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Review

Recent Advances of Sensitive Electrochemical Sensing Platforms for Rapid Detection of Phthalate Acid Esters

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Abstract: As a kind of plasticizer, phthalic acid esters (PAEs) are often added to plastics to enhance elasticity, transparency, durability and prolong service life. However, it does not chemically bind to plastics and is easy to migrate to the environment. It is difficult to degrade in the environment, and it is also enriched in the human body through the food chain and respiration, which will lead to obvious adverse reactions such as decreased learning and memory function and neurobehavioral disorders. Due to the toxicity, universality and low concentration limitations of PAEs in the environment and food, it is essential to achieve rapid and sensitive detection of PAEs in soil, atmosphere, water and food. Electrochemical (EC) sensors have the advantages of simplicity, fast, low cost, portability, easy operation, high specificity and high sensitivity, so they are applied for the detection of PAEs. Although there are a large number of studies on the detection of PAEs by EC sensors, there is no review on this aspect. In this review, we introduce the detection of PAEs from classical EC sensors, electrochemiluminescence (ECL) sensors and photo-electrochemical (PEC) sensors in the past five years. This review is beneficial to understanding the construction of EC sensors and the detection mechanism of PAEs. We also propose that the development of rapid, accurate and real-time detection methods of PAEs is key to assessing risk and preventing related diseases.

Keywords: phthalate acid esters; electrochemical sensor; determination

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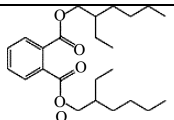
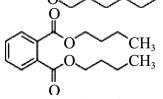
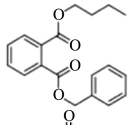
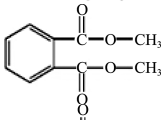
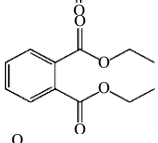
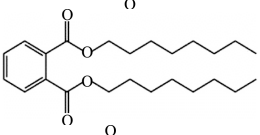
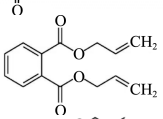
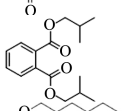
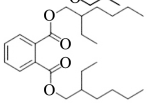
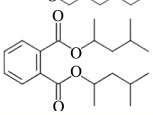
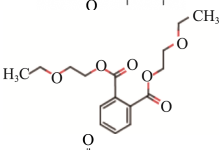
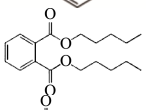
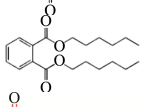
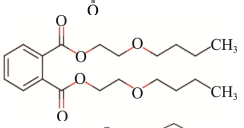
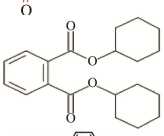
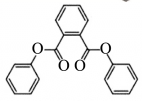
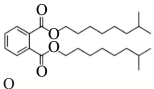
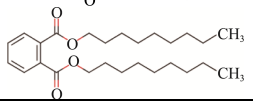
1 Introduction

Phthalic acid esters (PAEs, $C_{8+x}H_{4+y}O_{4+z}$) are a class of chemical compounds composed of dialkyl or alkylaryl esters of 1,2-benzenedicarboxylic acid, which are esters containing benzene rings[1]. PAEs as plasticizers are extensively added to personal care products (nail polish, shampoo), drugs, solvent adhesives, medical equipment, food packaging, agricultural films and building materials[2]. PAEs are not chemically bound to the polymer, so they can easily release into the environment, and finally enter human body from various potential sources causing environmental pollution and threatening human health[3]. With the development of industrialization of human society, a large number of PAEs are used in plastic products. At present, there are more than 30 kinds of PAEs, and the most commonly used 18 kinds are shown in Table 1. Some studies have detected PAEs in the water of the Yangtze River, and found that the concentration of dibutyl phthalate (DBP) in the water exceeds the surface water standard of China, the content of bis(2-ethylhexyl) phthalate (DEHP) and diisobutyl phthalate (DIBP) in the water is high, and DIBP is also high in the sediment[4]. Under the action of river input and atmospheric deposition, PAEs will diffuse and accumulate in the ocean, with low to high potential risks to marine organisms at

Table 1 The names, abbreviations and structural formulas of 18 commonly used PAEs

Name	Abbreviation	Molecular formula	Structural formulas
Bis(2-ethylhexyl) phthalate	DEHP	$C_{24}H_{38}O_4$	
Dibutyl phthalate	DBP	$C_{16}H_{22}O_4$	
Benzyl butyl phthalate	BBP	$C_{19}H_{20}O_4$	
Dimethyl phthalate	DMP	$C_{10}H_{10}O_4$	
Diethyl phthalat	DEP	$C_{12}H_{14}O_4$	
Di-n-octyl phthalate	DNOP	$C_{24}H_{38}O_4$	
Diallyl phthalate	DAP	$C_{14}H_{14}O_4$	
Diisobutyl phthalate	DIBP	$C_{16}H_{22}O_4$	
Bis(2-methoxyethyl) phthalate	DMEP	$C_{14}H_{18}O_6$	
Bis(4-methyl-2-pentyl) phthalate	BMPP	$C_{20}H_{30}O_4$	
Bis(2-ethoxyethyl) phthalate	DEEP	$C_{16}H_{22}O_6$	
Dipentyl phthalate	DPP	$C_{18}H_{26}O_4$	
Dihexyl phthalate	DHXP	$C_{20}H_{30}O_4$	
Bis(2-n-butoxyethyl) phthalate	DBEP	$C_{20}H_{30}O_6$	
Dicyclohexyl phthalate	DCHP	$C_{20}H_{26}O_4$	
Diphenyl phthalate	DPhP	$C_{20}H_{14}O_4$	
Diisononyl ortho-phthalate	DINP	$C_{26}H_{42}O_4$	
Dinonyl phthalate	DNP	$C_{26}H_{42}O_4$	

different nutrient levels. At the same time, PAEs will be directly diffused into the sediment as a large amount of plastic waste and microplastics sink into the seabed, which has a huge negative impact on marine biota[5-7]. PAEs in the ocean will enter the seafood organisms and accumulate, and ultimately be absorbed into the bod through the food chain. In addition, the extensive use of agricultural films, fertilizers and pesticides containing PAEs will cause persistent soil pollution[8-10]. Crops also absorb PAEs through their roots during growth[11], and most fermented products such as liquor and bread with grain as raw materials have detected the presence of PAEs[12]. PAEs in plastic packaging bags of food will migrate to food and cause food pollution. Studies have shown that the concentration of PAEs in food and air in China is the highest in the world, while the concentration of PAEs in indoor dust and personal care products is at a medium level[13]. In a word, PAEs are a kind of typical environmental estrogens. Single PAEs usually cause harm to highly exposed individuals[14], and the main way of PAEs exposure is food intake for people[15]. Existing studies have shown that the important metabolite of PAEs, phthalate monoester, has an inhibitory effect on the important phase II metabolic enzyme sulfotransferases (SULTs) in the human body[16]. Long-term intake of PAEs can lead to obvious depressive behavior, decreased learning and memory function, increased biomarkers related to chronic stress in plasma and brain tissue, decreased neurotransmission activity, and neurobehavioral disorders[17]. Especially, children may face the risk of anti-androgen effects due to personal and cumulative exposure to PAEs, and childhood exposure to PAEs or active or passive smoking during pregnancy may be a risk factor for childhood asthma[18-20]. The United States Environmental Protection Agency (U.S. EPA), European Union (EU), and China have added six PAEs (including DEHP, DBP, butyl benzyl phthalate (BBP), dimethyl phthalate (DMP), diethyl phthalate (DEP) and di-n-octyl phthalate (DNOP)) to the list of priority control pollutants. The molarity of DEHP in drinking water should be lower than 8 μg/L (20.5 nmol/L), which is one of the lowest molarity limits of pollutants including heavy metal ions, pesticides and polycyclic aromatic hydrocarbons recommended by the World Health Organization (WHO)[21]. The rapid and sensitive detection methods of PAEs are highly desired due to their toxicity, pervasiveness, and low concentration limits in the environment as well as food[22]. Therefore, it is an inevitable trend to carry out detection studies of PAEs to assess risks.

