

Review

Recent advances in the detection of microplastics in the aqueous environment by electrochemical sensors: A review

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ABSTRACT

Microplastics (MPs), as an emerging contaminant, have become a serious threat to marine ecosystems due to their small size, widespread distribution and easy ingestion by organisms. Therefore, it is necessary to develop various analytical techniques to detect MPs in real water environment. Among these detection techniques, the advantages of electrochemical sensors, such as easy operation, high sensitivity and low cost, provide the possibility of online real-time detection of MPs in real water environment. The aim of this article is to analyze and compare the advantages and disadvantages of different MPs detection techniques. Compilation of various electrochemical sensors, we compiled various electrochemical sensors, evaluated the recent advances in carbon materials, metals and their oxides, biomass materials, composite materials, and microfluidic chips in electrochemical sensors for detecting MPs, and in-depth investigated their detection mechanisms and sensing performances, proposed hotspot nanomaterials for electrochemical sensors that could be used to detecting MPs and gave an outlook on the last years of electrochemical sensors in the area of microplastic detection. Finally, the challenges of electrochemical sensors for the detection of MPs are discussed and perspectives for this area are presented.

1. Introduction

Plastic pollution has always posed a major threat to the global ecosystem. >30 million tons of plastic waste are generated worldwide every year (Nguyen et al., 2024). Due to their longevity, corrosion resistance and stability, plastics persist in the atmospheric, geological and water cycles and form smaller sizes (Chandra and Walsh, 2024). If the size of the plastic is <5 mm, it is called "microplastic". The term microplastics was first introduced by Richard C. Thompson (Thompson et al., n.d.). Microplastics are categorized according to their production route into primary microplastics (first produced in micrometer size) and secondary microplastics (degraded through physical and chemical processes) (Wang et al., 2019). About 20 million tons of this plastic waste ends up in the marine system in a direct or indirect form (Nguyen et al., 2024). The main sources of microplastics in the marine system include beach tourism, commercial fishing, maritime vessels and offshore industries (Osman et al., 2023). Fig. 1 shows the sources, formation and impacts of microplastics in marine systems. Marine aquatic organisms ingest or are exposed to microplastics in various forms (e.g., intravenously, subcutaneously, intraperitoneally, orally, and through dermal

exposure), which has toxic effects on aquatic organisms (Osman et al., 2023). Worse, microplastics can act as carriers of other pollutants, including through adsorption and bioaccumulation, thereby affecting humans and ecosystems (Amelia et al., 2021).

In recent years, microplastics have also been classified as one of the emerging pollutants due to the serious threat to the environment and human health (Babaei et al., 2024). Currently, states and international coalitions have introduced regulations and policies to combat microplastic pollution in marine systems. The United Nations Environment Assembly (UNEA) resolution "Ending Plastic Pollution" states that in the coming years or decades, plastic waste entering the oceans will be reduced to zero (Usman et al., 2022); The United States enacted the Microbead-Free Waters Act in 2017, which prohibits the use of small (<5 mm) intentionally manufactured plastic beads for rinsing personal care products (McDevitt et al., 2017); China also prohibits the disposal of plastic waste in water bodies in its "Solid Waste Pollution Prevention and Control Law" (Zhang et al., 2018); Australia has enacted the "Recycling and Waste Reduction Act" which prohibits the export of plastic waste (Recycling and Waste Reduction Act, 2020); New Zealand's Waste Minimization Act bans the manufacture of detergents

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containing plastic microbeads (Reddy, n.d.); South Korea launched the Plastic Waste Control Program (PWCP) in 2018 to, among other things, comprehensively manage plastic waste (Shin et al., 2020). It can be seen that the number of global policies and regulations on dealing with microplastics is increasing, but there are no unified standards for dealing with microplastics in different countries, and the microplastics laws and regulations introduced by different countries have certain limitations. It is difficult to implement and carry out and there is still microplastic pollution (Casella et al., 2024). In addition to working to reduce microplastic emissions and pollution, countries have also made efforts to monitor and assess microplastics in the aquatic environment, particularly in countries with long coastlines, abundant inland rivers and lakes, and polar regions like the Arctic, where it is necessary to understand the types, abundance and impacts of microplastics in the actual aquatic environment (Uhrin et al., 2022; Martin et al., 2022), and the detection of microplastics in the actual water environment has become a hotspot of concern for all countries (Zambrano-Pinto et al., 2024). Currently, microscopy, thermal analysis and spectroscopy are mainly used to detect microplastics. However, most microplastic detection techniques require sample pretreatment (Shruti et al., 2022); When it comes to microplastics in the submicron and nanometer range, many technologies have limitations that prevent traces of microplastics from being detected. Despite the existence of more mature technologies, their expensive equipment, long response times and low recovery rates do not meet the need for real-time in situ detection of microplastics in aquatic environment. In response to these problems, electrochemical sensors have been developed to detect microplastics (Kamel et al., 2024). Among many detection technologies, electrochemical sensors are widely used in the detection of pollutants in aquatic environments due to their high sensitivity, large detection range, high selectivity and low cost (Chen et al., 2024). Currently, electrochemical sensors are mainly used to detect endocrine disruptors (bisphenol A and its derivatives) in seawater (Yi et al., 2023), antibiotics (Joseph et al., 2022), and important pollutants such as heavy metal ions (Cd^{2+} , Pb^{2+} , Hg^{2+}) (Djebbi et al., 2022) (Akbari Hasanjani and Zarei, 2019) (Li et al., 2016) (Ridwan et al., 2023). When using electrochemical sensors to detect microplastics, researchers have focused on the use of different materials to improve the selectivity and detection performance of the sensors for microplastics (Oliveira et al., 2022). For example, carbon materials, metals and their oxides, biomass materials and composites, etc. (Du et al., 2023; Gongi

et al., 2022; Jebril et al., 2022; Noumani et al., 2024). In current studies, nanomaterials such as MOFs (metal-organic framework materials) with new applications for microplastic removal and quantum dots that can be used to track microplastics, with their excellent electrochemical properties and microstructures, are also potential functional materials for electrochemical sensing (Tammina et al., 2023; Xiong et al., 2024). In addition, the combination of electrochemical sensors and microfluidics is also a good means for detecting microplastics (Ece et al., 2023).

This paper provides an overview of the main techniques used in recent years to detect microplastics in marine systems. Here, recent advances in the detection of microplastics by electrochemical sensors are discussed, electrochemical sensors are categorized based on different electrode material types, the main mechanisms by which the sensors detect them are analyzed, the detection limits and detection limits of the different sensors are compared and hot nanomaterials that can be applied to electrochemical sensors are described. Finally, the limitations of electrochemical sensors are discussed and possible perspectives for future studies on electrochemical sensors for detecting microplastics in marine systems are presented, taking advantage of the portable, low-cost and online real-time detection potential of electrochemical sensors.

2. Techniques for the detection and analysis of microplastics

In marine systems, the main components of microplastics are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyamide (PA) and polyethylene terephthalate (PET). They come in various forms, most commonly in the form of fibers, fragments, films, microspheres, etc. (Guo and Wang, 2019). The density of microplastics influences its distribution in seawater; Since PE and PP have a lower density than water, they float above the surface of the water; While PS, PVC, PA and PET have a higher density than water, they sink in water (Andrady, 2017). Furthermore, microplastics in the marine environment can cause weathering and aging through photooxidation, mechanical abrasion and biodegradation (Zhang et al., 2024b). Weather influences and aging also change the nature of microplastics. For example, microplastics are photooxidized and break down into, among other things, low molecular weight alcohols, aldehydes, ketones and acids; mechanical abrasion accelerates the cracking of the microplastic and increases its hydrophilicity; and bacteria, fungi, algae and other microorganisms break them down into inorganic molecules such as CO_2

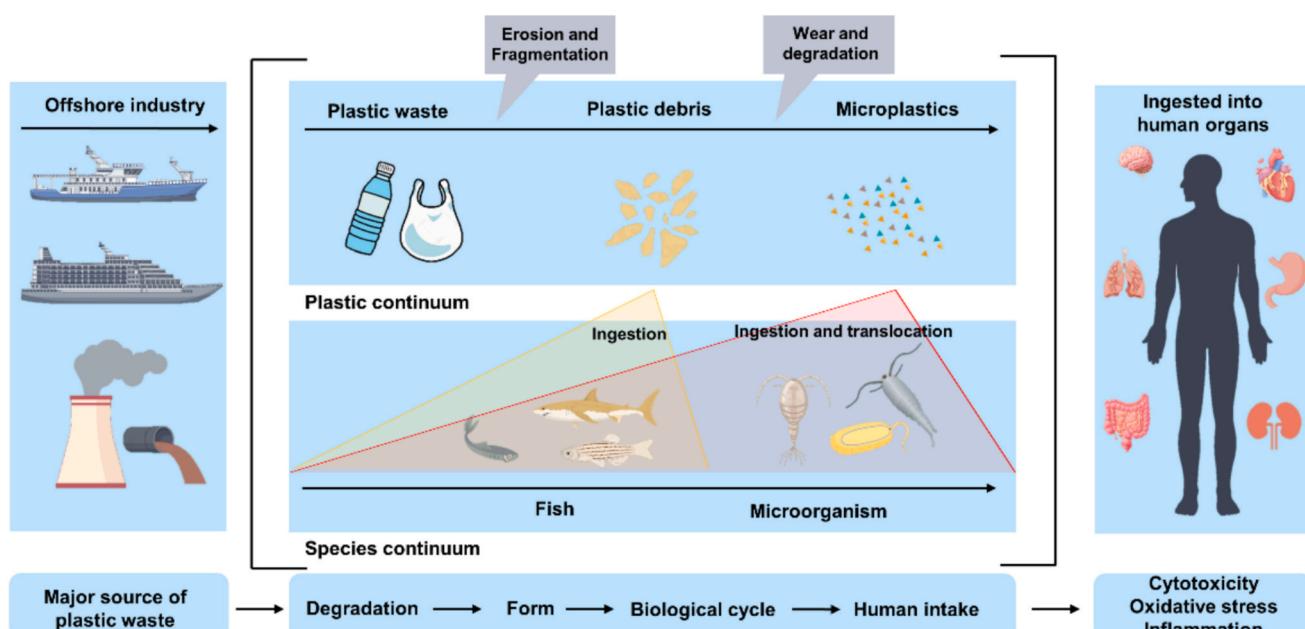


Fig. 1. Main sources, occurrence and effects of microplastics in marine systems on marine organisms and humans.

and H₂O. (Biale et al., 2022).

