Review

Voltammetric determination of mercury(II)

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A R T I C L E   I N F O

A B S T R A C T

Monitoring mercury provides a real challenge in analytical and environmental science, yet solutions are urgently needed due to the adverse effects of mercury on human health and the environment. Electrochemical techniques, more specifically voltammetric techniques, for determination of mercury(II) [Hg(II)] have inherent advantages. We review the state of the art in voltammetric determination of Hg(II) through quantitatively comparing different approaches classified according to the type of working electrode used. As much modern electroanalysis uses nanomaterials for the design of optimal electrode surfaces, this aspect is covered fully.

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Contents

1. Introduction

Mercury(II) [Hg(II)] is one of the most well-known toxic contaminants in aquatic ecosystems and even low-level Hg(II) exposure is considered to be a significant human health hazard because accumulation of Hg(II) through the food chain in the human body can lead to serious problems to the central nervous system and damage to the brain, kidney, lungs, and the developing fetus [1]. Unfortunately, anthropogenic Hg emissions will increase in the future [2], so ongoing contamination is a global problem and rapid, reliable determination of trace Hg(II) has become increasingly desirable.

So far, various commonly used analytical methods, including cold-vapor atomic absorption spectroscopy, cold-vapor atomic

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fluorescence spectroscopy, inductively coupled plasma-mass spectrometry and inductively coupled plasma-atomic emission spectrometry, can be employed for sensitive, selective determination of Hg(II) [3]. However, these traditional central-laboratory measurements require expensive, sophisticated instruments, high operating costs and complicated sample-preparation processes, which are time consuming and unsuitable for routine in-field monitoring of a large number of samples. Also, samples may change during their collection, so efforts are ongoing to design rapid, inexpensive methods for detection of Hg(II). Currently, methods, such as colorimetry and fluorimetry, have been developed to allow miniaturization and field applications [4]. Imperfect, these still exhibit some features that limit their practical use, such as cross-sensitivity toward other metal ions and the sophistication needed to synthesize probe materials. Compared to other techniques, electrochemical techniques, more specifically voltammetric techniques, are potentially most promising for determination of Hg(II) in the field, due to their inherent advantages, such as high sensitivity and selectivity, rapid analysis time, impressive cost effectiveness and miniaturization.

In the past decade, with rising interest in developing a reliable, time-saving, low-cost and easy-to-operate method for determination of Hg(II) in the field, a few reviews focused on optical sensors (fluorescent and colorimetric) [1,5–7]. Also, there are a few reviews with some discussion on voltammetric determination of Hg(II), if unavoidably fragmentary and incomplete [4,8–10]. As far as we know, no review focused specifically on the worthwhile topic of voltammetric determination of Hg(II). Furthermore, great progress was recently made in applying nanomaterials to voltammetric determination of Hg(II) and the number of papers devoted to this topic has grown rapidly in the past five years. Thus, a dedicated review is considered timely to evaluate the success to date and to identify the remaining challenges in this topic.

In this article, we review the state of the art in voltammetric determination of Hg(II) through quantitatively comparing different approaches, including the main details of methodology, design, mechanism and performance, to arrive at some important conclusions. As *TrAC* requires a concise review covering the latest advances, we focus our discussion on the past five years. Relevant information relating to the performance of different approaches is presented in several tables.

2. Principle of voltammetric determination

Voltammetry involves monitoring the current generated upon application of a potential sweep. There are several types of voltammetric techniques, such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), differential pulse voltammetry (DPV) and square wave voltammetry (SWV), depending on the potential-time waveforms of the applied potential function [11]. As they offer better signal-to-noise ratios, DPV and SWV can offer better sensitivity than LSV and CV [12], so DPV and SWV are the most commonly used methods.

The sensitivity for voltammetric determination of Hg(II) can be greatly enhanced through the introduction of a pre-concentration step, in which Hg(II) is accumulated on the surface of the working electrode by a faradaic or an adsorptive process. Then, the analytical signal is generated by the subsequent anodic stripping voltammetry (ASV), which is the voltammetric technique most applicable to the voltammetric determination of trace Hg(II), because the pre-concentration step offers voltammetric approaches with high sensitivity and a low limit of detection (LOD). In detail, in the faradaic pre-concentration step, Hg(II) is reduced to Hg(0) and deposited on the surface of the working electrode via application of a negative potential. In the adsorptive pre-concentration step, Hg(II) is

pre-concentrated via chemical accumulation, which is based on the formation of complexes with suitable ligands on the surface of the working electrode. Then, Hg(II) in the complexes is electrochemically reduced to Hg(0).

Following the pre-concentration step, the detection step is performed by sweeping the electrode potential in the anodic direction to re-oxidize Hg(0) to Hg(II), and the oxidation current (stripping current) is recorded as a function of scan potential. The position of the oxidation peak (stripping peak) and the peak current are used for Hg(II) identification and quantification, respectively.

