

Mini Review

Polymer-based Electrochemical Sensing Platform for Heavy Metal Ions Detection - A Critical Review

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Electrochemical sensors have the advantage of fast analysis, low cost, high sensitivity, flexible and diverse technique, and excellent adaptability for in-situ analysis. This review introduces the recent advances in the field of electrochemical sensing of heavy metal ions (HMIs) based on polymers modified electrodes. In particular, the unique properties of polymers, excellent bridging ability, absorbing ability for HMIs, different conducting polymers and composites, and highly selectively ions imprinted polymers used for the detection of HMIs are highlighted.

Keywords: Electrochemical sensors, heavy metal ions, polymers, ions imprinted polymers, conducting polymers

1. INTRODUCTION

Heavy metals ions (HMIs) are substances that seriously pollute the environment, mainly including arsenic, cadmium, lead, mercury and chromium [1-5]. They are present in the atmosphere, soil and water, which can cause serious problems in all organisms even in small quantities because of their wide distribution, persistence, bioaccumulation and high toxicity [6-9]. Therefore, developing fast and accurate methods for the analysis of low-concentration HMIs is of great significance, not only in environmental samples (water, soil and biological), but also in food, medicine and biological samples [10,11].

Many analytical methods have been reported for the determination of HMIs, such as atomic absorption spectrometry, cold vapor atomic fluorescence inductively coupled plasma techniques (both optical and mass spectrometry modalities), X-ray fluorescence spectrometry, etc [12]. However, these techniques require sophisticated instrumentation, trained technicians, complicated preconcentration

process before measurement and time-consuming processes. Compared with aforementioned methods, electrochemical method is promising as an alternative method due to its merits of fast analysis, high sensitivity, cost-effectiveness, simple operation and easy miniaturization, which is also adaptable for in-situ analysis, point-of-care and in vivo real time analysis [13,14].

Traditional mercury electrode based voltammetry has been considered as a very powerful method for the analysis of HMIs. These mercury based electrodes includes the hanging mercury drop electrode (HMDE) [15-19], the dropping mercury electrode (DME) and mercury film electrode (MFE). These classic mercury devices have the advantages of high sensitivity, good reproducibility, and high accuracy, with a wide range of hydrogen evolution potential, and the possibility of forming amalgam to obtain a clean surface. However, the voltammetry established for mercury electrodes is being limited due to the toxicity of mercury [11]. Recent advances in various novel materials, especially the development of polymeric materials, have opened a new area for electrochemical sensor with flexible electrochemical techniques, such as amperometry (AMP), differential pulse anodic stripping voltammetry (DPASV), potentiometry (POT), differential pulse voltammetry (DPV), anodic stripping voltammetry (ASV), square wave anodic stripping voltammetry (SWASV), cyclic voltammetry (CV), and differential pulse stripping voltammetry (DPSV) [20,21].

Polymeric materials are attracting attention due to their low cost, compatibility and strong adsorption properties, and bridging and embedding ability for other materials [22-24]. Niu synthesized a series of silica-loaded salicylaldehyde-modified PAMAM dendrimers ($\text{SiO}_2\text{-G}_0\text{-SA}\sim\text{SiO}_2\text{-G}_{2.0}\text{-SA}$) and analyzed by fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM) and thermogravimetric analysis (TGA). The feasibility of removing Hg (II), Pb (II) and Au (III) from aqueous solutions by these adsorbents is described, and the adsorption mechanism is proposed [25-27]. Qu prepared novel bifunctional silica-based hybrid materials SG-HE-S-AO and SG-HO-S-AO containing sulfur and amidoxime by heterogeneous and homogeneous methods, and studied static saturation adsorption of Ag (I), Pb (II), Cu (II), Ni (II) and Hg (II) [28,29]. Four silica gel (SG) functionalized by silica gel-loaded diethylene triamine (DETA) chelating resins SG-DETA-1, SG-DETA-2, SG-DETA-3 and SG-DETA-4, were studied for its high adsorption properties for Ag^+ [30], Cu^{2+} [31], Ni^{2+} [32], Hg^{2+} [33] and Pb^{2+} [34]. Zhu studied a high density amino sorbent based on polyurethane foam (PUF) to remove Pb (II). The effects of equilibration time, solution pH, initial Pb (II) concentration and temperature were investigated. The results show that the adsorption of Pb (II) on PEI-PUF has high pH dependence and endothermic, and can be applied for the practical applications [35].