Hydrophobicity is an important property of microplastics, and in aquatic environments, hydrophobic organic pollutants (POPs) are adsorbed to microplastics, further increasing the potential environmental hazards of microplastics. Electrostatic interaction is another important property of microplastics. Most microplastics are negatively charged, while heavy metal ions in seawater are positively charged. Microplastics adsorb positively charged heavy metal ions through electrostatic attraction (Li et al., 2022b). In addition, microplastics can form forces such as hydrogen bonds, π-π bonds and van der Waals forces and have physicochemical properties such as functional groups and a high specific surface area, which can also impact the environment of marine systems. However, due to the diversity of microplastic types and particle sizes as well as the complex physicochemical properties in the actual marine system, their further detection and analysis is required. This chapter provides a systematic summary of the main microplastic analysis and detection techniques and discusses the advantages and disadvantages of each technique.

2.1. Electrochemical analysis techniques

Electrochemical analysis as a solution for the cost-effective detection of microplastics is one of the most sought-after analytical techniques for the online detection of microplastics (Noumani et al., 2024). Compared to traditional spectral and thermal analysis methods, more cost-effective microcircuit sensor platforms are built with sensing materials and detection elements (Kamel et al., 2024). In addition, electrochemical methods for both qualitative and quantitative analysis of microplastics only require a small amount of sample from the environment. Electrochemical sensing is an important branch of electrochemical analysis (Saputra, 2023). Includes potentiometric, amperometric, and impedance sensors that can detect samples in the environment in various ways (Baranwal et al., 2022). And in the sensor strategy, environmental factors such as pH (Adeel et al., 2020), temperature (Zu et al., 2024), and interference (Tang et al., 2022) can affect the lifespan and accuracy of the sensor. Therefore, when designing the sensor platform, it is necessary to adjust the optimal pH value, study the appropriate temperature of the electrode material and study the noise immunity to achieve the best sensor performance. The unique advantage of electrochemical sensors is their detection speed. The electrochemical reaction usually occurs within a few tens of seconds or minutes, and understanding the microscopic physicochemical interaction between the test sample and the working electrode is the key to improving the speed of the sensor (Liu et al., 2021). Selection of suitable modified electrode materials according to the properties of microplastics. Electrochemical sensors have long been ideal for research in biology, medicine, and the environment, and materials with excellent electrochemical properties have been integrated into electrochemical analyzes to improve the sensitivity and specificity of the sensors (Baranwal et al., 2022; Baig et al., 2019).

2.2. Microscopic analysis techniques

Microscopic analysis is currently the most common technology for detecting microplastics. An optical microscope can be used to determine the abundance, size, shape, color and other physical properties of microplastics in water samples. It has the advantages of easy operation, low cost, etc., but the optical microscope cannot detect microplastics with a particle size of several micrometers or nanometers, and using the visual counting method will cause a large error due to the operator's subjectivity and the transparency of the microplastics. However, optical microscopy cannot detect microplastics with particle sizes of several micrometers or nanometers, and the visual counting method can introduce large errors due to operator subjectivity and the transparency of microplastics, but optical microscopy can be optimally combined with techniques such as fluorescence, staining, polarization and digital holography. In one study, Labbe et al. (2020) added optical elements to a

microscope for polarization and optical detection of microplastics. Here, the use of the Nile Red dye enables the detection of microplastics by generating different fluorescence depending on the hydrophobicity and excitation with an LED flashlight. However, Nile Red dye bursts easily under laser irradiation and is expensive. Based on the drawbacks of Nile Red dye, Lee et al. (2024) developed a low-cost DBB dye for detecting microplastics and applied it to a smartphone-based fluorescence microscope. The results showed that DBB can effectively color microplastics to emit fluorescence and identify different fluorescent colors using a smartphone-based optical microscope to detect microplastics. In another study, Burke et al. (2024) developed a low-cost, 3D printer-based scanning microscope, the EnderScope, and presented the utility and feasibility of the microscope concept. In the concept's presentation, the microscope is based on the mechanics of a 3D printer (Creality Ender 3), which can automatically scan and detect microplastics in seawater over a large area. According to Běhal et al. (2022), optical microscopy can be used to analyze microplastics using digital holography. Using polarized holographic microscopy, microplastics such as PA, PP and polyester can be recovered and applied to a fully optical fingerprint profile based on the Jones matrix form. With polarized holographic microscopy, microplastics such as PA, PP and polyester can be detected and applied in a complete optical fingerprint according to the Jones matrix form. Electron microscopy can also be used to detect microplastics, allowing microplastics of different shapes, colors and sizes to be accurately distinguished. For example, Raharinaivo et al. (2024) used a combination of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) to quantify microplastics in the ocean. Furthermore, the technology was able to distinguish between 38 microplastic-like particles and microplastics from Madagascar.

2.3. Thermal analysis techniques

Pyrolysis-gas chromatography-mass spectrometry (py-GC-MS) is also a commonly used technique for detecting microplastics. It is based on the principle that trace amounts of polymer samples are rapidly heated in an inert atmosphere to produce cleavage products, which are introduced directly into the gas chromatography system for separation and then into the mass spectrometer for detection to determine the composition of the samples by qualitative and quantitative analyzes of characteristic fragment ions after high-temperature cleavage. It is able to analyze microplastics qualitatively and quantitatively; It is also able to detect traces of very small plastic particles. However, the accuracy of co-pyrolysis of mixed component microplastics is a challenge for py-GC-MS to detect microplastics (Peñalver et al., 2020). Therefore, in Lou et al.'s study (Lou et al., 2022), the detection method for microplastics was improved and 1-octadecene, pentane and bibenzyl were selected as new indicators for PE, PP and PS, reducing the upper limits of quantitative uncertainty to 25 %, 32 % and 24 %, respectively, for PE, PP and PS, and increased the accuracy of quantification of microplastics. In addition, the quantitative performance of the py-GC-MS technique for microplastics was enhanced by the use of tandem mass spectrometry in a study by Albignac et al. (2023). The detection limit for microplastics was as low as 15–70 ng by selecting the appropriate indicator for the polymer and optimizing the in-process multi-reaction monitoring. When detecting microplastics, due to the lack of particle size information in the py-GC-MS technique, it is necessary to use the py-GC-MS technique in combination with Fourier transform infrared spectroscopy (FTIR) to estimate the particle size refine information on microplastics. The two techniques have a high potential to complement each other in terms of quantification. The complementarity between the two techniques was also demonstrated in a study by Roscher et al. (2022) who used FTIR spectroscopy and py-GC-MS techniques to analyze wastewater from two German wastewater treatment plants for each month of a year in which FTIR spectroscopy identified 11 μm of microplastics in the wastewater and then obtained supplementary mass data by py-GC-MS techniques. The results showed that polyolefins were the most abundant polymers in

wastewater. Transmission electron microscopy coupled with py-GC–MS enables the morphological and analytical characterization of microplastics, allowing the identification and localization of microplastics in soil fractions, thus enabling the monitoring of microplastics over time (Watteau et al., 2018).

Thermogravimetric analysis technique (TGA) is another commonly used technique for thermal analysis of microplastics for testing purposes. It is a thermal analysis technique based on the principle of measuring the mass of the sample to be tested as a function of temperature under programmed temperature control and is used to study the thermal stability and composition of materials. It offers the advantages of high quantification, small sample size and high resolution. However, in TGA testing, various factors such as sample size, temperature rise rate, sample dosage, etc. affect the analysis results, resulting in data errors in the analysis process, which require TGA to be used in conjunction with other analysis techniques for the detection of microplastics. TGA combined with FTIR spectroscopy can characterize microplastics in the environment (Yu et al., 2019). Samples in the environment are pyrolyzed in a thermogravimetric analyzer and the resulting gases are then analyzed using FTIR spectroscopy, which enables the quantitative detection of microplastics in seawater due to the different temperature profiles and absorption spectra of different types of microplastics. Differential scanning calorimetry (DSC) is a technique that can replace or complement FTIR spectroscopy, which was demonstrated by Majewsky et al. (2016) used to clearly distinguish and quantitatively analyze PE and PP in the environment. Peñalver et al. (2021) combined mass spectrometry with TGA to detect small amounts of PS microplastics in air, with detection and quantification limits of 7.7 and 25.8 ng m⁻³, respectively. TGA can also be used in conjunction with optical microscopy (Maja et al., 2023), thermal extraction and desorption (Dümichen et al., 2015), gas chromatography (David et al., 2018) or even multi-techniques for the purpose of accurate quantification of microplastics in the environment.

2.4. Spectral analysis techniques

As an important analytical tool, spectroscopy is often used to determine the physical structure and chemical composition of substances. Fourier transform infrared spectroscopy (FTIR) is based on the mathematical principles of the Michelson interferometer and Fourier transform, in which light from an infrared source is split into two beams and interfered with after passing through the interferometer. As these two light beams pass through the sample, they interact with the molecules in the sample and produce absorption spectra that correspond to the vibrational frequencies of the molecules. Yang et al. (2023) used micro-FTIR spectroscopy and simple analysis software to analyze microplastics in the range of 10 μm–500 μm. Different pretreatment methods were used to identify microplastics in different water samples for different impurities. Aging microplastics in seawater pose a major challenge for spectral analysis. Zeng et al. (2024) used FTIR and a deep convolutional neural networks (CNNs) model based on machine learning techniques to classify aging microplastics. The addition of the CNN model eliminates the need for pre-processing of the original image and also enables the analysis of aged microplastics. This deep convolutional neural network-based model can scale with aging plastics and is a promising analytical technique. Tagg et al.'s approach, based on micro-FTIR imaging with focal plane array reflectance (FPA), enables automated detection, identification and understanding of microplastics in complex samples with high organic matter content, and the amount of microplastics in different stages of a wastewater treatment plant (Tagg et al., 2020).