The latter adsorptive pre-concentration step is called adsorptive stripping voltammetry [13]. However, many works have confused the two concepts and procedures by referring them collectively as ASV. So, we here follow previous authors, and classify both of them as ASV. Depending on the types of voltammetric techniques selected in the stripping step, there are commonly three types of ASV:

- linear sweep anodic stripping voltammetry (LSASV);
- differential pulse anodic stripping voltammetry (DPASV); and,
- square wave anodic stripping voltammetry (SWASV).

As evaluated in published reviews [9,10,14,15], stripping voltammetry has been established and continues to be the leading technique in electrochemical determination of trace Hg(II).

Commonly, voltammetric determination of Hg(II) is performed in an electrochemical cell that consists of a three-electrode system – a working electrode on which Hg(II) is deposited, a reference electrode and a counter (or auxiliary) electrode. Because electrochemistry is based on processes occurring at the surface of the working electrode, the performance of voltammetric determination of Hg(II) strongly depends on the properties of the working electrode. The ideal working electrode should possess the following characteristics: reproducibility, selectivity, sensitivity, long-term stability, portability, rapid detection, ease of use, and cost effectiveness. Driven by these needs, great efforts have been made in design, fabrication, and application of working electrodes to further this analytical procedure, which we discuss in detail in the following sections.

3. Metal electrodes

Among various metal electrodes, the gold (Au) electrode is generally favored, since it has a high affinity for Hg(II), which enhances the pre-concentration effect. Different types of Au electrodes, such as solid [16], film [17], microelectrode arrays [18,19], microwire [20] and screen-printed [21], have been reported for stripping voltammetric determination of Hg(II). Their performance is shown in Table 1.

Major drawbacks in the use of Au electrodes are the structural changes of their surface caused by formation of amalgam and the difficulty in recovery [22]. These phenomena can lead to loss of reproducibility and reliability. The chemically-modified electrodes emerged to overcome this obstacle, and we discuss them in detail in the following sections.

Another problem in stripping voltammetric determination of Hg(II) is the interference of halide ions (e.g., Cl$^-$), due to the formation of insoluble calomel, which precipitates onto the electrode surface, so reducing the active electrochemical area and hence decreasing the sensing performance. To overcome this problem, Compton's group reported the detection of trace Hg(II) over the range 10–200 ppb at Au ultra-microelectrode arrays by LSASV without the interference of 0.1 M and 1 M chloride media, despite calomel formation [18]. Even if calomel precipitates onto the array

Table 1
Comparison of performance for voltammetric determination of Hg(II) at metal electrodes

Electrodes	Technique	Linearity range	Sensitivity (μA ppb^{-1})	LOD (ppb)	Ref.
Gold solid electrode	SWASV	0–100 ppb	1.03	0.40	[16]
		0–25 ppb	1.45		
		1–5 ppb	2.78		
Gold film electrode	DPASV	1–3 ppb	0.273	0.17	[17]
Gold ultra-microelectrode arrays	LSASV	10–200 ppb	0.11 nC/ppb	3.2	[18]
Gold microelectrode array	DPASV	2–20 ppb	–	0.8	[19]
Gold microwire electrode	SWASV	0–47 ppb	–	2.4	[20]
Screen-printed gold electrodes	SWASV	5–30 ppb	0.0358	1.1	[21]
Screen-printed gold electrodes	SWASV	–	0.04	0.9	[23]
On-chip integrated Au–Ag–Au three-electrode	DPASV	10–1000 ppb	0.0066	3	[24]
Sb film electrode	SWASV	10–100 ppb	–	1.3	[25]

Abbreviation: LOD, Limit of detection.

during the accumulation step, the signal is not adversely affected, due to the large number of microelectrodes making up the array.

Berg et al. also found that the adsorption of halide ions causes a gradual decrease in the height and the potential of the Hg peak, when using an Au microwire electrode in SWASV [20]. However, this effect is eliminated by including an anion-desorption step in the analysis prior to each scan, so it is more reproducible and suitable for use in seawater samples. To eliminate further the interferences of organic and inorganic species present in real matrices, a sample pre-treatment step, such as on-line medium exchange [17] and an optimized digestion method [23], coupled to voltammetric determination of Hg(II) by an Au-based electrode, was also developed. Through the sample pre-treatment step, a low LOD of 0.17 ppb was obtained – the lowest of the Au-based electrodes listed in Table 1.

Recently, with the development of microfabrication techniques, an Hg(II) detector with an on-chip integrated Au–Ag–Au three-electrode system and a microfluidic channel, was fabricated [24]. The three-electrode system consists of a silver reference electrode and two Au electrodes used as working and counter electrodes, respectively. As a lab-on-a-chip device, it demonstrates great potential for the application of *in-situ* or on-line mercury-pollutant analysis. Considering that Au is not a cheap material, an antimony (Sb)-film electrode has been developed [25]. As shown in Table 1, although the performance of the Sb-film electrode (LOD: 1.3 ppb; sensitivity: not given) is not superior to an Au-solid electrode, its performance has been comparable with some Au-based electrodes [e.g., Au-ultra-microelectrode arrays (3.2 ppb) and Au-microwire electrode (2.4 ppb)].