In addition, some people have studied the effects of grafting [36], branching [37], cross-linking [7,38], copolymerization [39], coated [40] and embedding [41] to combine the polymer with other substances to achieve the high adsorption ability [42] for HMIs. For example, Liu prepared porous acrylonitrile (AN)/methyl acrylate (MA) copolymer beads by suspension emulsion. The cyano group in the AN/MA copolymer beads is converted to an amidoxime (AO) group and the HMIs in the aqueous solution are removed by reaction with hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) [39]. Zhang synthesized polydopamine (PDA) polymers modified with magnetic nanoparticles ($\text{Fe}_3\text{O}_4/\text{PDA}$) and used to remove various contaminants such as Cu^{2+} , Ag^+ and Hg^{2+} [41]. Then, the SiO_2 shell was coated on Fe_3O_4 nanoparticles by hydrolysis of Na_2SiO_3 , and modified by $\text{Fe}_3\text{O}_4@\text{SiO}_2$ by silanization

reaction to form $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SH}$ adsorbent, and the Hg^{2+} in water was adsorbed and removed [43]. Qu studied two types of chitosan coated cotton fibers (SCCH and RCCH) for the removal and recovery of Hg^{2+} ions in aqueous solutions [44]. Chen developed a new surface modification method by iron (III)-mediated atom transfer radical polymerization to regenerate the activation of resin-supported N-chlorosulfonamide groups on the surface of polystyrene by electron transfer. The polyacrylonitrile (PAN) was grafted onto the surface of polystyrene (PS) to remove Hg^{2+} from the solution. Other HMIs such as Pd^{2+} , Ag^+ and Cu^{2+} did not interfere with the binding of Hg^{2+} [36]. Sun combined a heterocyclic compound with an open chain crown ether (OCE) to form a new functionality groups, which was loaded on a PS substrate to obtain a novel chelating resin to remove transition HMIs, such as Cu (II), Hg (II), Au (III), Ag (I) and Pd (II) [45-47]. Wang synthesized a novel chitosan derivative by cross-linking reaction of chitosan Schiff base with sodium alginate and used to remove Cd (II) ions. The balance and kinetic data fit well with the Langmuir and pseudo second-order models. Thermodynamic parameters indicate that at higher temperatures, the process is spontaneous and therefore adsorption is efficient. In addition, the regenerated adsorbent after five cycles can retain 87.15% of the adsorption capacity compared to the newly prepared adsorbent [48].

Polymer based materials is attracting more and more research interests in the construction of electrochemical sensing platform for HMIs. This review discusses the design and sensing mechanisms of recent electrochemical sensors of HMIs based on ions imprinted polymers (IIPs), conducting polymers and composites, and electroactive polymers. Table 1 summarizes recent studies on the detection of HMIs based on polymers modified electrodes, including electrode materials, detection methods, analytes, detection limits, and linear ranges.

Table 1. Electrochemical sensing performances for the detection of HMIs based on different polymers modified electrodes.

Electrodes	Methods	Analytes	Linear range	Detection limit	references
CPE/IIP	DPV	Cd^{2+}	2.0-200 ng mL^{-1}	0.31 ng mL^{-1}	90
CPE/IIP	DPV	Cd^{2+}		4.95 $\mu\text{g L}^{-1}$	91
CPE/IIP	DPASV	Cd^{2+}	4-500 nM	1.94 nM	50
CPE/IIP	DPSV	Pb^{2+}	1-810 nM	0.6 nM	51
GCE/IIP- Cu^{2+}	DPV	Cu^{2+}	10-1000 μM	5.99 μM	52
GO/IIP- Cu^{2+} /ISE	POT	Cu^{2+}	0.0001-0.001 mM	0.0004 mM	53
CPE/IIP	DPSV	Cd^{2+}	0.5-40 $\mu\text{g L}^{-1}$	0.15 $\mu\text{g L}^{-1}$	92
Au@PEDOT/GCE	LSV	Hg^{2+}	0.5-20.0 μM	0.05 μM	93
GPE/IIP- Pb^{2+}	DPASV	Pb^{2+}	0.4-10 nM	0.11 nM	54
Nafion/SWCNTs/GCE	ASV	Cd^{2+}	40-4000 nM	4 nM	94
NCBFE	SWASV	Cd^{2+} Pb^{2+}	1-20 $\mu\text{g L}^{-1}$	0.1 $\mu\text{g L}^{-1}$ 0.4 $\mu\text{g L}^{-1}$	95
pGO/PPy/GE	DPASV	Cd^{2+}	1-100 $\mu\text{g L}^{-1}$	0.05 $\mu\text{g L}^{-1}$	69
Nafion-Bi-NMC/GCE	DPASV	Cd^{2+} Pb^{2+}	2-10 $\mu\text{g L}^{-1}$ 0.5-10 $\mu\text{g L}^{-1}$	1.5 $\mu\text{g L}^{-1}$ 0.05 $\mu\text{g L}^{-1}$	96
Nafion-G/GCE	DPASV	Cd^{2+} Pb^{2+}	1.5-30 $\mu\text{g L}^{-1}$ 0.5-50 $\mu\text{g L}^{-1}$	0.02 $\mu\text{g L}^{-1}$ 0.02 $\mu\text{g L}^{-1}$	97