In China, the national standard method for the detection of PAEs is based on Chromatography, which can be divided into gas chromatography (GC) and high-performance liquid chromatography (HPLC), both of which are mostly combined with mass spectrometry (MS) to achieve a qualitative and quantitative analysis of substances. The research and development of selective extraction and determination of various PAEs in samples by GC-MS has been relatively mature[23-27]. Compared with GC method, HPLC combined with different detectors (diode array detector and/or MS) has the advantages of simple sample preparation and no derivatization technology[28]. However, this method is slow, requires professionals to use complex and expensive instruments in professional laboratories, and requires the consumption of a large amount of organic solvents, so its detection is extremely inconvenient[29]. EC sensors have the advantages of simplicity, fast, low cost, portability, easy operation, high specificity and high sensitivity, so they are widely noticed for the detection of PAEs[30,31]. This review summarizes the application of EC sensors in the detection of PAEs from three aspects: classical EC sensor, ECL sensor and PEC sensor. According to the characteristics of these three sensors, the EC methods for detection of PAEs in recent years (2019-2023) were reviewed from enhancing interfacial charge transfer by nanomaterials and improving specificity by aptamer, molecularly imprinted polymer (MIP) and antibody (Ab) (Fig.1). This review is beneficial for readers to understand the development trend of EC sensors in the detection of PAEs, and guides the rapid, real-time and accurate detection of PAEs by EC sensors.

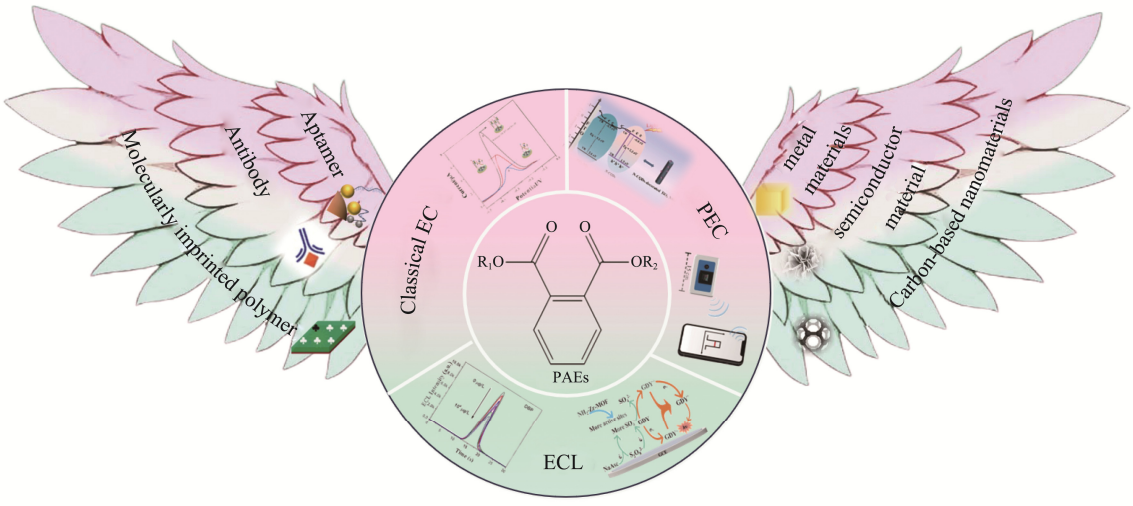


Fig.1 EC sensor based on nanomaterials and recognition elements for detection of PAEs.

2 Application of EC sensors for the detection of PAEs

The EC sensor can realize the qualitative or quantitative analysis of the analyte, because it can convert the concentration of the analyte into an electrical signal proportionally[32]. Due to the advantages of low detection limit (LOD) as low as picomolar , rapid response and low cost for sensing, EC sensor has become the most commonly used sensor type so far[33]. For the sake of further improving the performance of EC sensors, some studies have combined the advantages of EC strategies to develop a new analytical technology, namely photo-electrochemical (PEC) technology[32]. Because the optical signal is faster in the transmission process and is less interfered, the sensitivity and accuracy of PEC sensors are usually higher than those of EC sensors[34]. There are also studies on the combination of electrochemistry and chemiluminescence to make the sensor have higher performance in terms of detection sensitivity and selectivity, that is, electrochemiluminescence (ECL) sensor, which has the prominent merits of high stability, high sensitivity and wide linear range. Its core is to use the EC process to generate luminous energy, which is used to detect specific substances in the solution[32].

2.1 Application of classical EC sensors for the detection of PAEs

To achieve the best analytical performance while controlling the lowest economic and environmental costs is the overall goal in the field of EC sensing. The EC sensor uses the redox activity of the target or its effect on the redox reaction of the system to achieve the detection of the target[35]. The realization of a high sensitivity EC sensor depends on the establishment of an effective electron transfer to obtain a good current density. Improving the sensitivity of the EC sensors is usually achieved by modifying biological, organic and inorganic materials on electrodes. Among them, biomodified electrodes are often used to catalyze specific chemical reactions. Organic or inorganic materials are usually used to increase the electrode surface area and/or conductivity to improve the signal of the sensor[36-39]. In recent years, PAEs have received extensive attention due to their harmful effects in the environment and food, and classical EC analysis has gradually been applied to PAEs detection (Table 2).

Carbon-based nanomaterials are most widely used in EC sensors[40]. Graphite nitride (C_3N_4), which has the advantages of non-toxicity and large specific surface area, is a two-dimensional polymer semiconductor with amino groups. The Au@Ni-CoHNB/PEI-g-C_3N_4 composite modified on the electrode can improve the sensing performance. Au–Pd core-shell nanobone (Pd@Au NB) carrying electroactive substances can be used as signal probes to achieve accurate quantification of target content. A large number of Au@Ni-CoHNBs are connected by Au-N bonds, which can provide more binding sites for Apt. At the same time, when DEHP is present, RecJf exonuclease will assist in the recovery of the target and reach signal amplification. Therefore, found on PEI-g-C_3N_4/Au@Ni-CoHNB nanocomposites and RecJf exonuclease-assisted signal amplification strategy, a EC aptasensor for detection of DEHP can be established[41]. Zhou et al.[42] firstly tried to form a functionalized corncob biochar (F-CC3) film on glassy carbon electrode (GCE) by casting F-CC3 on GCE. The obtained GCEs were further modified to prepare an EC sensor with excellent sensitivity and high selectivity for the detection of DBP. The interlayer spacer using conductive F-CC3 can effectively inhibit the aggregation of CTS, form a good porous structure, increase the effective surface area, and thus improve the conductivity, as shown in Fig.2 (A). This study provides a novel idea for sensitive and rapid detection of PAEs by using the microscopic and structure-activity relationship between F-CC3 biomass matrix materials and PAEs molecular structure. Carbon nanotubes (CNTs) is a kind of carbon-based nanomaterials with stability and high modifiability, which have been widely studied and have a profound application history in the field of EC. It is also an important transition to modern material strategies. Due to the strong van der Waals interaction of single-walled CNTs (SWCNTs), aggregation and deficiencies are caused, destroying the polymer matrices and nonuniform thin layers. SWCNTs are difficult to overcome these deficiencies, and they are often pushed to the side of modern graphene materials and multi-walled CNTs (MWCNTs)[37,38]. Abeysinghe et al.[43] developed a new PAE sensing platform (bucky paper) using highly conductive MWCNT. Bucky paper can reduce the conductivity by adsorbing PAEs in the solution. This novel method has shown its potential to distinguish DEHP, diphenyl phthalate (DPhP) and dioctyl phthalate (DOP) from other aromatic molecules (e.g., naphthalene, bisphenol A, xylene and toluene). Zhao et al.[44] constructed an EC sensor by modifying diisononyl ortho-phthalate (DINP) MIP on a GCE. The proposed system has the advantages of highspeed immediateness detection capability, simple operation process, no sample pretreatment, low cost, short detection time, good stability, and high sensitivity. MWCNTs loaded with Au nanoparticles (NPs) can enhance the conductivity of the composite material. Based on this, a MIP EC sensor with high sensitivity and selectivity for the determination of DBP can be constructed. By modifying MWCNTs and Au NPs on the electrode surface, the chemical stability can be enhanced and the electron transfer rate can be accelerated. As shown in Fig.2 (B), by loading surface MIP synthesized using SiO_2 microspheres as carriers that can recognize DBP on the surface of MWCNTs and AuNPs modified electrodes, an EC sensor for detecting DBP can be successfully constructed[45,46]. Graphene material has