4. Organic and biological receptor-modified electrodes

The term "chemically-modified electrode" designates an electrode with a chemically-active species deliberately immobilized onto its surface. In order to enhance the sensitivity and the selectivity for voltammetric determination of Hg(II), chemically-modified electrodes have been widely used. A range of substrate electrodes for modification have been studied for the voltammetric determination of Hg(II) with carbon proving the most popular electrode material. The most popular carbon-based-substrate electrode is the glassy-carbon electrode (GCE), and the other carbon-based-substrate electrodes commonly used are boron-doped diamond electrode (BDDE), carbon-paste electrode (CPE) and screen-printed carbon electrode (SPCE). More information about these substrate electrodes could be found in the published reviews [10,26,27]. Au electrodes are also popular substrate electrodes for modification, and the modification can partly eliminate the passivation of the bare Au electrode, because the attached modified layer can prevent the adherence of interfering substances. Common methods for immobilizing a modifier include chemisorption, covalent binding, self-assembled monolayer and polymerization.

Many organic and biological modifiers, such as organic molecules, polymers and DNA, are used as receptor material for voltammetric detection of Hg(II). These modifiers are generally based on two types of interaction: ion exchange and complexation, the latter being more selective due to the specific interaction between the specially-designed receptor and Hg(II). Their performance is shown in Table 2.

4.1. Organic group-based modification

The organic molecules as receptors commonly contain functional groups with high affinity toward Hg(II). Sulfur-containing (sulfur atoms or thiol groups) receptors are mostly used due to their high affinity for Hg(II) [28]. Recently, a GCE modified with Langmuir-Blodgett (LB) film of p-tert-butylthiacalix[4]arene (TCA, which contains four sulfur atoms) was designed for the determination of trace amounts of Hg(II) [29]. Compared with bare GCE and

Table 2
Comparison of performance for voltammetric determination of Hg(II) at organic and biological receptors modified electrodes

Electrodes	Technique	Linearity range	Sensitivity (μA ppb^{-1})	LOD (ppb)	Ref.
LB-TCA/GCE	DPASV	0.1–30 ppb	0.513	0.04	[29]
thiophenolate/CFMEs	ASV	10–2000 ppb	–	–	[30]
polyviologen/GCE	DPASV	1–100 ppb	0.0143	0.3	[33]
polyamide/GCE	DPASV	2–1604 ppb	–	2	[34]
IIP/CPE	DPASV	0.5–100 ppb	3.49	0.1	[37]
MPMBT/GCE	SWASV	0.2–32 ppb	2.14	0.02	[38]
ssDNA/Au electrode	DPV	20–400 ppb	–	20	[40]
ssDNA/Au electrode	DPV	0.2–400 ppb	–	0.1	[41]
ssDNA/Au electrode	DPV	0.02–1000 ppb	–	0.012	[42]
super-sandwich DNA/Au electrode	DPV	0.02–200 ppb	–	2×10^{-6}	[43]
PTO/Au electrode	DPASV	0.04–0.2 ppb	9.08	0.012	[44]

Abbreviations: LOD, Limit of detection; LB, Langmuir-Blodgett film; TCA, p-tert-butylthiacalix [4]arene; CFME, Cylindrical carbon-fiber microelectrode; IIP, Ion-imprinted polymer; MPMBT, Microporous poly(2-mercaptobenzothiazole); ssDNA, Single-stranded DNA; PTO, Polythymine oligonucleotide.

modified GCE using the direct coating method, the LB-film-modified electrode can greatly improve measurement sensitivity by a factor of about eight. However, a non-covalently attached monolayer deposited with the LB technique is easily lost in repeated applications. Thiophenolate (containing thiol groups)-layer-modified cylindrical carbon fiber microelectrodes (CFMEs) are also used for the determination of Hg(II) using ASV [30]. In terms of sensitivity and ease of regeneration, mono or thin layers of organic molecules can meet the requirements well. However, for *in-situ* monitoring, the stability and the durability of polymeric films assembled on the electrodes are preferred.