Raman spectroscopy is an analytical technique based on the principle of light scattering that can provide information about the molecular vibrations of microplastics to identify their chemical composition. The advantages are that samples do not need to be pretreated, in-situ detection occurs and the chemical specificity is high. In the last two

years of research (2023–2024), Raman spectroscopy has also become a popular technique for detecting microplastics (Araujo et al., 2018). A systematic review of Raman spectroscopic techniques for microplastic detection was presented in the study by Dai et al. (2024). It is mainly classified into four cutting-edge techniques: surface-enhanced Raman scattering, Raman tweezers, tip-enhanced Raman scattering and Raman mapping and imaging. However, it also reflects the inherent limitations of Raman spectroscopy, particularly in the complex sample pretreatment and difficult standardization of microplastic evaluation. Kim et al. (2024b) constructed a 3D plasma gold nanopore structure based on surface-enhanced Raman spectroscopy (SERS) and machine learning to handle complex sample preprocessing; Feng et al. (2023) used Raman spectroscopy and a multi-model machine learning approach to identify microplastics, an evaluation method for automated microplastic monitoring. Moreover, more and more researchers are working on rapid detection of microplastics for real-time in situ detection. Wu et al. (2024) increased the imaging speed of the spectra by one to two orders of magnitude using linear scanning Raman spectroscopy, and this system can identify microplastics with particle sizes of 500 nm. In the study by Ruan et al. (2024), a SERS based on Ag nanoparticles and NaI sols was used to amplify the PS signal to accelerate the detection of PS microplastics.

2.5. Other analysis techniques

Microfluidics technology is widely used in the analysis of environmental pollutants due to its low cost, easy operation and high efficiency. Based on the designable structure and small size of microfluidic chips, portable sensors can be developed for in-situ detection of microplastics in seawater. Due to its low cost, easy operation and high efficiency, microfluidics technology is widely used for the analysis of environmental pollutants. Based on the designable structure and small size of microfluidic chips, portable sensors can be developed for in situ detection of microplastics in seawater (Milani et al., 2015). Many also see this as a new technology for detecting microplastics (Ece et al., 2023). In recent years, microfluidic devices have been applied to analyze and detect microplastics in aquatic environments. In the IEEE International Symposium on Oceanometry, Valentino et al. (2022) combined microfluidic devices with digital holography and artificial intelligence, a portable device that promises to enable in situ detection of microplastics in seawater. Moreover, microfluidics, as a low-cost device for collecting microplastics, offsets the problem that techniques such as optical microscopy and Raman spectroscopy require complex pre-processing of microplastics. Furthermore, machine learning, deep learning and neural networks, important branches in the field of artificial intelligence, can also be used as tools in the analysis of microplastics. Meng et al. (2024) used machine learning principal component analysis (PCA) with laser-induced fluorescence to classify nine microplastics using a PCA scorecard with a detection limit of 0.03 for ocean microplastics. Artificial intelligence saves work effort and provides guidance for the future identification, classification and detection of microplastics.

Fig. 2 shows the advantages and disadvantages of different microplastic analysis techniques. Recent studies on microplastic detection, have described in situ detection of environmental samples and provided practical guidance (Abimbola et al., 2024; Zhang et al., 2025; Wang et al., 2023a; Zhang et al., 2024a). However, most reviews focus on improving of existing microplastic analysis techniques to increase the accuracy, sensitivity, and scope of quantitative analysis of microplastics (Praveena et al., 2024; Ribeiro et al., 2024; Shi et al., 2024). This article focuses on the research for new analytical techniques for in situ detection of environmental samples. Among the many analysis and detection techniques, electrochemical sensors are characterized by high sensitivity, high accuracy and a large measuring range. In addition, electrochemical sensors are simple, inexpensive and easy to automate. Therefore, electrochemical methods are expected to enable online in-situ detection of microplastics in aquatic environments. For example,

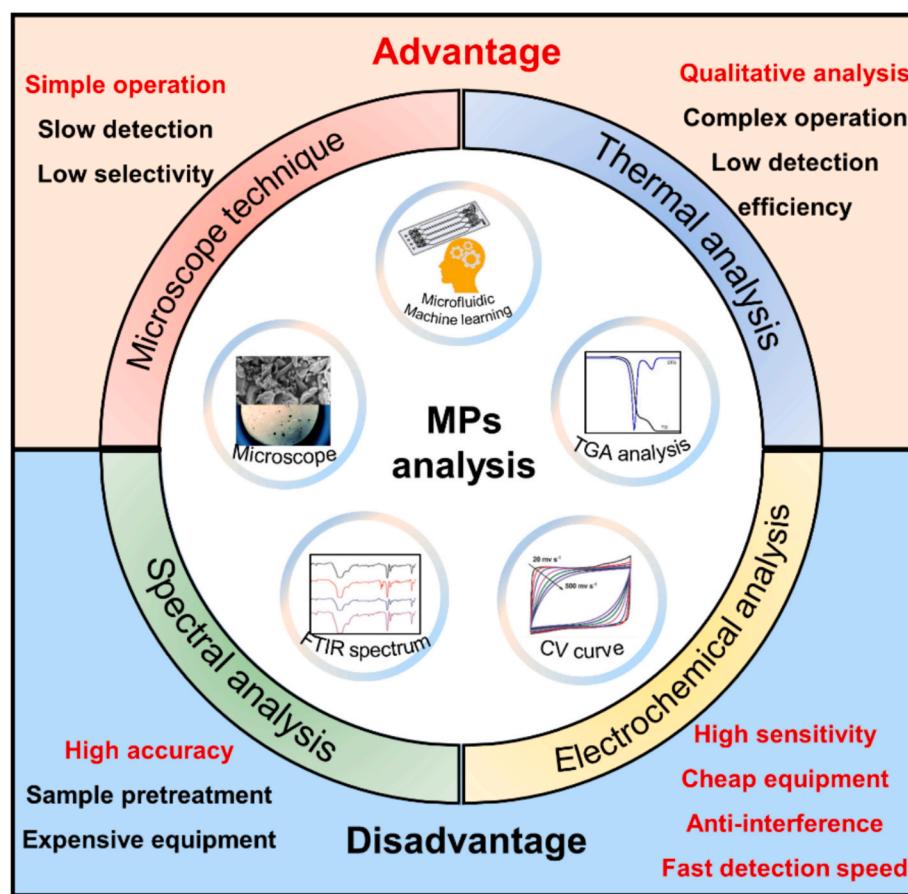


Fig. 2. Main microplastic analysis techniques and their advantages and disadvantages.

electrochemical sensors by sampling and analyzing microplastics in seawater, lake and river water can be a new technology for the detection of microplastic. This article focuses on the application of electrochemical sensors in microplastic detection.

3. Electrochemical sensors for detecting microplastics

As one of the most important electrochemical analysis techniques, electrochemical sensors offer the advantages of electrochemical analysis. In terms of sensor specificity, Fig. 3 shows the sensing strategy and detection mechanism of electrochemical sensors for microplastics, whose hydrophobicity and electrostatic force are the main properties of electrochemical sensors. The optimal sensitivity and higher detection range of microplastic detection were achieved by configuring different electrode materials. The detection performance of electrochemical sensors based on different materials and their detection mechanisms for microplastics are summarized in Table 1. For different working electrode materials, their detection mechanisms and sensing strategies for microplastics are slightly changed.

3.1. Carbon-based electrochemical sensors

Carbon materials are widely used as electrode materials due to their abundant sources, low cost, excellent electrochemical properties and environmental friendliness (Zhu et al., 2022). In recent decades, graphene, carbon nanotubes, carbon nanofibers and other carbon nano-materials have become hotspots for electrode materials (Jian et al., 2017). In electrochemical sensors, carbon materials are usually used as electrode preparation and modification materials due to their large specific surface area, tunable structure, high electron transfer rate, etc. (Liu et al., 2022). The glassy carbon electrode (GCE), a commonly used

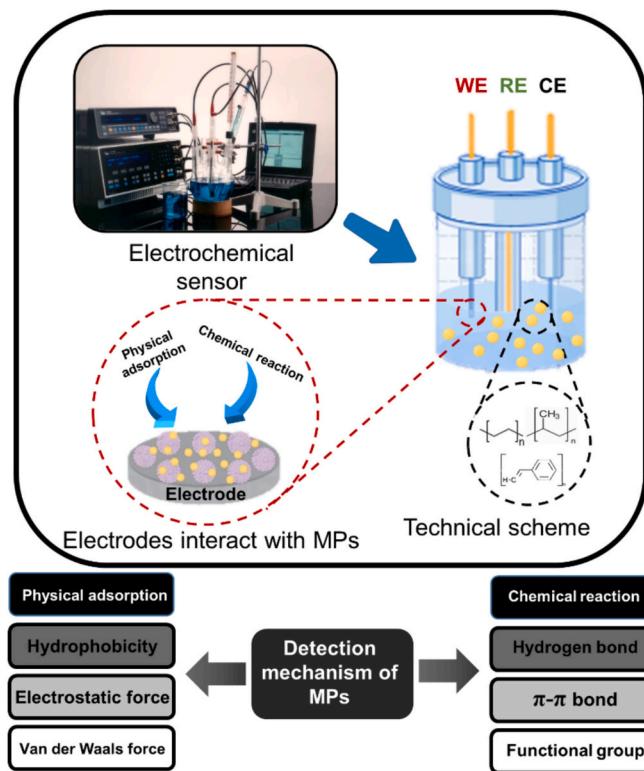


Fig. 3. Sensing strategy of an electrochemical sensor for microplastics and its detection mechanism.

Table 1

The ability of electrochemical sensors to detect microplastics and their detection technique based on different materials.

