86 0731 88822754. Fax: +86 0731 88823701. E-mail: zgming@hnu.edu.cn (G.M. Zeng), tanglin@hnu.edu.cn (L. Tang)

Abstract

Sensors integrating chemical, biological, materials, electronics sciences, and etc., are considered as a promising technology that can bring great convenience and change to the world. Pollutant detection is one of the significant missions of sensors in the background of serious global environmental problems. As an accurate, selective, simple and inexpensive detection method, sensors are very suitable for environmental detection. Environmental samples, however, are very complex and unexpectedly relative to other ecosystems, which makes sensors a long way to go in practical application. Thus far, sensors have been developed with greater sensitivity, simpler and more efficient detection, better environmental adaptation, and etc. for pollutants detection. This review critically and comprehensively highlights the sensing strategies, and points the way of sensor development in environmental application. The sensitive and efficient, simple and miniaturized, low-cost, in-situ sensor strategies are comparatively reviewed in consideration of sensor development in pollutants detection.

Keywords

Sensors, environmental pollutant, detection, practical application, development

Specifications Table [Every section of this table is mandatory. Please enter information in the right-hand column and remove all the instructions]

Subject	Environmental Science and Engineering
Specific subject area	Sensor, environment pollutant detection, nanomaterials
Type of data	Table： Typical pollutants detections with different types of sensor, sensor unit, detection range, limitation and time in environmental samples Figure： 1. The structure of the review. 2. Various sensing strategies based on nanoparticles involving AuNPs, QDs and magnetic nanoparticles as signal amplifier, biological molecular materials carrier, substrate of sensing unit. 3. Applications of conductive polymer materials, e.g. PPy, PANI and PTh in sensing strategies. Thereinto, strategy for different DNA comformotions functionalization with PTh 4. Sensors based on mesoporous materials involving non-functionalization, binding with biological molecular materials and fluorophore, and Love Wave sensor fabrication. 5. Different detection strategies for sensors, included strategy of magnetic force combination, expanding response area by gold nanoclusters, AuNPs wrapped in hydrogel, : nanomaterials nanocarriers for biomolecular materials loadinge, and application strategy of glucose meter in pollutant detection. 6. Various signal amplifier strategies involving different actions of nanomaterials, fluorescence enhancement (QD enhancement, liposome amplification), DNA recycling reaction, and proteins binding (various activities and antibodies) 7. Sensors based on different specific biological molecules including DNA (double helix, G-quadruplex, double strand breaking at special nucleotide sites, mispairing double helix, and loops), enzyme, and immunoglobulin (reaction between antigen and antibody, or signal amplifying of immunoglobulins combined with nanomaterials and proteins) 8. Different miniaturization sensors. 9. Fast preparation and maintaining bioactivity via chemical crosslinking and electronic effects in sensor fabrications 10. Efficient detection involving fast responses and reliable detection 11. Different multichannel sensors strategies for pollutants detections
How data were acquired	No data

Data format	No data
Parameters for data collection	No data
Description of data collection	No data
Data source location	No data
Data accessibility	No data
Related research article	G. Zhou, J. Chang, S. Cui, H. Pu, Z. Wen, J. Chen, Real-time, selective detection of Pb(2+) in water using a reduced graphene oxide/gold nanoparticle field-effect transistor device, ACS Appl. Mater. Interfaces 6(2014) 19235-19241. J. Ping, Y. Wang, J. Wu, Y. Ying, Development of an electrochemically reduced graphene oxide modified disposable bismuth film electrode and its application for stripping analysis of heavy metals in milk, Food Chem. 151(2014) 65-71. P. K. Sahoo, B. Panigrahy, S. Sahoo, A. K. Satpati, D. M. Li, D. Bahadur, In situ synthesis and properties of reduced graphene oxide/Bi nanocomposites: as an electroactive material for analysis of heavy metals, Biosens. Bioelectron. 43(2013) 293-296. D. Chen, H. Feng, J. Li, Graphene oxide: preparation, functionalization, and electrochemical applications, Chem. Rev. 112(2012) 6027-6053. Y. Liu, X. Dong, P. Chen, Biological and chemical sensors based on graphene materials, Chem. Soc. Rev. 41(2012) 2283-2307. F. Perreault, A. Fonseca de Faria, M. Elimelech, Environmental applications of graphene-based nanomaterials, Chem. Soc. Rev. 44(2015) 5861-5896.