4.2. Polymer-based modification

Trace-metal-ion detection based on conductive polymer-modified electrodes has received considerable attention, due to their superior electrical conductivity, good adhesion properties, enhanced rigidity and suitable structure [31,32]. An electropolymerized anion-exchange polymer (polyviologen)-modified GCE (PVGCE) has been used to detect Hg(II) by DPASV [33]. This PVGCE could improve the detection limit of Hg(II) in the presence of a high concentration of chloride, because Hg(II) forms negative complex ions $HgCl_4^{2-}$ that can be accumulated by the anion-exchange characteristic of polyviologen. In addition, to improve the selectivity of the conductive polymer, functionalization of conducting polymers with a specific group would increase the scope of analysis. A poly (EDTA-like)-film-modified electrode has been fabricated by electropolymerization of pyrrole-containing monomers substituted with specific complexing groups [34]. This polyamide electrode was reported to show significant selectivity towards Hg(II), even in the presence of a large excess of other metal cations.

For the above-mentioned complexing modifiers, the specificity of receptors toward target Hg(II) is always based on a conventional Lewis acid-base complexation interaction. Although these particular receptors (Lewis base) can exhibit specific interactions with Hg(II), some other soft Lewis acids [such as Cd(II), Pb(II), Cu(II), and Ag(I)] also can exhibit specific interactions with the receptors. Consequently, these receptors usually provide an unremarkable selectivity toward Hg(II) in the presence of some potential interfering metal ions. Therefore, a highly selective modifier is still urgently needed in this field.

Molecularly-imprinted polymers (MIPs) are promising highly selective synthetic receptors with molecular recognition sites designed for a particular analyte [35]. This kind of polymer has become attractive as replacements for biological receptors in electrochemical-sensing applications [36]. The MIP technique can also be used to prepare polymers containing inorganic cation-selective sites, as the so-called ion-imprinted polymers. Recently, a highly selective, sensitive voltammetric sensor based on a Hg(II) ion-imprinted polymer-modified CPE was reported [37]. As shown in Table 1 and Table 2, the proposed sensor provides a high sensitivity of 3.49 µA ppb^{-1}, which is superior to the Au-based and organic receptor-modified Hg(II) sensors mentioned above. And, there is no interference, even when concentrations of potential interfering Cu(II) and Cd(II) are 100 and 500 times as much as that of Hg(II), which shows a good selectivity for Hg(II).

The sensitivity of the imprinted electrode depends on the amount of effective imprinted sites on the electrode surface. However, the traditional imprinting techniques suffered from low binding capacity, poor site accessibility, and slow binding kinetics because most imprinted sites were embedded in high rigid polymer matrix interior. To create more effective imprinted sites and to improve site accessibility, our group recently reported a surface-ion-imprinting strategy in electropolymerized microporous poly(2-mercaptobenzothiazole) (MPMBT) films (Fig. 1) [38]. Due to their higher proportion of surface-imprinted sites, larger sur-

face-to-volume ratio, the complete removal of Hg(II) templates and larger affinity to Hg(II) templates, the Hg(II)-MIP-modified GCE can not only strikingly improve the sensitivity by a factor of 5.9 times over the non-imprinted electrode, but also obtain good repeatability with a relative standard deviation (RSD) of 2.5% for 10 repeat measurements. In addition, a 50-fold excess of Pb(II), 100-fold excess of Cd(II), Zn(II) and Cu(II) over Hg(II) hardly causes significant change in the stripping peak current of Hg(II), which shows good selectivity for Hg(II).

4.3. DNA-based modification

Hg(II) ions possess a unique property of strongly and highly selectively binding in between two DNA thymine bases (T) and subsequently forming stable T-Hg^{2+}-T base pairs [39]. Based on this property, several DNA-based receptor-modified electrodes were developed for voltammetric detection of Hg(II) in recent years. The fundamental mechanism for such sensors is based on a change in the electrochemical response of an electroactive label bound to bio-organic molecule probes. One way is to modify the electrode with redox-tagged oligonucleotides, and then adjust the distance of redox labels from the electrode surface via an Hg(II)-induced conformational switch [40–42]. Another way is to amplify the signal by hybridizing multiple signal probes [43].

Han and Kim et al. developed a reusable electrochemical sensor for detection of Hg(II), based on the Hg(II)-induced conformational change of ferrocene(Fc)-labeled DNA from an open structure to a restricted hairpin structure (Fig. 2A) [40]. Furthermore, this electrode was able to regenerate by simply unfolding the ferrocene-labeled DNA in cysteine.

Similarly, Liu and Yu et al. reported an Hg(II) sensor that relied on the cooperative coordination between Hg(II) and short Fc-tagged poly-T oligonucleotides immobilized on the electrode surface [41]. Such interaction induced a conformational switch of the Fc-tagged oligonucleotides from single-strand to a duplex-like structure, which drew the Fc tags away from the electrode surface and thus substantially decreased redox current (Fig. 2B).

Also, Wu and Yu et al. developed an electrochemical Hg(II) sensor based on target-induced structure-switching DNA [42]. This system comprises two DNA strands, one an oligonucleotide immobilized on the electrode surface, and the other an Fc-tagged oligonucleotide complementary with the first strand. The stable T-Hg^{2+}-T base pairs induced the folding of the first strand into a hairpin structure, which resulted in the release of the Fc-tagged oligonucleotide from the electrode surface and substantially decreased redox current (Fig. 2C).