CNSs/PPy/SPE	SWASV	Hg ²⁺ Pb ²⁺		0.0128 nM 0.0014 nM	70
PPy/rGO/SPE	SWASV	Cd ²⁺ Cu ²⁺	0.1-500 mg L ⁻¹	0.097 mg L ⁻¹ 0.064 mg L ⁻¹	98
PPy/AP-ITO	DPV	Cd ²⁺ Pb ²⁺ Cu ²⁺	10-1200 nM 10-1500 nM	8.95 nM 0.99 nM 11.1 nM	72
PANI-co-PDTDA/PtE	DPV	Cd ²⁺ Pb ²⁺ Hg ²⁺	0-0.01 µg L ⁻¹ 0-1 µg L ⁻¹ 0-1 µg L ⁻¹	0.0008 µg L ⁻¹ 0.000938 µg L ⁻¹ 0.000789 µg L ⁻¹	99
PEDOT/GO/GCE	DPSV	Hg ²⁺	0.01-3.0 µM	2780 µM	77
PPy/rGO/GCE	SWASV	Pb ²⁺	0.5-450 nM	0.3 nM	100
Fe ₃ O ₄ /PANI/GCE	DPV	Cd ²⁺ Pb ²⁺		0.3 nM 0.03 nM	84
Cd ²⁺ -IIP/CPE	DPV	Cd ²⁺	1-500 nM	0.52 nM	101
EDTA- PANI/SWCNT/SSE	DPV	Cu ²⁺ Pb ²⁺ Hg ²⁺	1.2-2000 µM 2-37 µM 2-2000 µM	0.08 µM 1.65 µM 0.68 µM	85
ZnO/rGO/PPy	DPV	Hg ²⁺	2-18 nM		102
IIP/CPE	DPASV	Hg ²⁺	2-500 nM	0.52 nM	103
PANI/GO/GCE	SWASV	Pb ²⁺	0.2-250 nM	0.04 nM	86
PPy-RGO/GCE	SWASV	Hg ²⁺		15 nM	104
Cd ²⁺ -NPs-IIP/GCE	DPV	Cd ²⁺	0.05-0.8 µM	0.0001 µM	105
RGO/CS/PLL/GCE	DPASV	Cd ²⁺ Pb ²⁺ Cu ²⁺	0.05-2.0 µg L ⁻¹ 0.05-2.0 µg L ⁻¹ 0.05-2.0 µg L ⁻¹	0.01 µg L ⁻¹ 0.02 µg L ⁻¹ 0.02 µg L ⁻¹	89
PANI/G/SPE	SWASV	Cd ²⁺ Pb ²⁺	1-300 µg L ⁻¹	0.1 µg L ⁻¹	106
rGO/SnO ₂ /PPy/GCE	SWASV	Cd ²⁺ Cu ²⁺ Hg ²⁺ Pb ²⁺	0.5-3 µM	0.00075 µM 0.00083 µM 0.00081 µM 0.00088 µM	107
PEI/RGO/Nafion/GCE	DPASV	Cu ²⁺	1-70 µM	0.03 µM	88
G/PANI/PS/SPE	SWASV	Cd ²⁺ Pb ²⁺	10-500 µg L ⁻¹	4.43 µg L ⁻¹ 3.30 µg L ⁻¹	108
Nafion-GO/GCE	DPASV	Cd ²⁺	0.2-15 µg L ⁻¹	0.005 µg L ⁻¹	109
Nafion-rGo/Si Substrates	SWASV	Cd ²⁺ Pb ²⁺ Cu ²⁺	50-300 nM	21.6 nM 9 nM 7.5 nM	110
Nafion/IL/G/SPE	SWASV	Cd ²⁺ Pb ²⁺	0.1-100 ng L ⁻¹	0.06 ng L ⁻¹ 0.08 ng L ⁻¹	111
Pb ²⁺ -IIP-MWCNT/PtE	DPV	Pb ²⁺	1-5 ppm	20000 ppm	112
TCPP-PPy/ITO	DPV	Pb ²⁺	0.6-3.4 µM	2.47 µg L ⁻¹	113
rGO/PPy/GCE	SWASV	Pb ²⁺	5-750 nM	0.047 nM	114