Table 2 Characteristics of the developed classical EC sensors and ECL sensor for PAEs detection

Target	Type of sensor	Functional nanomaterials modified electrode	Recognition element	Type of signal response	Linear range (mol/L)	Limit of detection (mol/L)	Real sample	References
DEHP	EC	3D rGO/NiHCF NPs	Aptamer	turn off	2.6×10^{-14}-2.6×10^{-9}	9.3×10^{-15}	plastic toys, plastic packaging	[49]
DEHP	EC	PANI-MWCNTs/ Cu MOF/Au NPs	Aptamer	turn on	2.6×10^{-10}-2.6×10^{-7}	7.7×10^{-11}	sesame oil, peanut oil, corn oil	[51]
DEHP	EC	Au Fs	Aptamer	turn off	7.1×10^{-10}-2.0×10^{-8}	5.9×10^{-14}	drinking water	[52]
DEHP	EC	PEI-g-C_3N_4/Au@ Ni-CoHNB	Aptamer	turn off	2.6×10^{-12}-2.6×10^{-7}	6.4×10^{-13}	liquor	[41]
DBP	EC	Au@Pt/PEI-rGO	Antibody	turn on	3.6×10^{-12}-3.6×10^{-7}	9.9×10^{-13}	liquor	[55]
DBP	EC	SiO_2COOH@MIP/Au NPs/MWCNTs/GCE	MIP	turn off	3.6×10^{-10}-3.6×10^{-5}	1.8×10^{-11}	tap water, Chinese Baijiu	[46]
DBP	EC	MIP/Au NPs/ MWCNTs/BDD	MIP	turn off	1.0×10^{-8}-1.0×10^{-5}	3.3×10^{-9}	lake water, tap water	[45]
DBP	EC	MIP-DBP-CTS/ F-CC3/GCE)	MIP	turn on	$0\sim1.8\times10^{-6}$	2.6×10^{-6}	rice wine	[42]
DBP	EC	N-doped graphene/ $CoSe_2$/Au NWs	Antibody	turn off	3.6×10^{-12}-3.6×10^{-6}	1.8×10^{-12} 2.6×10^{-12}	liquor	[50]
DBP	EC	Au NPs/antigen/ chitosan/MWCNTs@ GONRs/GCE	Antibody	turn off	——	2.5×10^{-8}	pure water, tap water, pond water, river water	[54]
DINP	EC	GCE/MIPs	MIP	turn off	5.0×10^{-8}-1.0×10^{-6}	2.7×10^{-8}	white liquor	[44]
DPrP	EC	Au NCs/PEI-w-$CoSe_2$	Antibody	turn off	1.0×10^{-11}-1.0×10^{-5}	1.4×10^{-12}	liquor	[53]
DEHP、 DNOP、DPhP	EC	MWCNT/buckypaper	Label-free	turn off	——	2.6×10^{-3}	——	[43]
PAEs	EC	EST/PANI/CNT/ CuNPeNF	Enzyme sensing	turn on	3.0×10^{-11}-8.0×10^{-11}	——	PET bottle stored drinking water, soft drinks, beverage, lake water	[56]
DEHP	ECL	NH_2-Zr-MOF/GDY	Aptamer	turn on	2.6×10^{-15}-2.6×10^{-7}	6.2×10^{-15}	river water, urban drinking water	[57]
DBP	ECL	MWCNTs/CdSe QDs	Aptamer	turn off	3.6×10^{-9}-3.6×10^{-8}	1.5×10^{-9}	——	[58]

recently been particularly noticed[47,48], which is a 2-D, planar sheet of sp2-hybridized carbon. In other words, it is between CNTs (1-D) and graphite (3-D) in terms of carbon-based nanomaterials[38]. The coupling of graphene (3D rGO) with nickel hexacyanoferrate NP (NiHCF NP) can not only improve the electron transfer ability of NiHCF NPs, but also provide more sites for aptamer immobilization. Based on this, an efficient DEHP EC sensing platform can be developed[49]. Fig.2 (C) shows a sensitive dual-mode competitive EC immunosensor for the quantitative determination of DBP on the strength of the response modes of square wave voltammetry and differential pulse voltammetry. The functionalized N-doped graphene/ $CoSe_2$ nanobelt composites can be used as a preliminary signal amplification platform for immunosensors. The limited Ab binding sites are competed by the immobilized coating antigen DBP-BSA and DBP. The concentration of DBP can be determined through DPV detection of the Thionine (Thi) signal and SWV mode detection of the current generated by the peroxidase-like ThiAu@Pt- catalyzed H_2O_2 and o-phenylenediamine reaction system. The method has good selectivity, stability and reproducibility, and has been successfully applied to the sensitive detection of DBP in actual samples[50]. The combination of materials, such as MWCNTs, Cu metal-organic frameworks (Cu MOFs) and Au NPs, can construct a highly sensitive EC aptasensor to detect of DEHP in edible vegetable oil[51].

As a typical inorganic material, metal materials are also used in the modification of EC sensors. It can be seen from Fig.3 that the electrode was modified with Au nanoflowers (Fs), and the surface of the refined electrode