Recently, a super-sandwich DNA structure was designed to amplify the voltammetric signal [43]. With the super-sandwich DNA structure, long concatemers containing multiple signal probes were created, and improved the electrochemical signal by about a factor of two compared with the traditional sandwich structure.

Different from the methods that rely on redox labels, a new sensing platform based on polythymine-oligonucleotide-modified Au electrode (PTO/Au) was established for voltammetric determination of Hg(II) with stripping approach [44]. In the linearity range 0.04–0.2 ppb, a high sensitivity of 9.08 µA ppb^{-1} was obtained, far beyond the sensitivity of organic-receptor-modified electrodes listed in Table 2.

As we discussed above, artificial receptors (e.g., organic group and imprinted polymer) and biological receptors (e.g., DNA) both have their own advantages and potential. As seen in Table 2, as a whole, the LODs for DNA-modified electrodes are lower than those of artificial-receptor-modified electrodes. Also a high sensitivity of 9.08 µA ppb^{-1} for a DNA-modified electrode is far beyond those for artificial-receptor-modified electrodes. Based on the above results, biological receptors possess specificity and high sensitivity that are
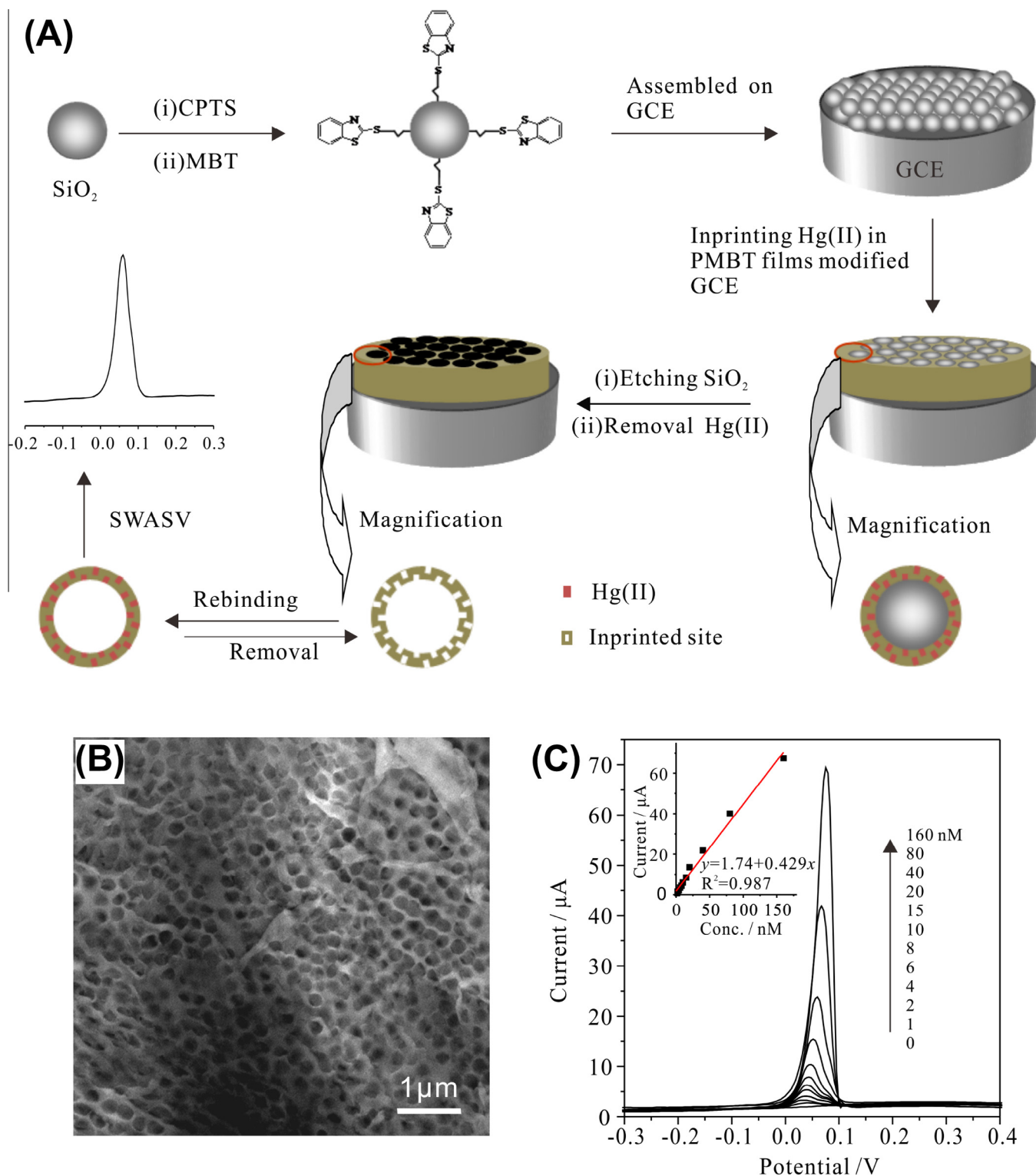
Fig. 1. (A) How Hg(II)-imprinted MPMBT/GCE can be formed. (B) Typical SEM image of the imprinted MPMBT films formed with 19 consecutive potential cycles on the GCE surface. (C) Typical SWASV stripping signals of Hg(II) on an imprinted MPMBT/GCE. Inset is the calibration plot of the SWASV peak current (background current was subtracted) *versus* the concentration of Hg(II). (From [38], ©2010 Elsevier B.V.).