Materials	Types	Particle size range	Line arrage	LOD	LOQ	Test water sample	Mechanism	Ref.
GCE	PS	0.1-10 μm	0.005-0.500 pM			Deionized water	Electrostatic interaction	(Vidal et al., 2023)
Graphene	PS	0.08-20 μm	0.01-25 mg L ⁻¹			Tap water	Electrostatic interaction and Hydrophobic interaction	(Du et al., 2023)
SF-1/AL-1	PS	100 nm	300-900 nM	\sim 0.526 nM/ \sim 0.44 nM		Fresh water, Tap water and Bottled water		(Kim et al., 2024a)
Pt	Amidine latex beads	1 μm				Milli-Q water	Electrostatic interaction	(Moazzzenzade et al., 2023)
Au	PS	20-330 nm				Deionized water	Electrostatic interaction and Hydrophobic interaction	(He et al., 2024)
AuNPs@Au	PS	70-280 nm			0.9 $\mu\text{g L}^{-1}$	Deionized water	Electrostatic interaction and Hydrophobic interaction	(Li et al., 2022a)
CHIT@MgO	HMT		0.5 μM -4 μM	0.03 μM	0.10 μM	River water , Drain water and Bottled water	Electrostatic interaction	(Noumani et al., 2024)
γ -Fe ₂ O ₃ /Pt/TiO ₂	Carboxylated PS	50 nm	10^6 - 10^{14} ml ⁻¹			Milli-Q water	Magnetic collection	(Urso et al., 2022)
CeO ₂ NPs	PE/PP	27-32 μm	0.2-1.0 mg mL ⁻¹	0.226 mg mL ⁻¹ / 0.338 mg mL ⁻¹	0.754 mg mL ⁻¹ / 1.13 mg mL ⁻¹	Seawater	Hydrophobic interaction	(Nguyen et al., 2024)
CNH@RhB	PS					Deionized water		(Zheng et al., 2023)
EPS	PS/PE/PA/ PMA			10^{-11} - 10^{-5} M		Deionized water	Hydrophobic interaction	(Gongi et al., 2022)
Binding peptide	PS/PP/PE					Deionized water and NaCl solution	Hydrophobic interaction	(Woo et al., 2022)
Carbon fiber@Ag	PE	1-10 μm				NaCl solution	REDOX	(Shimizu et al., 2017)
AuSNPs@CB	HQ/CC/RC			1.7 μM /5.1 μM /4.5 μM		Tap water, Dam water and Bog water	REDOX	(Jebrib et al., 2021)
Cu ₃ SnS ₄ @GA@CHIT@BSA	PS	50-200 nm		0.06 $\mu\text{g mL}^{-1}$	0.14 $\mu\text{g mL}^{-1}$	Tap water and River water	Protein corona	(Xiao et al., 2024)

working electrode for electrochemical sensors, also has the ability to detect microplastics. In a study by Vidal et al. (2023), an electrochemical sensor based on μ GCE electrodes was used to detect PS-MPs. The sensing mechanism of this work is that negatively charged PS-MPs undergo electrophoretic migration, and since μ GCE has strong adsorption of PS-MPs, the PS-MPs are adsorbed on the working electrode, causing the FcMeOH mediator used for charge transfer to block the charge. In their work, PS-MPs were quantitatively characterized using EIS impedance spectroscopy, which can detect PS-MPs with sizes of 0.1–10 μm in the range of 0.005–0.500 pM. Graphene, as a nanocarbon material, is extremely advantageous for sensing applications due to its electrocatalytic activity, adsorption capacity, high porosity and electrical conductivity (Pengsomjit et al., 2024). Based on the hydrophobicity and electrostatic force of graphene, it can adsorb microplastics through hydrophobic and electrostatic interactions (Mehmood et al., 2023). In addition, the carbon ring of graphene can interact with microplastics containing aromatic rings through π - π , which increases the adsorption of microplastics containing aromatic rings (Pei et al., 2013). In the study by Du et al. (2023), graphene nanomaterials were obtained from petroleum wastes and used as electrodes in a spectroelectrochemical impedance sensor to detect PS-MPs. The data were processed using PCA and SVD. The results of PCA and SVD showed that the sensor had good performance in detecting the particle size range of PS from 0.08 to 20 μm . Among many carbon materials, biochar materials appear in public perception due to their natural microstructure, functional diversity,

structural adaptability and other characteristics (Sakhya et al., 2020). More importantly, biomass carbon materials offer a sustainable and cost-effective way to be a candidate for a cleaner and more sustainable functional material in the future (Yameen et al., 2024). Based on biomass carbon materials, Kim et al. (2024a) fabricated electrochemical sensor electrodes for the detection of PS-NPs at 100 nm using carbonized natural starfish (SF-1) and *aloe vera* (AL-1) and compared the detection efficiencies of the two biomass carbon materials separated. The results showed that the AL-1-modified GCE electrode had better detection parameters with a detection limit of \sim 0.526 nM, while the SF-1-modified GCE electrode had a detection limit of \sim 0.44 nM. As shown in Fig. 4, the difference in sensing parameters of the two biomass carbon materials may be due to the presence of elements such as Ca, K, Mg, etc. in AL-1 to form functional groups with C, O and S, and this metal-carbon framework can support PS oxidation, thereby increasing current.

3.2. Metals and their oxides based electrochemical sensors

3.2.1. Precious metals

Among a wide range of metallic materials, precious metals stand out in terms of electrochemical sensing response and stability due to their chemical inertness, corrosion resistance and good electrical conductivity (Karakovskaya et al., 2021; Thoeny et al., 2023). Au and Pt as electrode materials have been used in the study of electrochemical sensors for detecting microplastics. Moazzzenzade et al. (2023) used a glass-coated

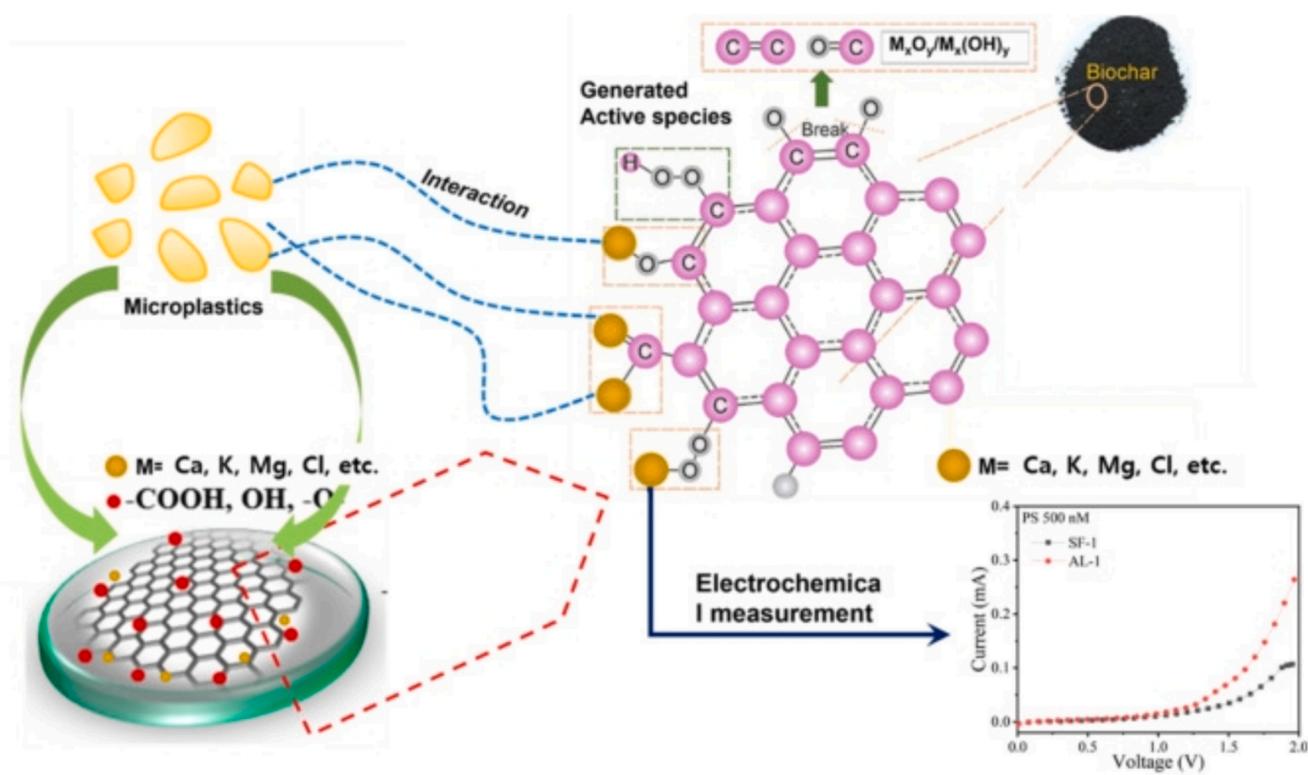


Fig. 4. Possible sensing mechanisms for PS detection on biochar-modified GCE surfaces (Kim et al., 2024a).