PPy/GO/GCE	DPV	Cd ²⁺ Pb ²⁺	5-150 µg L ⁻¹	2.13 µg L ⁻¹ 0.41 µg L ⁻¹	115
PANI-VOPO ₄ /GCE	I-T	Pb ²⁺	2-200000 nM	1.36 nM	116

CPE: Carbon paste electrode; GCE: Glassy carbon electrode; ISE: Ion selective electrode; GPE: Graphite paste electrode; GE: Gold electrode; SPE: Screen printed electrode; SSE: Stainless steel electrodes; NCBFE: Nafion-coated bismuth-film electrodes; LSV: Linear sweep voltammetry; POT: Potentiometry

2. POLYMER-BASED ELECTROCHEMICAL SENSORS FOR THE DETECTION OF HMIs

2.1 Imprinted polymers

IIPs, as highly selective electrode materials, has been widely used to detect HMIs, because of their outstanding advantages such as strong selectivity, mechanical and chemical stability, low cost, relative ease and simple synthesis procedures [49]. Alizadeh and Amjadi reported a novel carbon paste electrode (CPE) modified by IIPs with appropriate recognition sites, which shows sensitive response and wide linearity to Pb²⁺, ranging from 1.0×10^{-9} to 8.1×10^{-7} M, and the detection limit is 6.0×10^{-10} M (S/N=3) [50]. Leila proposed an electrochemical preconcentration method using IIPs nanoparticles modified CPE (IIPs/CPE) for the DPASV determination of Cd²⁺ in the environmental and biological samples. The calibration plot was linear in the concentration range of 4-500 nM ($R^2=0.9936$) with a sensitivity of $918 \mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$ and a detection limit of 1.94 nM. The recovery rate of all actual samples is higher than 95%, indicating excellent performance of the proposed voltammetry method [49]. An developed an electrochemical sensor on glassy carbon electrode (Cu²⁺-IIPs/GCE) for the detection of Cu²⁺ in water. The electrochemical performance of Cu²⁺-IIPs/GCE was evaluated by DPSV. The response of Cu²⁺-IIPs/GCE to Cu²⁺ was linear from 1.0×10^{-5} to 1.0×10^{-3} M. The detection limit was found to be 5.99×10^{-6} M (S/N=3) [51]. Topcu studied a novel copper (II) selective electrode based on graphite oxide (GO)/IIPs composite for electrochemical monitoring of Cu²⁺ ions. The fabricated electrode exhibited a linear response to Cu²⁺ over the concentration range of 1.0×10^{-6} - 1.0×10^{-1} M. The detection limit of the fabricated electrode was determined to be 4.0×10^{-7} M [52]. Mojtaba synthesized highly selective lead IIPs by a thermal precipitation polymerization method using a terpyridine-based ligand as a complexing agent, which was successfully incorporated in graphite paste electrode (GPE) as the recognition element for lead ion (Pb²⁺). DPASV technique was used to evaluate the modified electrode. The constructed IIPs-GPE revealed a linear response toward Pb²⁺ over the concentration range from 0.4 to 10 nM and 10 nM to 1.0 µM. The limit of detection was evaluated to be 0.11 nM (S/N = 3) [53].