hardly achievable by artificial receptors. But the stability and the reproducibility of biological receptors when operating under harsh conditions are still worrisome, and their present price remains too high for commercial application. Artificial receptors are cost effective and have long-term stability unachievable by biological receptors.

5. Nanomaterial-modified electrodes

In the past decade, nanotechnology has offered exciting prospects in voltammetric determination of Hg(II). In the past five years, an explosion of research in this field has yielded myriad approaches by introducing various kinds of nanomaterials to modify
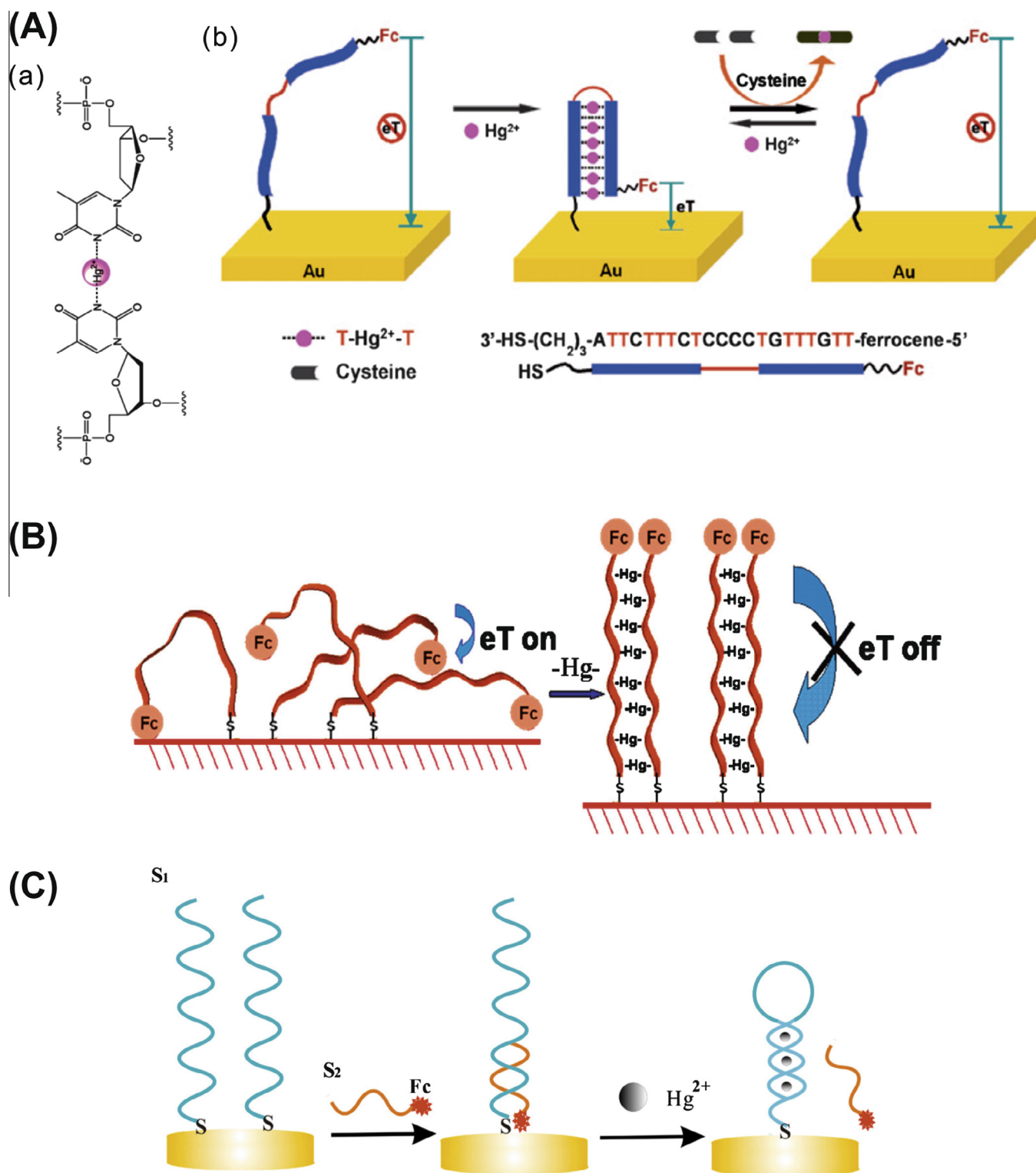
Fig. 2. Electrochemical sensor for Hg^{2+}-ion detection. (A) (a) Formation of T-Hg^{2+}-T base pair. (b) In the presence of Hg^{2+}, the conformational change results in increased efficiency of electron transfer (eT) between the Fc redox moieties and the electrode surface. (From [40], ©2009 the Royal Society of Chemistry). (B) A duplex-like complex forms when two proximate probes cooperatively coordinate with Hg^{2+}, inducing conformational switch and drawing Fc tags away from the electrode with decreased redox current. (From [41], ©2009 American Chemical Society). (C) In the presence of Hg^{2+}, mercury-mediated base pairs induce the folding of the S1 into a hairpin structure, which results in the release of the S2 from the electrode surface with a substantially decreased redox current. (From [42], ©2009 Elsevier B.V.).