Pt electrochemical microelectrode sensor to detect amidine-modified latex beads in drinking water. To detect latex beads, they used a blocked particle impact method. Here, the redox mediator is replaced by an oxidation-reduction reaction (ORR), which generates an electric field in which 1-μm-sized positively charged latex spheres migrate and collide with negative-potential Pt microelectrodes, the “kiss-and-run” event in the study, which generates a blocking signal. This approach is promising for detecting positively charged particles inside cells. In another study, He et al. (2024) developed a sandwich microelectrode sensor for the detection of PS-NPs using β-mercaptopropylamine-modified Au electrodes. The so-called “sandwich” structure of the detection strategy is shown in the sensor strategy diagram in Fig. 5(a), in which the positively charged β-mercaptopropylamine-modified Au electrodes can capture negatively charged PS NPs through electrostatic interactions; The ferrocene molecules (Fc) then bind to PS-NPs as electrochemical beacons via hydrophobic interactions and generate DPV peaks. In the so-called “sandwich” structure detection strategy, the positively charged β-mercaptopropylamine modified Au microelectrode can capture the negatively charged PS NPs through electrostatic interactions, and the ferrocene molecule (Fc), which is an electrochemical beacon, can do so through hydrophobic interactions bound to the PS-NPs to generate the DPV peak current response. In the selectivity study of the sensor, potential interferences such as organic molecules, inorganic ions and small particles were introduced to conduct selectivity experiments on the sensor respectively. As shown in Fig. 6(a), (b), the sensor responds to the strong interferences with only small electrical signals due to the introduction of their charged nature, water solubility and ability to trap the electrode surface. This practical sandwich microelectrode sensor has a detection range of 20–330 nm and is a good means for microplastic nanodetection. Similarly, Li et al. (2022a) employed this sandwich structure as a sensing strategy (Fig. 5(b)). Unlike the study of He et al., they used positively charged Au nanoparticles to modify the Au electrode. Furthermore, their work illustrated the influence of hydrophobicity and charge density of four nanoplastics (PP, PE, PS and PA) on the sensor and concluded that this sensor is more sensitive to highly negatively charged and highly

hydrophobic nanoplastics. For the sensor selectivity parameter, this study not only analyzed the effects of organic molecules and inorganic ions on sensor selectivity, but also compared the charge properties of PS-NPs and proved that electrostatic interactions are an important feature for the detection of PS-NPs. As shown in Fig. 6 (c), (d), and (e), the sensor reacts with current only to negatively charged PS-NPs, while it only shows a weak current response to other substances. The detection limit of this sensor for PS-NPs with diameters of 70–280 nm was 0.9 μg·L⁻¹. Although it is currently difficult to analyze mixed nanoplastic samples, this inexpensive, simple, and sensitive approach shows promise.

3.2.2. Metal oxide

Compared to precious metals, the cost of metal oxides is more acceptable to everyone. Furthermore, metal oxides are widely used in electroanalysis due to their strong electrocatalytic activity and organic trapping ability (Maduraiveeran et al., 2018). In the production of nanometal oxides, researchers often control the morphology and size of nanometal oxides through various manufacturing methods to form nanomaterials with high specific surface area such as particles, flakes, flowers, etc. (Lane and Zimmerman, 2019). In the field of sensing, this tunable multifunctional nanometal oxide will also improve the electrochemical performance of sensors (Hussain et al., 2023). For example, Noumani et al. (2024) on chitosan (CHIT) composites with MgO nanosheets as a sensor platform for the detection of hexamethylenetetramine (HMT) microplastics. Such MgO nanosheets (Fig. 7(a)) have the advantages of low cost, large specific surface area and good stability. The possible mechanisms for sensory detection of HMT include the negatively charged CHIT-MgO NS/TTO electrode and HMT with 12 protons, which can undergo charge transfer and electrostatic interactions; HMT can bind to metal ions as a strong chelator and reduce their electrocatalytic efficiency (Swathi et al., 2021). These two mechanisms reduce the DPV current of the sensor to achieve detection. In addition, the study evaluated the sensor's immunity to interference by using impurity concentrations 10–200 times higher than HMT. As shown in Fig. 6(f), the

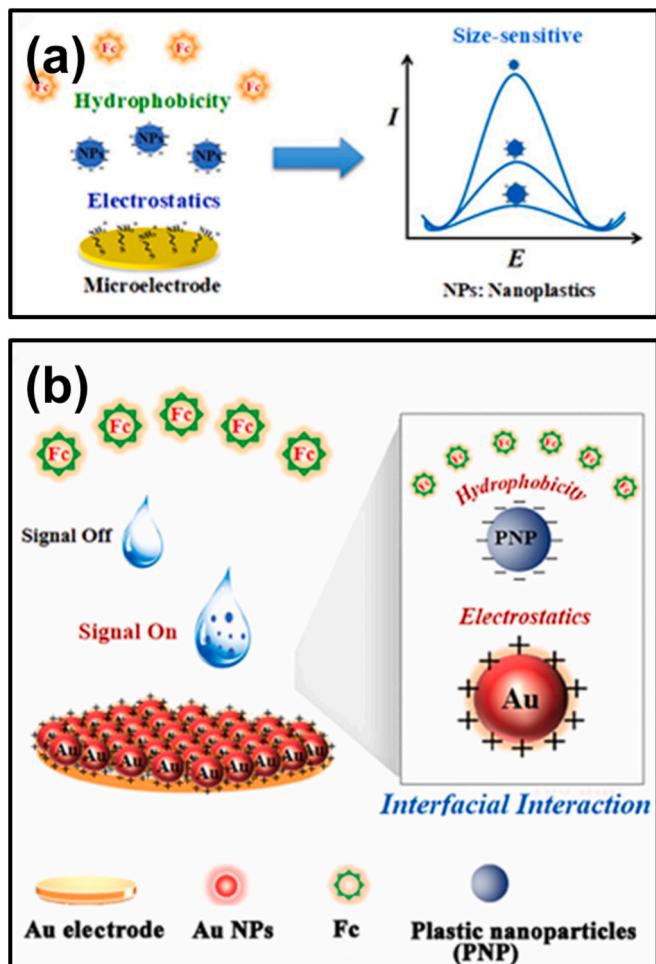


Fig. 5. (a) Schematic representation of sensor detection with Au electrodes (He et al., 2024), (b) Schematic representation of sensor detection with Au NPs (Li et al., 2022a).

sensor showed good selectivity for certain HMT concentrations even in an environment where different interfering substances interacted with each other. The chitosan and magnesium oxide nanosheet-based sensing platform had a detection limit of $0.03 \mu\text{M}$ and a quantification limit of $0.10 \mu\text{M}$ for HMT microplastics with a linear range of $0.5 \mu\text{M}$ to $4 \mu\text{M}$. Among metal oxides, magnetic metal oxides rely on the spontaneous arrangement of their internal electron spins to have magnetic properties after magnetization, and soft magnetic materials with iron oxides are corrosion-resistant and highly absorbent, with good adsorption properties (Wang et al., 2023b). Based on magnetic nanometal oxides, Urso et al. (Urso et al., 2022) utilized Mxene-derived $\gamma\text{-Fe}_2\text{O}_3/\text{Pt}/\text{TiO}_2$ microbots as a means to capture and detect nanoparticles (NPs). In the report, they constructed Mxene-derived TiO_2/Pt with excellent photocatalytic properties as a microrobot for capturing NPs and incorporated magnetic nano- $\gamma\text{-Fe}_2\text{O}_3$ into the lamellar structure of TiO_2/Pt to collect magnetic NPs (Fig. 7(c)). The captured NPs were quantified by electrochemical impedance spectroscopy (EIS). The NPs detected in the study were 50 nm carboxylated polystyrene particles, and the detection range was $10^6\text{-}10^{14} \text{ ml}^{-1}$ NPs at a concentration. This microrobot can instantly sense and detect NPs in water without requiring H_2O_2 as propulsion fuel. In recent years, they have performed well in the field of sensing based on the unique electronic and lattice structures of rare earth oxides, optical properties, electrochemical properties, catalytic properties, magnetic properties, etc. (Kowsuki et al., 2023). In the field of electrochemical sensor detection of microplastics, the excellent durability and hydrophobicity of rare earth oxide nanoparticles have

attracted attention (Azimi et al., 2013). The hydrophobic properties of cerium oxide nanoparticles (CeO_2NPs) were used to detect PE and PP microplastics in aquatic environments by Nguyen et al. (2024). The hydrophobic CeO_2NPs are attracted to the hydrophobic MPs; The oxygen-containing functional groups contained in the CeO_2NPs also form coordination bonds with the MPs (Fig. 7(b)). These two effects improve the sensitivity performance of the sensor. In the sensing strategy, the MPs in the surrounding area collide with the CeO_2NPs on the GCE electrode, resulting in charge transfer. This particle-electrode collision is an effective means of detecting MPs. The detection limit of this sensor for PE-MPs ($27\text{-}32 \mu\text{m}$) was 0.226 mg mL^{-1} .

3.3. Biomass materials based electrochemical sensors

The toxicity of microplastics as a typical pollutant in the environment, especially in aquatic environments with a large number of biological species, cannot be ignored (Xiang et al., 2022). When detecting microplastics in marine systems, the effects of microplastic toxicity need to be assessed (Wang et al., 2021). Traditional electrochemical sensors for carbon and metal materials are difficult to assess the toxicity of microplastics, while electrochemical sensors for biomass materials play a role in toxicity detection (Adekunle et al., 2019). On this basis, Zheng et al. (2023) proposed to detect the toxicity of PS-MPs using electrochemical biosensors based on carbon nanohorns (CNH), a nanocarbon material with low toxicity that can be well used for biosensing, and RhB, an electropolymerized membrane that can increase electroactive surface and catalytic activity. In their work, human liver cells (L-02) were used as test samples and energy supply cells, and selected intracellular ROS, glutathione, SOD activity and MMP changes as indicators of cytotoxicity, oxidative stress and apoptosis to analyze toxicity of PS-MPs alone and their toxicity in combination with typical pollutants such as bisphenol A (BPA), pentachlorophenol (PCP) and lead (Pb^{2+}). The results showed that the concentrations of these four pollutants in L-02 cells were $286.34 \mu\text{g mL}^{-1}$, $78.85 \mu\text{M}$, $67.87 \mu\text{M}$ and $60.12 \mu\text{M}$, respectively. This biosensor improves the understanding of the cytotoxicity of typical pollutants under the guidance of PS-MPs. Among the many aquatic organisms, microorganisms are crucial for breaking down microplastics. Among them, algae as primary producers have been shown to degrade hydrocarbons (Zhai et al., 2023). In other words, algae can also adsorb microplastics in marine systems. To this end, Gongi et al. (2022) developed a biosensor based on cyanobacterial extracellular polymers (EPS) to detect four common microplastics in the ocean. EPS is mainly composed of substances such as sulfated polysaccharides and proteins (Delattre et al., 2016). Among them, polysaccharides physically capture the particulate material, while peptides in proteins also adsorb MPs through hydrophobic interactions. In addition, EPS contains complex molecules such as amino acids, which further adsorb MPs by establishing hydrogen bonds, Coulomb forces, and electrostatic interactions. Etc. In their work, EPS was used as a membrane deposited on Au electrodes and EIS was used for quantitative characterization of PS, PE, polyamide (PA), and poly(methyl acrylate) (PMA) in nylon form. The results showed that this biosensor can detect samples at low concentrations with detection limits as low as $10^{11}\text{-}10^{15} \text{ M}$. As building blocks of proteins, peptides are also hydrophobic and have an affinity for microplastics (Simm et al., 2016). Woo et al. (2022) investigated the binding affinity of various MPs for hydrophobic peptides and developed an engineered peptide biosensor to detect PS and PP microplastics. In the report, PS-binding peptide (PSBP), PP-binding peptide (PPBP), and PE-binding peptide (PEBP) were determined using different methods. For example, using PS Binder software and based on hydrophobicity intensity sequences, etc. More importantly, this plastic-binding peptide binds selectively to MPs in both deionized water and NaCl solution at a concentration of 3.5 % and is independent of the surface oxidation of MPs, and the peptide biosensor is effective in detecting MPs advantageous in marine systems. However, the study did not report on the use of plastic-bound peptides in sensors, but only verified the selectivity of the