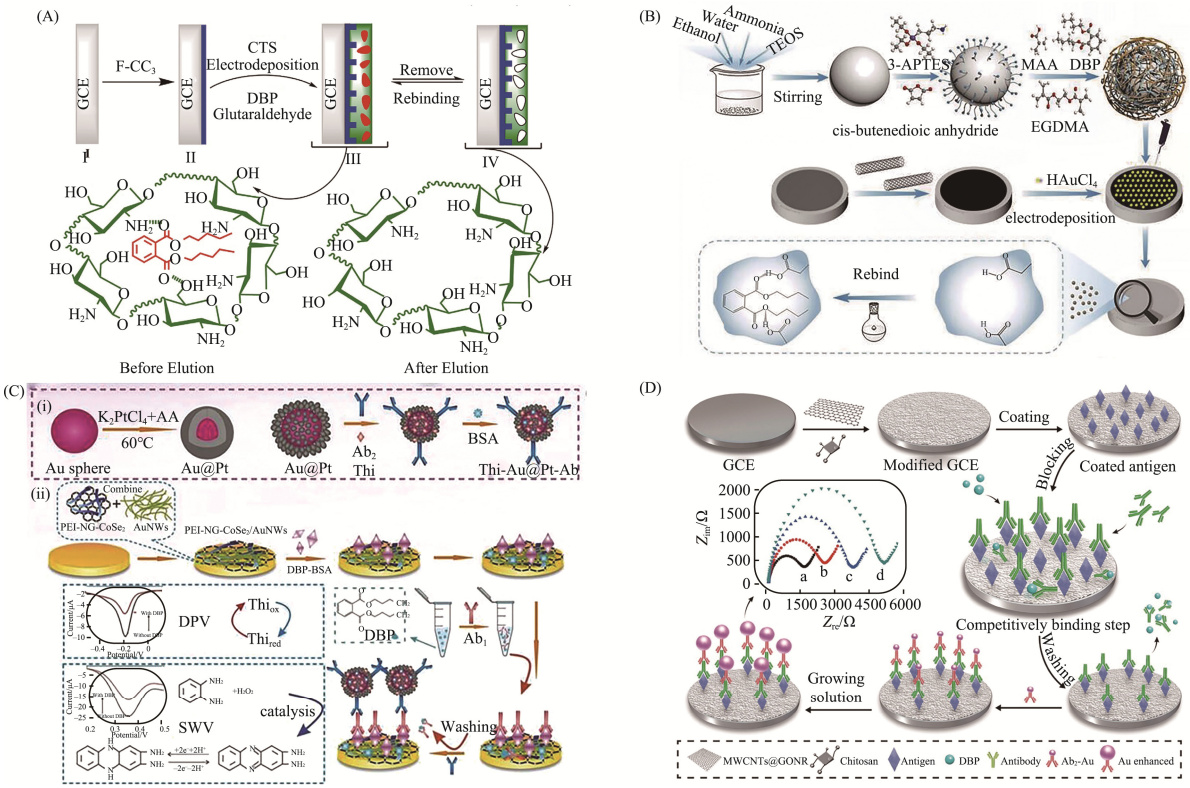


Fig.2. Scheme for (A) preparation of the MIP-DBP-CTS/F-CC3 EC sensor[42]; (B) preparation of SiO_2-COOH@MIP/Au NPs/MWCNTs/GCE sensor[46]; (C) preparation of Thi-Au@Pt-Ab_2 signal label (i) and EC immunosensor for detection of DBP (ii)[50] and (D) EC immunosensor for detection of DBP[54].

Adapted from [42, 46, 50, 54], with permission from Journal of Electroanalytical Chemistry, 2021; Food Chemistry, 2022; Sensors and Actuators B: Chemical, 2021; Biosensors and Bioelectronics, 2017.

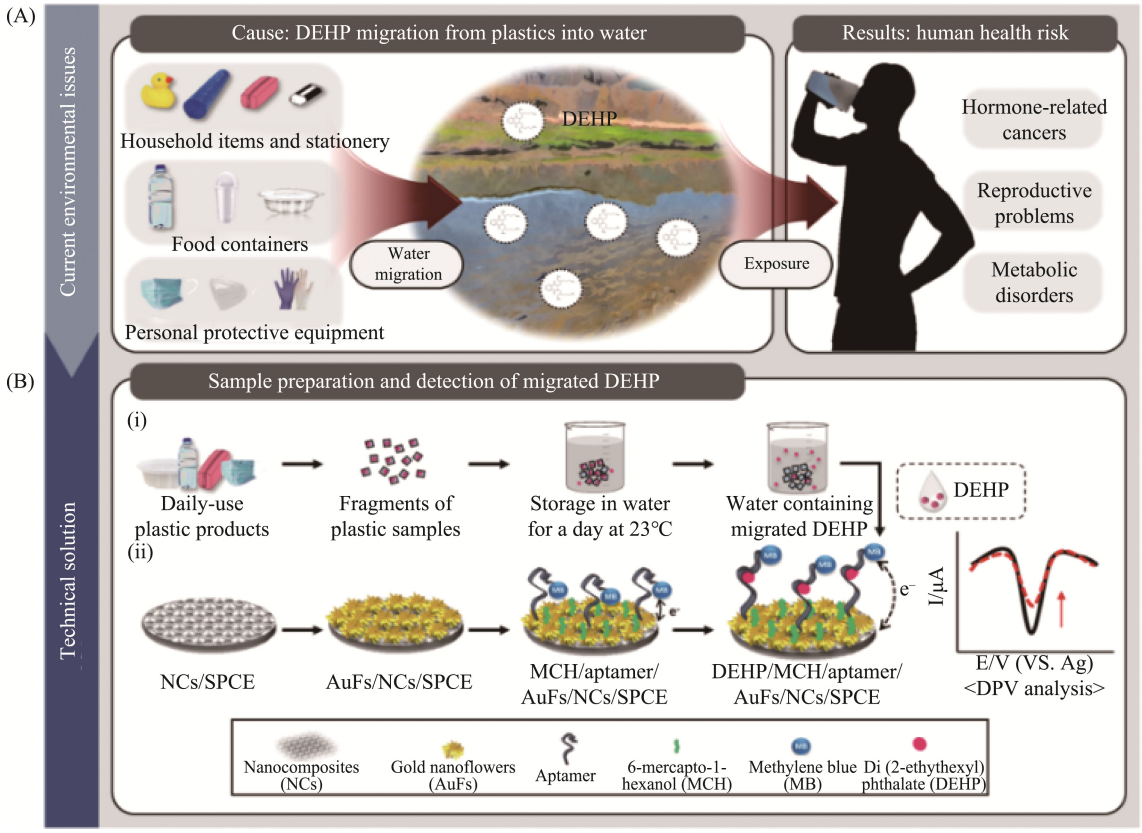


Fig.3 (A) Schematic diagram of the problems faced by the migration of DEHP from plastics to water, and (B) Scheme for (i)the fabrication of plastic products for daily use for the analysis of migrated DEHP, and (ii)the preparation of an EC aptasensor for DEHP detection[52].
Reproduced from [52], with permission from Sensors and Actuators B: Chemical, 2022.

showed enhanced electrocatalytic performance. Highly sensitive monitoring of DEHP can be achieved by capturing DEHP using a methylene blue-coupled aptamer immobilized on the surface of the Au Fs structure[52]. The composite material formed by Au nanocubes (NCs) uniformly anchored on the surface of PEI-w-$CoSe_2$ through Au-N bonds can improve the conductivity and available surface area of the electrode. The immunosensor based on this construction can detect dipropyl phthalate (DPrP) by monitoring the change of oxidation current of different concentrations of DPrP[53]. Au NPs induce signal amplification. The catalytic precipitation promoted by NADH can make the Au NPs larger, resulting in electrostatic repulsion and electron transfer resistance increased significantly after the combination of AuNPs-labeled secondary Ab and anti-DBP, which makes the signal amplified. Therefore, a simple, signal-amplified, label-free DBP EC impedance immunosensor can be established based on the indirect competitive binding system between coated antigen/ chitosan/MWCNTs@GONRs/GCE (modified electrode), target (DBP) and anti-DBP Ab, shown as Fig.2 (D)[54]. The researchers combined Au with other nanomaterials. The composite material can modify the electrode as a signal amplification platform, which can not only improve the sensing performance, but also immobilize the Ab. The composite material can also accurately quantify the content of the target by carrying electroactive substances as signal probes. It shows a new route for the monitoring of DBP and DEHP in the food field[41,55]. In order to overcome the cumbersome extraction procedures and complex detection instruments involving PAEs extraction, an enzyme for detecting PAEs can be introduced into the sensor. Annamalai et al.[56] developed a sensor, and analyzed the GCE modified with esterase and nano-components. It was proved that the developed enzyme-based EC sensor can be effectively used to the determination of PAEs in humans. The enzyme was introduced into the sensor to detect PAEs in beverages stored in PET bottles and lake water contaminated by industrial wastewater.