2.2 Conducting polymer and Conducting Polymers based composites

Conducting polymers (CPs) is the dominant material in the field of materials science, such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (3,4-ethoxythiophene) (PEDOT). They are usually combined with inorganic nanomaterials to form HMIs sensitive sensors [54], due to its unique

physical, chemical, and electrical properties, as well as excellent environmental stability, low cost, easy fabrication, and superior conductivity [55]. The design of composite materials such as PPy [56], PANI [57] and PEDOT [58] for electrochemical sensors has been successfully reviewed. In the past two decades, CPs has also attracted a lot of interests in CV and AMP detection [59].

2.2.1 Polypyrrole

As one of the most promising materials, PPy has shown great potential in building electrochemical sensors [60-62]. In addition to being biocompatible, it has the advantages of simple preparation, low cost and high electrical conductivity [63]. There have been many studies on the functionalized PPy used for the detection of HMIs [64-67].

Song prepared a porous GO-PPy (pGO/PPy) polymer nanocomposite modified sensor for electrochemical trace analysis of Cd (II). The electrochemical performance of pGO/PPy electrode was evaluated by DPSV and SWASV. The cadmium sensor prepared by pGO/PPy nanocomposite showed high sensitivity in the linear range of $1 \mu\text{g L}^{-1}$ - $100 \mu\text{g L}^{-1}$, and the detection limit was $0.05 \mu\text{g L}^{-1}$ [68]. Wei first synthesized PPy/carbon nanospheres (PPy/CNSs) and selectively detected Hg (II) and Pb (II) on modified screen printing electrodes (SPE) at ultra-low concentrations. The method is based on the selective adsorption of HMIs by PPy/CNSs. Combing the advantages of CNSs and PPy, the sensitivity of SWASV method to Hg (II) and Pb (II) is $0.113 \mu\text{A nM}^{-1}$, $0.501 \mu\text{A nM}^{-1}$, and the detection limit is 0.0041 nM and 0.0214 nM for Pb^{2+} and Hg^{2+} , respectively [69]. Lo studied the electrodeposition of a PPy film doped with benzenesulfonic acid (BSA) on an aminobenzenediazonium-modified flexible ITO electrode, which was also applied for the determination of Pb^{2+} , Cu^{2+} and Cd^{2+} metal ions in aqueous medium. The aminophenyl (AP) adhesive layer was modified onto ITO by electroreduction of the in situ generated parent diazonium compound. The ITO-AP-PPy electrode was used to detect Cu^{2+} , Cd^{2+} and Pb^{2+} by DPV with detection limits of 11.1, 8.95 and 0.99 nM, respectively. In addition, the modified electrode exhibits good reproducibility, and successfully used for the detection of HMIs in actual wastewater samples [70].

2.2.2 Poly (3,4-ethoxythiophene) (PEDOT)

PEDOT is an important conductive polymer, which has attracted significant amount of attention toward HMIs, due to its long-term electrochemical stability [71], high conductivity [72], excellent optical transparency [73], good color changing performance [74], and superior electrocatalytic property.

Zuo reported an electrochemical determination method of Hg^{2+} at trace levels based on PEDOT nanorod/GO nanocomposite modified GCE (PEDOT/GO/GCE) by DPSV. The effect factors, such as accumulation time, pH values and deposition potential were optimized. Under optimum conditions, the peak current and Hg^{2+} concentration found good linearity within the range of 10.0 nM-3.0 mM. At a signal-to-noise ratio of 3, the detection limit is found to be 2.78 nM [75]. Edgar prepared a PEDOT-sodium lauryl sulfate (SDS) coated ruthenium membrane electrode (SbFE) (PEDOT-SDS-SbFE) and

used to determine Pb (II) and Cd (II) by ASV. The PEDOT-SDS-SbFE showed good oxidation signals at -0.12 and -0.40 V, respectively, and had higher currents than unmodified electrodes. The RSD for $47.0 \mu\text{g L}^{-1}$ Pb (II) was 1.5% for seven successive assays [76]. Xu reported a method for detecting Cu (II) and Hg (II) by DPASV using S-doped carbon (S-C) nanoflakes and gold nanoparticles (AuNPs) modified electrode. The modified electrode exhibits enhanced electrochemical response compared to the bare GCE due to the effective complexing ability and electrocatalytic activity of S-C as well as the good conductivity of AuNPs. Under optimal conditions, the peak current exhibits a linear response to Cu (II) and Hg (II) concentrations ranging from 0.64 to 63.55 $\mu\text{g/L}$ and 4.01 to 300.89 $\mu\text{g/L}$ with detection limits of 0.19 $\mu\text{g/L}$ and 1400 $\mu\text{g/L}$ (S/N=3), respectively. The modified electrode was also used for the detection of Cu (II) and Hg (II) in lake water samples with satisfied results [77].