electrodes. These nanomaterials include, but are not limited to, noble metal nanoparticles (NPs), carbon nanotubes (CNTs), graphene and mesoporous silica. Also, nanomaterials are suitable for modification with a wide range of organic and biological receptors, giving rise to highly-selective Hg(II)-sensing systems. Their performance is shown in Table 3.

Table 3
Comparison of performance for voltammetric determination of Hg(II) at nanomaterial-modified electrodes

Electrodes	Technique	Linearity range	Sensitivity ($\mu A\ ppb^{-1}$)	LOD (ppb)	Ref.
Au NPs/GCE	SWASV	0.01–0.5 ppb	6.5	1.5×10^{-4}	[47]
		1–5 ppb	2.6		
		5–50 ppb	1.4		
Cys/Au NPs/CILE	SWASV	2–20000 ppb	–	0.46	[49]
MB-DNA/Au NPs/gold electrode	DPV	0.2–20 ppb	–	0.1	[50]
DNA/Au NPs/gold electrode	SWV	0.1–20 ppb	–	0.1	[52]
MB-DNA/Au NPs/gold electrode	DPV	0.2–100 ppb	–	0.064	[53]
Gold nanoelectrode ensembles	SWASV	0–14 ppb	2.95	0.02	[54]
Au NPs/PEDOT/GCE	DPASV	0.5–11 ppb	–	0.83	[55]
Au-Pt NPs/NFs/GCE	SWASV	0.1–10 ppb	7.993	0.008	[56]
GA/chitosan/CNPE	LSASV	1.3–16.6 ppb	0.75	1.96	[60]
Fast Violet B/MWCNTs/GCE	DPASV	0.2–2.8 ppt	–	0.0002	[61]
Au NPs/CNTs/GCE	DPASV	0.1–1 ppb	0.59	0.06	[62]
		1–10 ppb	0.083		
		10–250 ppb	0.45		
PMBT/Au NPs/SWCNTs/ GCE	DPASV	0.08–19 ppb	3.74	0.016	[63]
Au NPs/graphene	SWASV	0.008–0.05 ppb	708.3	0.006	[69]
		0.1–60 ppb	7.37		
Cysteamine/graphene/Au electrode	SWASV	1–8 ppb	0.066	0.6	[70]
AuNPs/GO-IL/GCE	DPASV	0.02–20 ppb	–	0.006	[71]
PPy-RGO/GCE	SWASV	0–20 ppb	0.618	3	[72]
BT-SBA/CPE	DPASV	400–2000 ppb	4.92	80	[74]
TFSF/GCE	DPASV	2–20 ppb	136.96	0.86	[75]
BT-SBA/GPCE	SWASV	0–20 ppb	2.04	0.18	[76]
AlOOH@SiO$_2$/Fe$_3$O$_4$/GCE	SWASV	2–30 ppb	1.24	0.00287	[77]
MBT/3D gold micro-/nanopore array electrode	SWASV	0.01–2 ppb	9.23	0.004	[78]

Abbreviations: LOD, Limit of detection; Cys, Cysteine; CILE, Carbon ionic-liquid electrode; MB, Methylene blue; PEDOT, Poly(3,4-ethylenedioxythiophene); NFs, Nanofibers; GA, Glutaraldehyde; CNPE, Carbon nanotube-paste electrode; PMBT: Poly(2-mercaptobenzothiazole); GO-IL, Ionic liquid-functionalized graphene oxide; PPy, Polypyrrole; RGO, Reduced graphene oxide; TFSF, Thiol-functionalized silica film; BTP, 2-benzothiazolethiol; SBA, SBA-15 mesoporous silica; GPCE, Graphite-polyurethane composite electrode; MBT, 2-mercaptobenzothiazole.