2.2 Application of ECL sensor for the detection of PAEs

When the ECL sensor is working, a definite voltage should be imposed on the electrode to make it undergo an EC reaction. The generated product (or product reacts with a certain element in the system) produces an excited state substance. When the substance returns to the ground state, it can emit light. By measuring the intensity of the luminescence, the monitoring and analysis of the substance to be measured can be realized[32]. The ECL chemiluminescence marker has a small molecular weight, a simple structure, a very stable label, and a particularly small effect on the function of the Ab. Therefore, the ECL sensor has better sensitivity, more ideal selectivity and better stability than the classical EC sensor. The ECL technology stems from the redox reaction on the electrode in the EC system, which causes electron transfer and energy emission on the electrode[59,60]. The luminescent material on the electrode surface has a significant effect on the analytical ability of the ECL sensor[61].

Dong et al.[57] combined a highly efficient electrocatalytic MOF (NH_2-Zr-MOF) with a graphdiyne (GDY) material to make a composite, which not only facilitates electron transfer in the whole EC reaction process, but also significantly enhances the overall EC active surface area, shown in Fig.4(A). In order to enhance the stability of ECL signal, nitrogen microbubbles with higher stability and higher mass transfer capacity were used into ECL system for the first time. Based on this, they constructed an ECL sensor to realize highly sensitive detection of DEHP. Among them, quite a few pores in GDY and NH_2-Zr-MOF can limit the redox reaction within a certain range, which will enhance the ECL intensity of GDY in the system. The porous MOF structure can enlarge the ECL emission of GDY by an autocatalytic and pore-limiting method. In the meantime, for the sake of further enhancing the property of the sensor, the accelerator sodium ascorbate (NaAsc) is integrated into the co-reaction system. As can be seen from Fig.4(B)[58], the working electrodes for ECL detection was prepared by bonding carbon conductive tape onto ITO glass and modifying it with MWCNTs and CdSe quantum dot (CdSe QDs). The bisphenol A (BPA) and DBP could quench the ECL emission of CdSe QDs, and the decreased ECL intensities had excellent linear relationships with the concentrations of BPA and DBP. Futhermore, we can couple the modified electrode in this study with a paper-based analytical device composed of

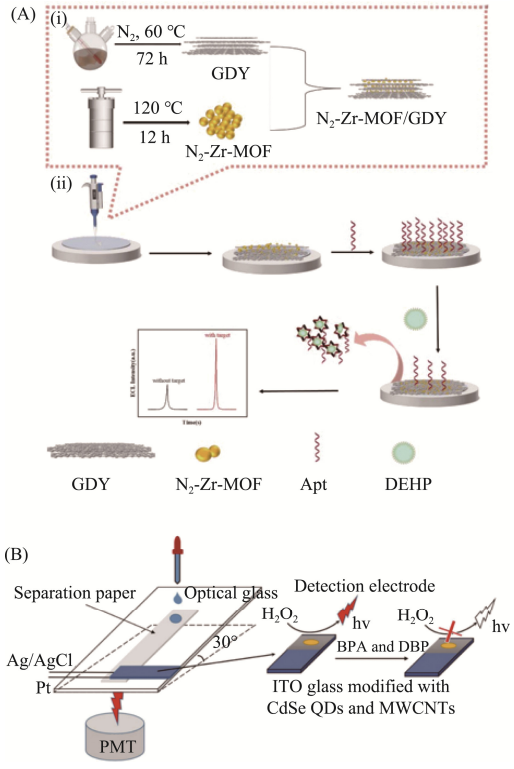


Fig.4 Schematic diagram of (A) material synthesis (i) and ECL sensor preparation process(ii)[57] and (B) paper chromatography ECL device for BPA and DBP detection[58]
Adapted from [57, 58], with permission from The Analyst, 2018; Sensors and Actuators B: Chemical, 2021.

chitosan-modified filter paper. The separation function of the paper-based device and the advantages of easy manufacture and convenient operation make the ECL sensors have the possibility of being applied to the separation and detection of various targets.

2.3 Application of PEC sensor for the detection of PAEs

When PEC sensor works, the light signal as the excitation light source can cause the photosensitive substance to react with the measured substance, and then produce a signal that has a linear relationship with the concentration of the measured substance. Therefore, we can achieve the analysis of the target by detecting the current/voltage signal. In addition, the PEC sensor has superior sensitivity because the relatively independent excitation signal and detection signal make its background signal lower[32]. In recent years, nanomaterials have attracted wide attention in the field of sensor design due to their exceptional physicochemical and opto-electronic properties, a high surface area-to-volume ratio and easy surface functionalization, and they have made breakthroughs in portability, miniaturization and fast signal response in sensor design. Many nanomaterials have different functions such as high conductivity, good catalytic activity, and optical and plasma properties. Reliable and sensitive nanomaterials portable sensors can achieve rapid and cost-effective real-time monitoring and detection of different analytes[62]. The properties of the PEC sensors for the detection of PAEs are presented in Table 3.

In the field of PEC sensors, there are many studies on semiconductor materials. As is known to all, the heterojunction structure can greatly enhance the carrier mobility. Meng et al.[63] constructed a PEC sensor for detection of DEHP based on the DEHP aptamers as the biological recognition elements and BiOI/ZnO nanoarrays (NRs) as the transducer species, which is illustrated in Fig.5(A). The built-in electric field can be generated between BiOI with narrow band gap and ZnO NRs, and the photocurrent response is obvious. Therefore, BiOI can be combined with ZnO NRs, which can not only promote the transmission and separation of charge carriers, but also enhance the visible light absorption. The PEC sensor based on this construction showed excellent sensing performance for the detection of DEHP. The constructed PEC sensor introduced a potential device for monitoring DEHP in the environment. Fig.5(B) shows that a Z-scheme heterojunction is formed between the prepared Cu_2O/Cu_3SnS_4 Fs, and the composite material is used as a photoactive material to construct a smartphone-based PEC point-of-care test (POCT). The competitive immunoassay on the electrode can significantly reduce the photocurrent signal and enhance the sensitivity of POCT. The smartphone is used to record and transmit PEC results during the operation of the sensor. The results show that the constructed sensor has excellent stability, repeatability, reproducibility and selectivity. This sensor provides a sensing platform for intelligent POCT for environmental monitoring and food safety[64]. Bismuth sulfide (Bi_2S_3), which forms a heterojunction structure with other semiconductor materials, has greatly improved sensing performance[65,66]. Studies have combined Bi_2S_3 with molecular imprinting to construct a MIP-PEC sensor for the determination of the plasticizer DOP. The role of Bi_2S_3 in this sensor is a photoelectric converter[67].