2.2.3 Polyaniline

PANI has abundant amino and imine functional groups on the surface [78,79], which has excellent physicochemical stability, environmental stability and biocompatibility. It has been widely used in detecting HMIs due to the synergy between PANI and HMIs [80,81].

Kong developed an easy-to-use electrochemical sensor for the quantitative detection of Pb^{2+} and Cd^{2+} . The core-shell type ferroferric oxide (PANI) (Fe_3O_4 @PANI) nanoparticles are used to construct the electrochemical sensing platforms. The specific surface area of Fe_3O_4 is large, which can improve the detection sensitivity. Under the optimal experimental conditions, the linear range of Pb^{2+} detection is in the range of 0.1-10 nM with detection limit of 0.03 nM, and the prepared electrochemical sensor has high sensitivity, good specificity and good stability. This analytical method has great application prospects in detecting other HMIs [82]. Deshmukh achieved the electrochemical determination of Cu^{2+} , Pb^{2+} , and Hg^{2+} using EDTA chelating ligands to modify PANI and SWCNTs based nanocomposites (PANI/SWCNTs). The detection limits of EDTA-PANI/SWCNTs/SSE for Cu^{2+} , Pb^{2+} , and Hg^{2+} were determined to be 0.08 μM , 1.65 μM and 0.68 μM , respectively [83]. Ying reported the significant effect of GO/PANI nanomaterials on high-sensitivity electrochemical measurements and removal of environmentally harmful lead (Pb^{2+}) ions [84].

2.3 Electroactive Polymers

Electroactive polymers, including nafion, polydopamine, poly-L-lysine (PLL), polyallylamine [85], and polyethyleneimine (PEI) [86], have been applied in HMIs sensing.

Guo coated RGO and chitosan (CS) hybrid matrix RGO-CS on the surface of GCE, then PLL were fabricated by electropolymerization with CV scan, and was used to prepare RGO-CS/PLL modified GCE (RGO-CS/PLL/GCE) for the simultaneous electrochemical detection of Cd^{2+} , Pb^{2+} and Cu^{2+} . The detection limits were 0.01 $\mu\text{g L}^{-1}$, 0.02 $\mu\text{g L}^{-1}$ and 0.02 $\mu\text{g L}^{-1}$ by DPASV, respectively. Moreover, PLL modified electrodes exhibited good stability, more active sites and strong adherence to electrode surface, which also enhanced the electrocatalytic activity [87]. Hu used PEI-RGO nanocomposites in combination with nafion as sensing materials, and used DPASV to analyze trace

amounts of Cu^{2+} in solution. The limit of detection ($S/N=3$) was calculated to be $0.3 \mu\text{M}$ and the sensitivity was up to $0.5274 \mu\text{A} \mu\text{M}^{-1}$. More importantly, trace level detection of Cu^{2+} is achieved in the presence of other coexisting interfering HMIs [88]. Li established a novel sensing platform for Cd^{2+} with DPASV based on nafion-GO nanocomposite film. The nanocomposite membrane combined with the advantages of GO and the cation exchange capacity of nafion improved the sensitivity for the Cd^{2+} determination [89].

3. CONCLUSIONS

In conclusion, this review provides an overview of polymer-based electrochemical sensors for the detection of HMIs, including IIPs, conducting polymer and electroactive polymers. The polymer-based electrochemical sensors show excellent merits including easy fabrication, low cost, high sensitivity and selectivity. The IIPs based potentiometry will be a promising method for the detection of HMIs in complex samples due to its high selectivity, excellent stability and repeatability. Miniaturization need to be extensively explored in future for in situ analysis, point-of-care, and in vivo analysis. For example, all-solid microelectrode could be used for the potentiometric sensing of HMIs in single cell. Thus the method and technique related to the flexible modification of polymer on a micro and even nano scale surface will be a challenging task in the future.

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