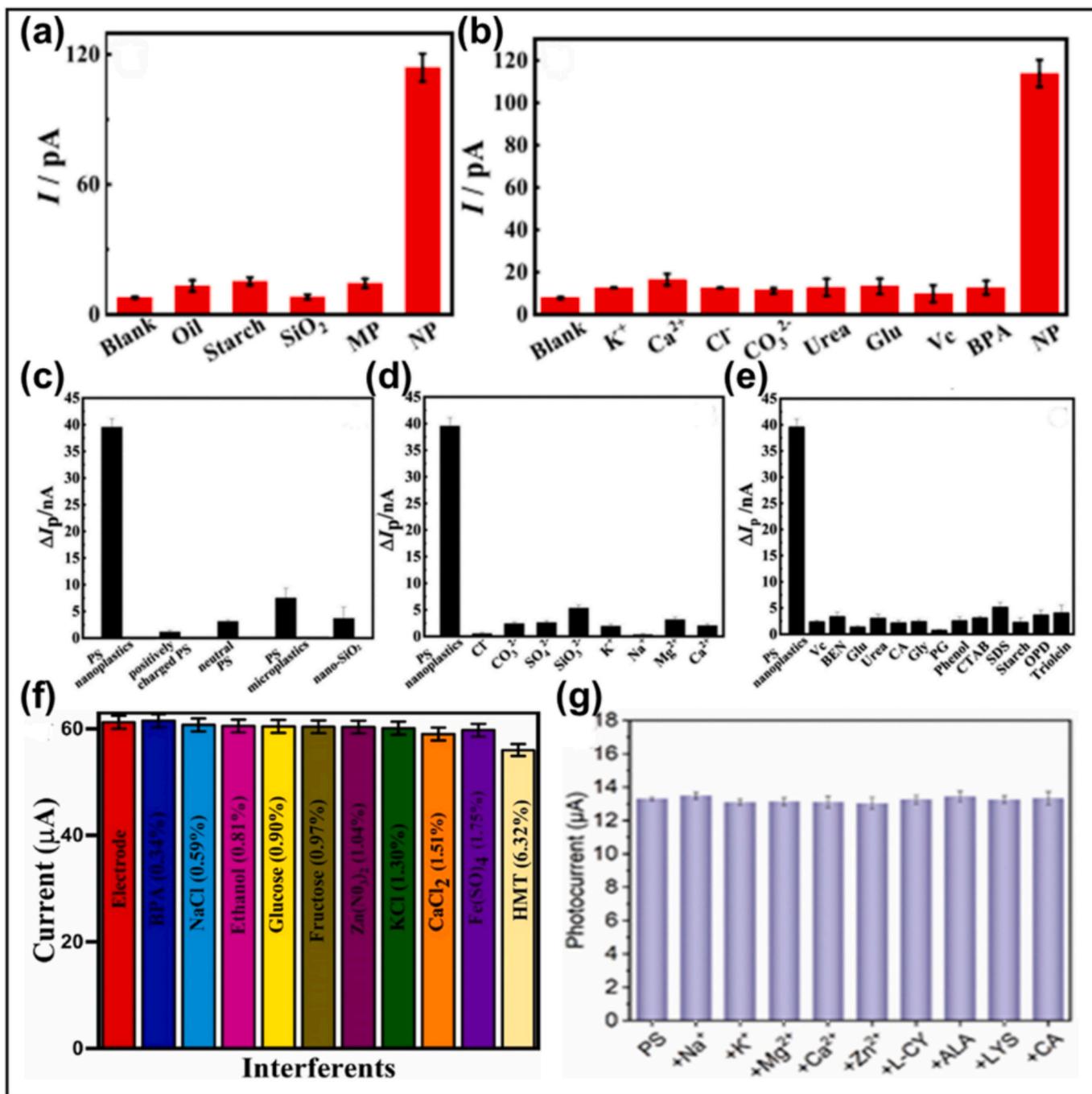


Fig. 6. (a), (b) Selectivity experiments of Au microelectrode sensors for the same concentration of organics, inorganic ions, MPs and NPs (He et al., 2024); (c), (d), and (e) Selectivity experiments of Au-NPs electrodes sensors for positively, neutral, and negatively charged PS-NPs, PS-MPs and SiO_2 -NPs, as well as inorganic ions and organic molecules (Li et al., 2022a); (f) CHIT MgO NS/ITO electrodes in PBS for HMT interference analysis (Noumani et al., 2024); (g) Anti-interference experiments with PEC sensors (Xiao et al., 2024).

peptides. The role of biomass materials is not only in the specific detection of MPs but also contributes to improving sensing capabilities. Vázquez Juiz et al. (2018) quantitatively characterized PS-MPs through tunable resistance pulse measurement (TRPS), which in turn uses humic acid (HA) to vary the pulse size distribution. Unlike traditional electrochemical sensors, TRPS is based on the Coulter principle, in which particles form a pulse signal when passing through an electrically sensitive area with a conductive liquid, and the size and number of particles are then characterized based on the pulse signal. In this study, PS-MPs flowed through the measurement channel with a reduced current between cells and transmitted a resistance pulse or “blocking” signal.

However, organic polymers (DOM) in the environment can interfere with the measurements by affecting the current, and the introduction of HA alters the variation of the electric field in the channel to correct the interfering effects of DOM. Although the complex composition of biomass materials can have an impact on the sensor analysis of MPs, electrochemical sensors based on biomass materials remain promising.

3.4. Composite-based electrochemical sensors

In the field of sensing, working electrodes are crucial, and researchers often embellish and modify them to optimize sensing

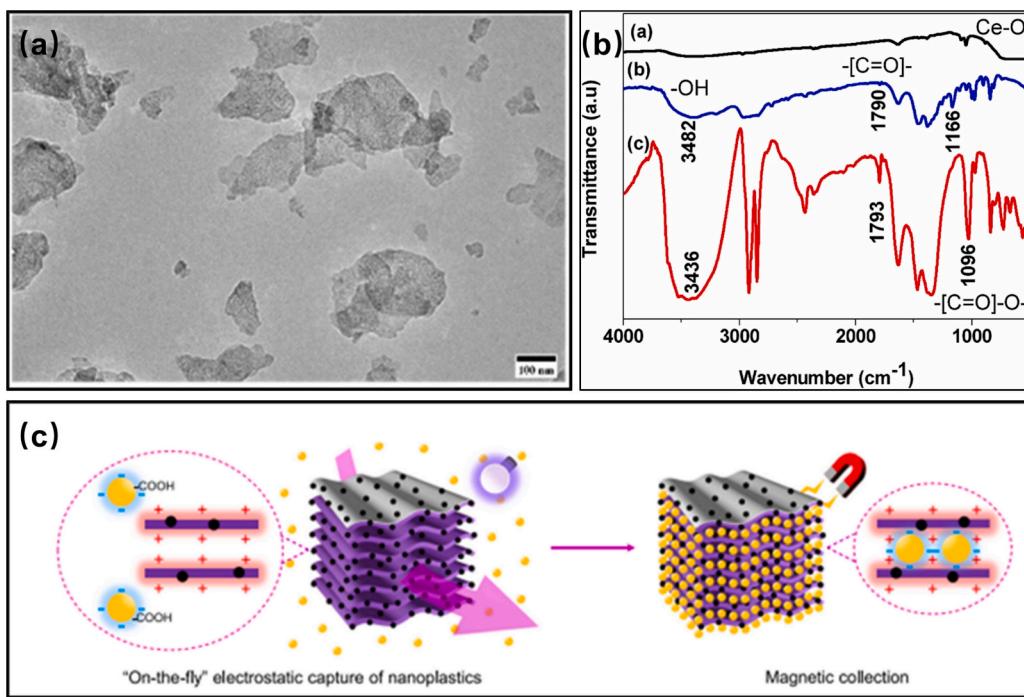


Fig. 7. (a) SEM image of magnesium oxide nanosheets (Noumani et al., 2024), (b) FTIR of cerium oxide nanosheets and their interaction with PE and PP (Nguyen et al., 2024), and (c) map of magnetic collection strategy of MPs based on γ -Fe₂O₃/Pt/TiO₂ nanomaterial (Urso et al., 2022).

performance and specificity detection through the use of the above-mentioned materials. However, a single material often does not achieve the desired detection results and several material composites are required. Composites can be associated with combining the advantages of two or more materials to further increase the detection performance of electrochemical sensors. Among electrochemical sensors for detecting MPs, metal and carbon composites are widely used. Shimizu et al. (2017) used a home-made microfilament electrode made of carbon fiber and Ag wire as a working electrode to detect PE-MPs based on the electrochemical sensing strategy of particle impact electrodes. They analyzed the nature of the “spikes” produced by the transient current

response, or the “spikes” produced by PE-MPs when they impinge on the microfilament electrode. The nature of the “spike” is analyzed. That is, during the impact of PE-MPs on the electrode, O₂ dissolved in PE-MPs is reduced to H₂O₂, while PE-MPs do not react, resulting in a transient current response. This method can be used to determine the distribution and concentration of PE-MPs with particle sizes of 1–10 μ m. In another study, Jebril et al. (2021) synthesized a nanocomposite of green gold nanoparticles (AuSNPs) and carbon black (CB). This composite material improves electron transfer and electrocatalytic properties, thereby increasing the conductivity of the sensor. When preparing the materials, they used *Malva sylvestris* leaf extract to synthesize the AuSNPs, and