Table 3 Characteristics of the developed PEC sensors for PAEs detection

Target	Type of sensor	Functional nanomaterials modified electrode	Recognition element	Type of signal response	Linear range (mol/L)	Limit of detection (mol/L)	Real sample	References
DEHP	PEC	BiOI/ZnO NRs	Aptamer	turn off	1.0×10^{-11}-5.0×10^{-7}	3.8×10^{-12}	soil	[63]
DEHP	PEC	N-CQDs-decorated TiO_2 NRs/BCP	Aptamer	turn on	1.3×10^{-13}-1.8×10^{-10}	4.4×10^{-14}	milk, river water	[72]
DEHP	PEC	GQDs-decorated TiO_2 NTs	Aptamer	turn off	7.8×10^{-13}-2.6×10^{-10}	2.6×10^{-13}	milk, plastic bag, lake water	[73]
DEHP	PEC	N, S-GQDs/TiO_2 NRs	Aptamer	turn on	2.6×10^{-16}-2.6×10^{-14}	2.6×10^{-16}	plastic bag, Fenhe water	[74]
DEHP	OPECT	MXene/Bi_2S_3/$CdIn_2S_4$	Label-free	turn off	1.0×10^{-12}-2.0×10^{-10}	2.4×10^{-13}	plastic, lake water, purified water	[82]
DBP	PEC	NH_2-UiO-66/ TpPa-1-COF	MIP	turn off	1.0×10^{-10}-1.0×10^{-4}	3.0×10^{-11}	tap water, Chinese Baijiu, chicken	[79]
DBP	PEC	$Cu_3(BTC)_2/Cu_2O$/ITO	MIP and aptamer	turn off	1.0×10^{-13}-1.0×10^{-9}	3.5×10^{-14}	bottled water	[77]
DBP	PEC	MIP/Au/TiO_2	MIP	turn off	5.0×10^{-8}-5.0×10^{-7}	7.0×10^{-10}	real water	[80]
DBP	PEC	Cu_2O/Cu_3SnS_4	Antibody	turn off	1.4×10^{-10}-1.4×10^{-6}	2.9×10^{-11}	Blank lake water, soybean oils	[64]
DBP	PEC	g-C_3N_4/SnO_2	Aptasmer	turn off	1.0×10^{-15}-1.0×10^{-9}	3.0×10^{-16}	tap water	[75]
DOP	PEC	$Cu_3(BTC)_2$@Cu_2O	MIP	turn off	2.5×10^{-11}-1.0×10^{-7}	9.2×10^{-12}	bottled water	[78]
DOP	PEC	Bi_2S_3	MIP	turn off	5.0×10^{-13}-7.0×10^{-11}	1.0×10^{-13}	Plastic bottled water,wastewater,soil extracts	[67]

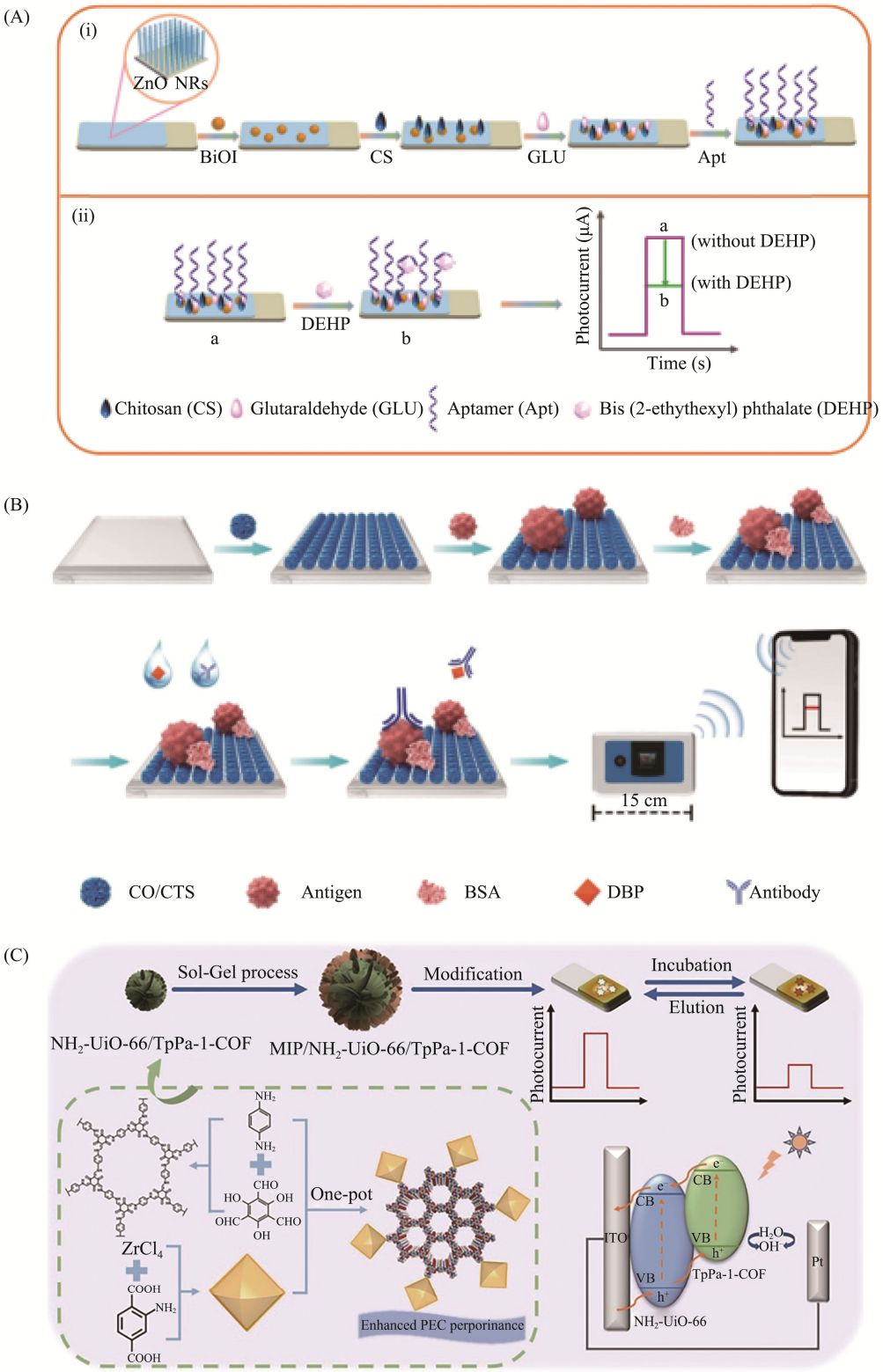


Fig.5 Schematic demonstration of (A) PEC aptasensing platform based on BiOI/ZnO NRs for detection of DEHP: (i) the assembly process of the PEC aptasensing platform, (ii) the recognition mechanism for detection of DEHP[63], (B) fabrication procedure for the PEC POCT platform for DBP detection[64] and (C) the preparation process of MIP-PEC sensor and the mechanism of photocurrent generation[79]. Adapted from [63, 64, 79], with permission from Biosensors and Bioelectronics, 2024; Journal of Hazardous Materials, 2023; Biosensors and Bioelectronics, 2023.

Various non-metallic nanomaterials, such as carbon dots (CDs), graphene QDs (GQDs) and carbon nitride have achieved great attention of late years[68-71]. Non-metallic nanomaterials are unquestionably more environmentally friendly than traditional semiconductor materials, which can efficiently increase the risk of potential toxicity to health and environment[69]. Therefore, the research on the combination of semiconductors and non-metallic materials is also a hot topic. Deng et al.[72] constructed a visible-light-driven highly efficient PEC aptasensor for specific

and sensitive detection of DEHP by combining N-doped carbon QDs-decorated TiO_2 nanorods (N-CQDs-decorated TiO_2 NRs) with biocatalytic precipitation (BCP). Among them, TiO_2 NRs, which are modified by N-CQDs, have exceptional PEC performance and increased visible light absorption capacity. The reason for the signal amplification is that horseradish peroxidase (HRP)-induced BCP causes a decrease in the PEC detection signal. GQDs are also mostly combined with TiO_2 nanorods to form composites for efficient and sensitive detection of DEHP. The anti-DEHP aptamer was used as a biorecognition element for the constructed PEC sensor to achieve specific recognition of DEHP. The photoelectric properties of the materials can also be improved by nitrogen and sulfur co-doping of GQDs. In the construction of PEC sensor, GQDs were uniformly and tightly anchored on TiO_2 NTs by electrostatic interaction, and anti-DEHP aptamer molecules were immobilized on GQDs modified TiO_2 NTs by cross-linking coupling method. [73,74]. Yang et al.[75] used g-C_3N_4/SnO_2 composite as a signal indicator and the target-induced cross-shaped DNA structure as a signal amplifier to construct a signal-quenched ultrasensitive PEC aptasensor for detection of DBP. The designed cross-shaped DNA structure is used for sequential recognition of the target due to its repulsive and separated tails, fixed directions and multiple recognition domains, reducing the steric hindrance of the reaction, thereby showing high signal amplification efficiency (Fig.6). The construction of this sensor provides a new nucleic acid signal amplification method, which provides a new method for improving the sensitivity of the PEC sensing platform for detection of PAEs.