Value of the Data

[Provide 3-6 bullet points explaining why these data are of value to the scientific community. Bullet points 1-3 must specifically answer the questions in red next to the bullet point, but do not include the question itself in your answer. You may provide up to three additional bullet points to outline the value of these data. Please keep points brief, with ideally no more than 400 characters for each point.

No data.

Data Description

No data.

Experimental Design, Materials and Methods

No experiment.

Ethics Statement

No experiment.

Acknowledgments

The study is financially supported by the Program for the National Natural Science Foundation of China (51521006, 51508175, 51378190), Science and Technology Plan Project of Hunan Province, China (2015SK2001), China Postdoctoral Science Foundation (2016M600490, 2017T100462).

Declaration of Competing Interest

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

References

[1] D. Chen, H. Feng, J. Li, Graphene oxide: preparation, functionalization, and electrochemical applications, *Chem. Rev.* 112(2012) 6027-6053.

[12] Y. Liu, X. Dong, P. Chen, Biological and chemical sensors based on graphene materials, *Chem. Soc. Rev.* 41(2012) 2283-2307.

[3] F. Perreault, A. Fonseca de Faria, M. Elimelech, Environmental applications of graphene-based nanomaterials, *Chem. Soc. Rev.* 44(2015) 5861-5896.

[4] G. Yang, C. Zhu, D. Du, J. Zhu, Y. Lin, Graphene-like two-dimensional layered nanomaterials: applications in biosensors and nanomedicine, Nanoscale 7(2015) 14217-14231.

[5] S. E.Zhu, R. Shabani, J. Rho, Y. Kim, B. H. Hong, J. H. Ahn, H. J. Cho, Graphene-based bimorph microactuators, *Nano Lett.* 11(2011) 977-981.

[6] M. M. Barsan, M. E. Ghica, C. M. Brett, Electrochemical sensors and biosensors based on redox polymer/carbon nanotube modified electrodes: a review, Anal. Chim. Acta 881(2015) 1-23.

[7] S. Kruss, A. J. Hilmer, J. Zhang, N. F. Reuel, B. Mu, M. S. Strano, Carbon nanotubes as optical biomedical sensors, *Adv. Drug. Deliv. Rev.* 65(2013) 1933-1950.

[8] S. K. Vashist, D. Zheng, K. Al-Rubeaan, J. H. Luong, F. S. Sheu, Advances in carbon nanotube based electrochemical sensors for bioanalytical applications, *Biotechnol. Adv.* 29(2011) 169-188.

[9] S. B. Yang, B. S. Kong, D. H. Jung, Y. K. Baek, C. S. Han, S. K. Oh，H. T. Jung, Recent advances in hybrids of carbon nanotube network films and nanomaterials for their potential applications as transparent conducting films, Nanoscale 3(2011) 1361-1373.

[10] X. Chen, J. Zhu, Z. Chen, C. Xu, Y. Wang, Y. Yao, A novel bienzyme glucose biosensor based on three-layer Au-Fe_3O_4@SiO_2 magnetic nanocomposite, *Sens. Actuator B-Chem.* 159(2011) 220-228.

[11] A. Merkoci, Nanoparticles-based strategies for DNA, protein and cell sensors, *Biosens. Bioelectron.* 26(2010) 1164-1177.

[12] K. Saha, S. S. Agasti, C. Kim, X. Li, V. M. Rotello, Gold nanoparticles in chemical and biological sensing, *Chem. Rev.* 112(2012) 2739-2779.

[13] R. Liu, H. H. Liu, Z. Ji, C. H. Chang, T. Xia, A. E. Nel, Cohen, Y. Evaluation of toxicity ranking for metal oxide nanoparticles via an in vitro dosimetry model, *ACS Nano* 9(2015) 9303-9313.

[14] R. Balint, N. J. Cassidy, S. H. Cartmell, Conductive polymers: towards a smart biomaterial for tissue engineering, *Acta Biomater.* 10(2014) 2341-2353.

[15] S. Nambiar, J. T. Yeow, Conductive polymer-based sensors for biomedical applications, *Biosens. Bioelectron.* 26(2011) 1825-1832.