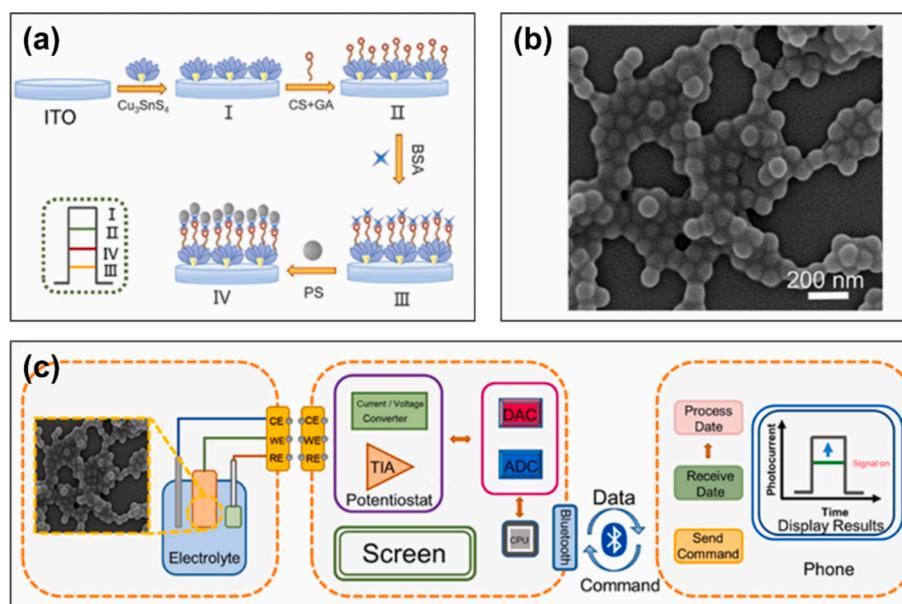


Fig. 8. (a) Schematic diagram of PEC sensor for PS-MP detection, (b) SEM image of PS modified with BSA, (c) Block diagram of smartphone-based PEC detection system (Xiao et al., 2024).

various active substances in the extract, such as polysaccharides, phenolic compounds and polyols, can act as stabilizers and reducing agents. In contrast to NPs, which are routinely detected, the sensor targeted three phenol isomers of the detected substances, namely hydroquinone (HQ), catechol (CC), and resorcinol (RC). In the results, the sensor modified with AuSNPs and CB composites could detect these three NPs simultaneously with detection limits of 1.7, 5.1, and 4.5 μM , respectively. Xiao et al. (2024) developed a photoelectrochemical sensor (PEC) to detect MPs based on the aggregation effect induced by protein corona. In Fig. 8(a), they prepared flower-shaped Cu_3SnS_4 as the photoelectric effect element, which was then modified with glutaraldehyde (GA), chitosan (CHIT), and bovine serum albumin (BSA). The recognition mechanism of the PEC sensor developed in this work is that proteins wrap MPs through hydrophobic interactions to form a protein coat called a protein crown (Li et al., 2021). Furthermore, the BSA adsorbed on the MPs and not adsorbed on the MPs leads to inhomogeneity of the charge on the surface of the MPs, which generates the attractive patch charge force. As shown in the SEM image of Fig. 8(b), the PS-MPs were adsorbed with BSA after the addition of BSA. To evaluate the interference immunity of the sensor, interfering substances present in the actual aqueous environment, such as inorganic ions and amino acids, were selected for this study. The results in Fig. 6(g) show that the PEC sensor is very little affected by the above-mentioned interfering substances and is highly selective for PS-MPs. In terms of sensor performance, the PEC sensor had a detection limit of 0.06 $\mu\text{g mL}^{-1}$ and a quantification limit of 0.14 $\mu\text{g mL}^{-1}$ for PS-MPs with particle sizes in the range of 50–200 nm. It was noted that in the study, the PEC sensor was linked to a digital multimeter (DMM) and the data was transmitted to a smartphone via

Bluetooth (Fig. 8(c)). This approach enables portable implementation of fast, real-time detection in real-world waters.

3.5. Microfluidic chips based electrochemical sensors

Electrostatic interactions are one of the key factors for the detection of MPs in marine systems. Microfluidic chips can enhance the selection efficiency of MPs by applying electric fields. Davies and Crooks (2020) report a continuous Faraday plasma concentration polarization (fICP) method for focusing, quantification and separation of MPs in a trident microfluidic channel. This method can be used to control the movement of charged MPs. Its microfluidic structure is shown schematically in Fig. 9(a). Briefly, through multiple electric field gradients (EFGs) formed by bipolar electrodes (BPEs) in the trident microfluidic channel, negatively charged MPs are focused, sorted and separated due to convection and electromigration. Although this method can detect MPs in the environment, the detection performance of this electrochemical method was not mentioned in the report. In contrast, in the study by Pollard et al. (2020), a resistive pulse sensor (RPS) was used that can characterize MPs and algae. Customizable 3D printing was used in the fabrication of the microfluidic chip in their study, and the lid and base of the fabricated microfluidic chip can be reused. The RPS classifies MPs and algae based on the transient current changes they generate by shifting the sensing region of the microfluidic chip to produce a specific signal. Interestingly, this signal not only distinguishes the two, but there is also a correspondence between the shape of the signal and the shape of the particle. The results show that the microfluidic RPS sensor has a detection limit of 14 particles per milliliter at a pressure of 100 mbar. In

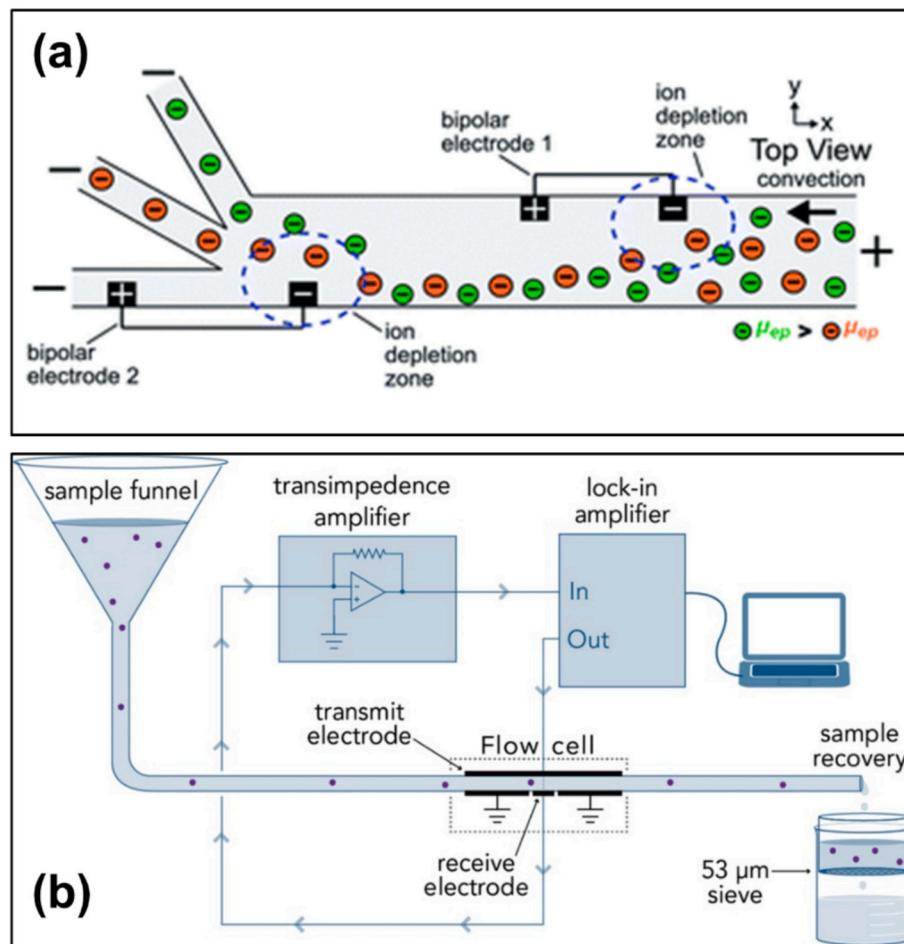


Fig. 9. (a) Schematic of the microfluidic structure used for continuous fICP experiments (Davies and Crooks, 2020), (b) Setup of the impedance spectroscopy experiment (Colson and Michel, 2021).

addition, Zhao et al. (2024) developed a microfluidic chip with a stretchable electrochemical sensor to create a bionic platform to simulate alveolar respiration. Toxicity monitoring of PS-NPs at 50 nm was achieved by analyzing NP-induced oxidative stress through the detection of H₂O₂ as reactive oxygen species (ROS). Although this bionic platform is not a direct detection of NPs, the excellent sensing performance of the microfluidic chip in combination with electrochemical sensors still offers potential. Another technique of flow cytometry, often combined with microfluidics, can also be used to detect MPs in aquatic environments, and Colson and Michel (2021) used high-throughput flow measurements of MPs based on flow cytometry and impedance spectroscopy (Fig. 9(b)). This impedance spectroscopy-based flow measurement not only enables the size quantification and recovery of PE-MPs in the range of 300–1000 μm, but also enables the discrimination of MPs from biological particles, air bubbles, etc. in samples through impedance settings and twelve-dimensional k-nearest neighbor (12-D k-NN) classification.