MOFs are extremely porous materials with stability and can achieve various interactions by containing both inorganic and organic parts in the structure, so they are ideal nanomaterials for PEC sensors. In addition, MOF-based sensors also have the advantages of high sensitivity, large porosity, controllable structure, simple functionalization, large surface area, and low LOD[62,76]. Yu et al.[77] proposed a dual recognition strategy of aptamer and MIP based on MOF and Cu_2O heterostructure. A new type of PEC sensor was prepared by modifying the complex formed by the incubation of aptamer with DBP on the surface of $Cu_3(BTC)_2$/Cu_2O/ITO and the controllable self-polymerization of dopamine. The $Cu_3(BTC)_2$/Cu_2O composite has high photocurrent, good stability and strong light absorption ability under visible light irradiation. The PEC sensor has high specificity for the detection of DBP due to the dual recognition mechanism of aptamer and MIP. Gao et al.[78] coated MOF material $Cu_3(BTC)_2$ on Cu_2O to form $Cu_3(BTC)_2$@Cu_2O heterostructure. The heterostructure exhibits strong light absorption ability, enhanced photocurrent and nicer stability under visible light irradiation. By imprinting DOP on the heterostructure as a photoelectric converter, a PEC sensor was established. The experimental results show that the method has good stability, reproducibility, sensitivity and selectivity in real

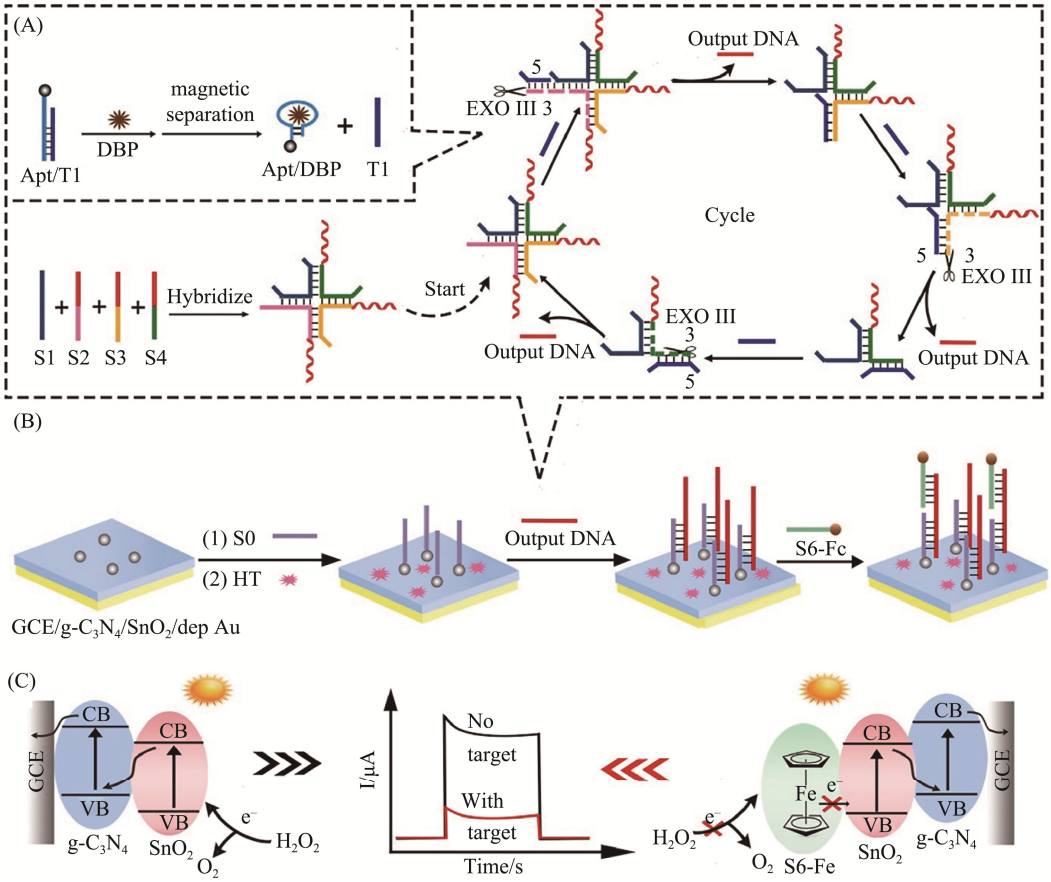


Fig.6 Schematic illustration of (A) the target-induced Exo III-assisted cruciform DNA Nucleic Acid signal amplification strategy; (B) the construction process of PEC sensor; (C) electron transfer mechanism of the proposed sensor[75].
Reproduced from [75], with permission from Analytica Chimica Acta, 2023.

sample analysis, indicating that MOF-based heterostructures have good application prospects in the field of PEC analysis. The combination of various nanomaterials will better improve the performance of the sensor. A novel MOF/COF heterostructure hybrid composite (NH_2-UiO-66/TpPa-1-COF) with eximious photoactivity was prepared by Yang et al.[79] The formation of heterojunction, strong light absorption ability and good energy band structure of the material have better photocurrent response. It can be used as a PEC sensitization layer to construct MIP-PEC sensors for highly sensitive and selective detection of DBP in Fig.5(C). Using MIP as the recognition element of the PEC sensor can improve the sensing performance of the sensor. Because the specific binding of the imprinting site to DBP hinders electron transfer, the photocurrent response of the sensor is reduced. In addition to MOF materials, other nanomaterials such as Au NPs also have good photoelectric effect and are widely used in photoelectric sensors[74].

Organic EC transistor (OECT) sensors have great potential for sensing applications owing to their favorable biocompatibility, intrinsic amplification and structural flexibility[81]. However, the activity of a few frail biomolecules may be affected by an applied external voltage. Organic PEC transistor (OPECT) sensing technology, which combines PEC and OECT sensors, has received great attention because it can make up for the shortcomings of OECT sensors. Zhang et al.[82] used MXene/Bi_2S_3/$CdIn_2S_4$ as the photoactive material and $Ru(NH_3)_6^{3+}$ as a signal enhancement molecule. Combining PEC analysis with an OECT, a novel OPECT aptasensor was established for the detection of DEHP. Based on the MXene/Bi_2S_3/$CdIn_2S_4$ photosensitive material, the OPECT sensor achieved a high current gain of nearly a thousand times at zero bias voltage (Fig.7). The constructed signal-on OPECT sensing platform achieved high sensitivity and high specificity detection of DEHP. The detection results of the sensor in real samples were satisfactory. Therefore, the successful construction of this OPECT sensing platform shows the huge potential of OPECT for the detection of DEHP.

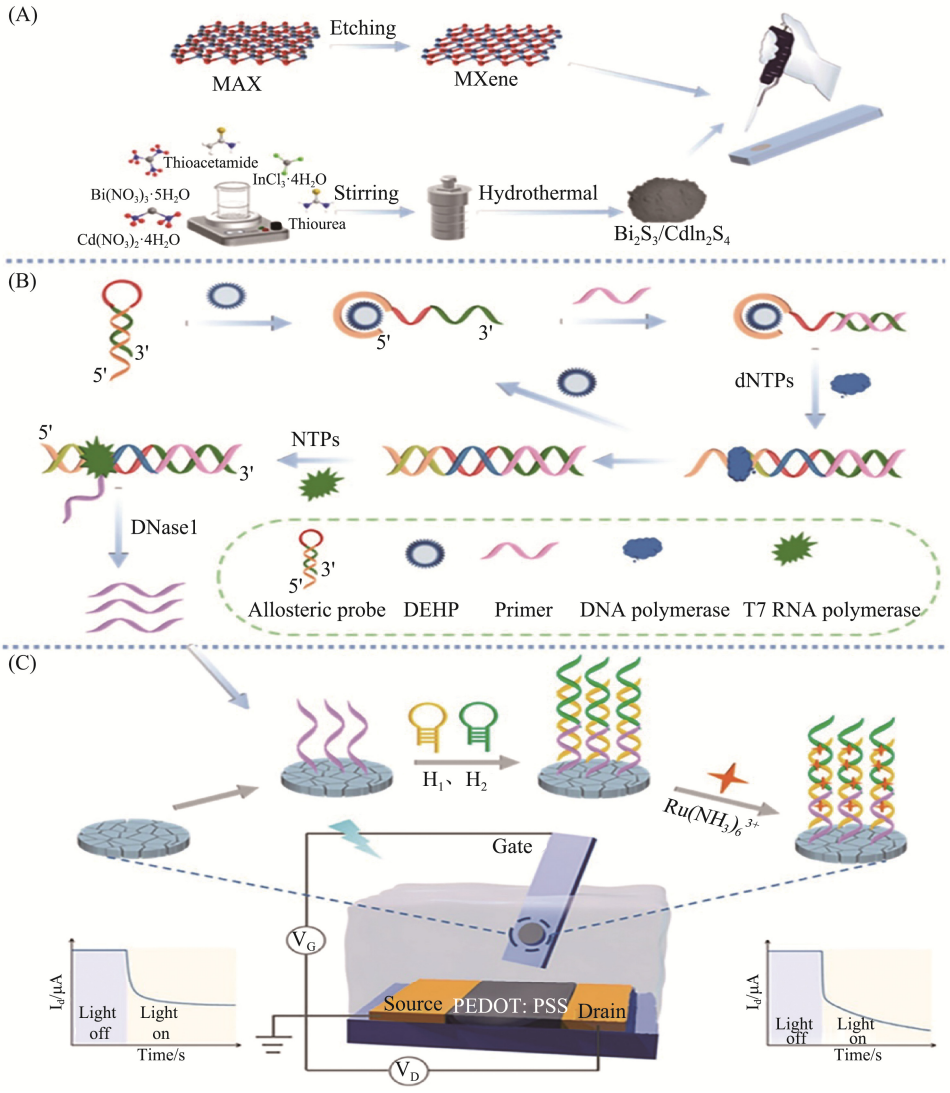


Fig.7 Schematic illustration of (A)the preparation of MXene and $Bi_2S_3/CdIn_2S_4$, (B)flow chart of allosteric probe-initiated catalysis and acquisition of target RNA, (C) and construction of OPECT sensor[82].
Reproduced from [82], with permission from Analytical Chemistry, 2024.

3 Summary and perspectives

PAEs have the characteristics of strong toxicity, wide distribution and great harm, which need more attention. PAEs in the environment and food not only have a huge negative impact on marine biota, but also may cause children to face anti-androgen effects and the risk of asthma. In addition, the important metabolite of PAEs, phthalate monoester, has an inhibitory effect on the important phase II metabolic enzyme SULTs of the human body. Long-term intake of PAEs can lead to obvious depressive behavior and neurobehavioral disorders. The limited low concentration of PAEs in the environment and food determines the importance of achieving sensitive detection of trace amounts of PAEs. Compared with GS-MS and HPLC-MS, the developed sensor for rapid detection of trace PAEs is a powerful tool for emerging disease warning and daily PAEs pollution risk monitoring. These EC sensors integrate Ab, aptamers or MIP as three main recognition elements. This review summarizes the classic EC sensors, ECL sensors and PEC sensors for detection of PAEs. Although varieties of EC sensors have been developed, only a few EC sensors can finally achieve portable or fast real-time detection. Therefore, PAEs still have a long way to go from the laboratory to the real-time detection site.

In the future, PAEs pollution can be prevented and controlled by raising public awareness of environmental protection and developing real-time rapid detection technology. Aptamer is a cost-effective, versatile and efficient new material and identification element. It can overcome the defects of poor chemical stability, high cost and short life of traditional elements (e.g., Ab, proteins and enzymes). The rapid and continuous development of smartphone electronic devices and the development of new algorithms have enabled smartphones to have different functions as detectors and instrument interfaces (such as multi-USB ports, Bluetooth or Wi-Fi). The high resolution of the mobile phone camera can quickly and accurately read the optical signal, thereby increasing the LOD and expanding the detection range. In addition, the communication and networking capabilities of smart phones provide a new idea for the construction of real-time and rapid PAEs detection, and provide data support for the prevention of PAEs pollution in the region. Real-time monitoring of PAEs can provide the latest information about PAEs pollution, thus reminding people to stay away from pollution sources and evaluate environmental remediation. The sensor can also be effectively used to monitor the abnormal levels of PAEs in the human body at an early stage, so as to warn the occurrence of diseases. In summary, the ultimate goal of sensor technology innovation is to develop a multi-functional platform with high sensitivity, high selectivity, portability, cost-effectiveness and easy to use and it can provide a variety of PAEs qualitative and quantitative detection services.

Abbreviation

EC	electrochemical	DINP	diisononyl ortho-phthalate	MOFs	metal-organic frameworks
ECL	electrochemiluminescence	DPrP	dipropyl phthalate	QDs	quantum dot
PEC	photo-electrochemical	DOP	dioctyl phthalate	GQDs	graphene QDs
GC	gas chromatography	DMP	dimethyl phthalate	N-CQDs	N-doped carbon QDs
MS	mass spectrometry	DEP	diethyl phthalat	GDY	graphdiyne
HPLC	high-performance liquid chromatography	BBP	benzyl butyl phthalate	CDs	carbon dots
MIP	molecularly imprinted polymer	DIBP	diisobutyl phthalate	CNTs	carbon nanotubes
BCP	biocatalytic precipitation	3D	three-dimensional	SWCNTs	single-walled carbon nanotubes
OECT	Organic EC transistor	NPs	nanoparticles	MWCNTs	multi-walled carbon nanotubes
OPECT	organic PEC transistor	Fs	nanoflowers	GCE	glassy carbon electrode
LOD	detection limit	NCs	nanocubes	Ab	antibody
DEHP	bis(2-ethylhexyl) phthalate	NR	nanorod	HRP	horseradish peroxidase
DBP	dibutyl phthalate	NWs	nanowires	SULTs	sulfotransferases
DPhP	diphenyl phthalate	NiHCF	nickel hexacyanoferrate	NaAsc	sodium ascorbate

Author Contributions:

Conceptualization-Xiuxiu Dong, Lili Zhang; Funding acquisition-Xiuxiu Dong, Minfu Wu, Qijian Niu; Investigation-Xiuxiu Dong; Project administration-Xiuxiu Dong; Supervision-Xiuxiu Dong; Roles/Writing - original draft-Xiuxiu Dong, Lili Zhang, Meicai Ge; and Writing - review & editing-Xiuxiu Dong, Minfu Wu, Qijian Niu.

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Data Availability:

The authors declare that the main data supporting the findings of this study are available within the paper and its Supplementary Information files.

Conflict of Interest:

The authors declare no competing interests.

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