4. Challenges and perspectives

4.1. Challenges

Electrochemical sensors are widely used in important areas due to their low cost, easy operation, stability and repeatability. Electrochemical sensors also offer potential advantages when detecting microplastics, as they do not require any pretreatment of the samples to be detected and have a high specificity for the detected microplastics. Although many electrochemical sensors for detecting MPs have been analyzed above, not all of them can be used in marine systems, and there are still many challenges for electrochemical sensors for detecting MPs in real marine systems, as described below:

1. The main sources of microplastics in marine systems are polyethylene and polypropylene, which account for >50 % of the content. However, currently available electrochemical sensors mainly detect polystyrene, and only a few electrochemical sensors detect polyethylene and polypropylene. For the wide range of microplastic types in marine systems, the detection of one or a few microplastic types alone is not sufficient. Electrochemical sensors must be able to detect and differentiate between a broader range of microplastic types.
2. Microplastics in actual marine systems vary in shape, but electrochemical sensors currently only detect bead-shaped microplastics; Microplastics range in size from millimeters to nanometers, and electrochemical sensors have detection and quantification limits that can detect microplastics as small as two to three orders of magnitude. There is currently no way to detect microplastics in full size and in any shape.
3. The complex environment and numerous contaminants in the marine system also make the detection of microplastics by electrochemical sensors significantly difficult, and most current research focuses on deionized water, NaCl solution or daily water, with very few direct detection of microplastics in actual seawater. When electrochemical sensors detect real seawater, heavy metal ions, organic pollutants, etc. affect the selectivity of the sensor for MPs.
4. Electrochemical sensors typically have a lifespan of six months or a year, which is shorter than other technologies, and the detection limit of an electrochemical sensor decreases with increasing use. In addition, electrochemical sensors can also cause errors in microplastic detection due to environmental factors such as temperature, pH and electrolytes.
5. The current electrochemical sensor platform for microplastics is still in the laboratory stage. Especially in the manufacturing of the sensor, the working electrode is usually small-scale, and the manufacturing method is also more complicated, which makes the commercialization of an electrochemical sensing platform difficult.

6. Due to their small size and pollutant-carrying nature, microplastics are easily ingested by marine organisms and therefore pose a threat to marine life; Worse, their cumulative effect, transmitted through the food chain, can also impact human health. Currently, electrochemical sensors are mainly used for quantitative analysis of microplastics, and the toxicity assessment of microplastics needs to be further improved.

4.2. Future perspectives

The working electrode, as the most important detection unit of electrochemical sensors, is currently a hotspot of electrochemical sensor research in the field of sensor technology by modifying the working electrode with modified nanomaterials.

Metal-organic frameworks (MOFs) have shown remarkable achievements as hotspot nanomaterials in various fields. In the field of sensing, the high specific surface area, porous structure and excellent electrocatalytic properties of MOFs can increase the performance of sensors (Sharma et al., 2023). On the one hand, the structure of MOFs can be specifically controlled through various manufacturing methods (Kalaj and Cohen, 2020); On the other hand, different functional groups can be introduced into MOF materials (Wu et al., 2023), providing unlimited possibilities for specific selectivity and functional diversity of sensors. However, although MOF materials are not currently used in electrochemical sensors, there is still potential for their development in the detection of MPs. S-tapered fiber (STF) sensors based on functionalized ZIF-8 material were used for detection of NPs in the study of Xiong et al. (Xiong et al., 2024). In this study, the strong electrostatic adsorption effect of ZIF-8 on PS-NPs as well as the π-π stacking and high specific surface area of the STF sensors were exploited to improve their sensitivity and specificity for the detection of PS-NPs. MOFs are effective MP adsorbents that adsorb MPs both chemically and physically (Verma et al., 2024). Currently, MPs in various forms have been removed from water using the ZIF series of MOF family (ZIF-8 (Pasanen et al., 2023), ZIF-67 (Wan et al., 2022)), MIL (MIL-88B (Feng et al., 2022), MIL-101 (Modak et al., 2023), etc.) and UIO-66 (Chen et al., 2020; Mohan et al., 2024). In other words, MPs can be selectively captured by each of these MOFs. Among other types of interaction binding, the primary methods for trapping MPs include hydrogen bonds, π-π bond stacking, electrostatic interactions, hydrophobic interactions, and van der Waals forces (Kumar Dey et al., 2023). Among them, Gao et al. (Gao et al., 2023) developed a novel MP trap based on MOF-545, which they named MOF-545 oxime. The π-π conjugated structure of the C=N group in MOF-545 oxime and its surface electrical features enhanced its interaction with MPs. Furthermore, the distinct microporous structure of the oxime increased the number of MP adsorption sites. The main tactic to improve MOF electrochemical sensing is to functionalize the surface and structure by incorporating specific functional groups. This changes the surface and structure and increases the MP selectivity. In terms of capture ability, it is crucial to increase the surface area of MOFs and control the size, shape, and structure of pores to enhance the capture efficiency of MPs. In addition, MOF synthesis should consider extending the lifetime of MOFs for the stability and repeatability of electrochemical sensors; Various environmental conditions such as pH, temperature and ion concentration also affect the impact of their sensing ability. Finally, the performance of electrochemical sensors is also significantly increased by composite materials made from MOFs or their derivatives, as well as components such as carbon nanomaterials, magnetic materials, etc.

Another nanomaterial that works well with sensors is quantum dots. For smaller MPs and NPs in the marine environment, more sensitive, highly selective and functionally flexible sensing platforms are required. Quantum dots (QDs) are the preferred option for nanosensing among a variety of nanomaterials due to their excellent photoelectrochemical qualities, high stability and electrocatalytic activity (Ananthanarayanan et al., 2014). Nowadays, biological (Kumar et al., 2020), medical

(Sharma and Das, 2019), and environmental (Chen et al., 2019) applications utilize sensing platforms based on metal and carbon-based quantum dots. MPs can be tracked and analyzed by carbon dots (CDs) in quantum dots. In their summary of the uses and developments of CD in MP analysis, Sai et al. (Tammina et al., 2023) reviewed the many chemicals that can be assayed with CD and discussed their potential for MP detection. Among them, CD fluorescence is a crucial detection method. Later, in a study by Liu et al. (Liu et al., 2024), the entry of MPs into soybean sprouts was monitored using the fluorescence of CD. Additionally, it was the first time that MPs were analyzed using CD. Intriguingly, they made CD, which is biocompatible, by using a natural material - shrub leaves - as a carbon source. The fluorescent material made from leaves is far more sensitive to light, has a higher signal-to-noise ratio and has a larger Stokes shift than traditional fluorescent materials made from small molecules and rare earths. Since the quantum effect becomes more noticeable as the nanomaterials shrink in size and the continuous energy bands change into discrete energy levels, the quantum confinement effect (QCE) (Faribod and Sanati, 2019) is more suitable for electrochemical sensing than the fluorescent characteristics of CDs. Additionally, quantum dots are the primary luminescence component of electrochemical light-emitting sensors (ECL) (Chen et al., 2018). Furthermore, bisphenol A has been detected in aquatic habitats using electrochemical sensors combining quantum dots and molecular imprinting technology (Tan et al., 2016). The multifunctional sensing potential of quantum dots can help identify MPs by solving the challenge of detecting particles smaller than 10 µm. It can also control hydrophilicity and hydrophobicity based on surface changes and other functional components. Therefore, the challenge in using quantum dots for electrochemical sensing is to understand how quantum dots work and then rationally produce and synthesize them.

In summary, to exploit the advantages of these sensors in the field of microplastic detection, the primary path for future development of the use of electrochemical sensors for MP detection should be as follows:

1. A common goal is real-time online detection, and electrochemical sensors are particularly promising. We can use portable current, voltage and resistance sensing elements and rely on a control unit to convert their signals to reduce dependence on electrochemical workstations. Using wireless technology, we can then connect to devices such as computers and cell phones to perform real-time online microplastic inspection.

2. A crucial component in the construction of electrochemical sensor systems is the large-scale production of working electrodes, which must be mechanized using sensible preparation methods. Among them, sophisticated and well-established preparation techniques such as 3D printing and micro-nanomachining prove promising for electrode preparation engineering.

3. In order to decipher how the sensors work, a better understanding of the electrochemical reactions and processes in microplastics is required. Electrochemical sensors can be improved by studying chemical reactions at the microscopic level using *in situ* and *ex situ* techniques, as well as using increasingly complex computational and quantum chemistry software to study their electrochemical mechanisms at the molecular, atomic and even electronic levels.

4. By leveraging the advantages of many technologies, the combination of electrochemical sensors and other technologies to detect microplastics has a promising future. Electrochemical sensors and microfluidic devices work perfectly together. To perform both qualitative and quantitative analysis of microplastics, microfluidic chips are used for screening and classification, while electrochemical sensors are used for precise identification and quantitative detection.

5. The current problem of microplastics, whose rapid and simultaneous quantification and characterization is a challenge, should be solved through the use of artificial intelligence technologies, which are developing rapidly. Intelligent algorithms from chemometrics and machine learning can be used to improve intelligent identification of microplastics and create models and platforms for the morphology, type,

content and particle size of microplastics in real water samples.

5. Conclusion

MPs pollution has become a global environmental problem, and detecting and managing MPs in actual water environment is even more challenging. Compared to traditional MPs detection techniques, electrochemical sensors have unique advantages thanks to their detection speed and cost efficiency, especially in the application of field samples in real aqueous environments, and provide the possibility of *in situ* online detection of MPs. In this paper, electrochemical sensors based on carbon nanomaterials, metal and its oxide nanomaterials, biomass materials, composite materials and microfluidic chips are introduced in detail, their detection mechanisms and sensing performances are analyzed, and the advantages of electrochemical sensors based on various materials in the field of MPs detection are discussed. It is proposed to use hot nanomaterials such as MOFs and quantum dots in electrochemical sensors to detect MPs. The future of electrochemical sensors is considered from the perspective of the physical and chemical properties of microplastics, the improvement of electrochemical sensing performance and the trend of real-time online detection, focusing on the advantages and disadvantages of current electrochemical sensors in detecting MPs. The mechanism of sensor operation and sensing techniques are crucial and require further MP studies. In conclusion, electrochemical sensors are interesting candidates for real-time online detection of MPs.

CRediT authorship contribution statement

Jinhui Liu: Writing – review & editing, Writing – original draft, Data curation. **Jiaqi Niu:** Supervision, Investigation. **Wanqing Wu:** Supervision, Funding acquisition, Formal analysis, Conceptualization. **Ziyang Zhang:** Investigation. **Ye Ning:** Data curation. **Qinggong Zheng:** Project administration.

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.

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Data availability

Data will be made available on request.

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