5.1. Metal nanoparticle-based modification

Metals in the form of NPs have generated enormous excitement in electrochemical analysis due to their unique size-dependent properties, such as high effective surface area, enhancement of mass transport and catalysis, which are different from that of the bulk material [26,45,46]. Recently, Compton's group addressed why NP-modified electrodes can differ from that of conventional unmodified macroscale electrodes [45]. Discrepancies occur due to a combination of electrode kinetics and mass transport. The changed electronic structure and adsorption behavior at the nanoscale induces the changes of electrolytic reaction mechanism and kinetics. The different morphology of electrode surface between NP-modified electrodes and conventional unmodified macroscale electrodes changes the mass transport characteristics at the interface. In addition to novel properties, metal NPs open up new approaches to manufacturing electrodes cost effectively by minimizing the expensive materials (e.g. Au and platinum) needed.

As we have mentioned above, Au is generally favored in this field since it has a high affinity for Hg(II). However, undesirable Au amalgam may be formed and destroy the surface feature of the electrode, which subsequently leads to the loss of reproducibility and reliability. In addition, surface passivation often occurs at a bare Au electrode. To overcome these problems, AuNP-modified electrodes have emerged as a promising option for the voltammetric determination of Hg(II) [47,48]. The renewable surface of AuNPs permits us to eliminate memory effects. Compared with the performance of Au-solid and Au-film electrodes listed in Table 1 (sensitivity: 2.78 $\mu A\ ppb^{-1}$, LOD: 0.17 ppb), the AuNP-modified electrode shows improved analytical performance as listed in Table 3 (sensitivity: 6.5 $\mu A\ ppb^{-1}$, LOD: 1.5×10^{-4} ppb). Moreover, AuNPs functionalized with organic receptors (e.g. amino acids) have been designed to improve selectivity toward Hg(II) [49]. As AuNPs serve a large surface area to enhance greatly the loading capacity for biological receptors (e.g., oligonucleotide) and possess a friendly biocompatible microenvironment to maintain their activity, various oligonucleotide-functionalized AuNPs have been employed to achieve signal amplification [50–53].

Nowadays, a key bottleneck for AuNP-modified electrodes is how to modify efficient AuNPs on the electrode surface. Commonly, AuNPs easily aggregate, so that the modified electrode may lose the electrochemical properties of the AuNPs. For this reason, Jena and Raj et al. constructed AuNPs on the thiol-functionalized sol-gel-derived three-dimensional silicate network by a colloidal chemical approach [54]. Giannetto et al. deposited AuNPs onto a conductive polymeric film [55]. Gong and Hu et al. loaded bimetallic Au-PtNPs onto the 3D interlaced network of organic nanofibers [56]. In these studies, the AuNPs were homogenously distributed in the matrix and behaved like micro-/nano-electrode ensembles. The resulting sensor exhibited a high sensitivity of 7.993 $\mu A\ ppb^{-1}$, which is far beyond Au-solid and Au-film electrodes shown in Table 1.

5.2. Carbon nanotube-based modification

CNTs have had considerable research attention, and recently published reviews have demonstrated that CNTs have great potential applications in electrochemical sensing due to their unique structure, chemical stability, anti-fouling capacity, electrical conductivity and electrocatalytic activity [57–59]. However, their native insolubility severely holds back the process of application. Proper functionalization of CNTs can not only enhance the dispersibility but also improve the selectivity, broaden their properties and expand their applications.

Various functionalized CNTs for voltammetric determination of Hg(II) were successful, with CNTs playing key roles as electrochemical transducers. A functionalized multi-walled CNT (MWCNT)-paste electrode modified with cross-linked chitosan

was developed for the determination of Hg(II). The chitosan cross-linked with glutaraldehyde can increase polymer stability in acidic solutions and enhance accumulation ability [60]. Also, a recent strategy of covalent modification of MWCNTs using Fast Violet B salt containing potential donor atoms towards Hg(II) improved the selectivity [61].

CNTs can also be employed as support materials for dispersion and stabilization of various inorganic nanomaterials and organic materials due to their large chemically-active surface and stability. Xu and Jin et al. proposed a microwave-radiation approach to synthesize AuNP/CNT composite rapidly, with the AuNPs being uniformly dispersed on the walls of the CNTs [62]. This composite was first applied to the determination of trace Hg(II) by ASV, with improved performance compared to conventional Au-based electrodes. As mentioned above, traditional ion-imprinting polymers suffer from low binding capacity, poor site accessibility, and slow binding kinetics. To solve these problems, our group recently reported an electropolymerized surface ion-imprinting polymer film at the surface of AuNP/single-walled CNT nanohybrids (AuNP/SWCNT)-modified GCE for the electrochemical detection of Hg(II) by DPASV [63]. Due to their larger surface area, AuNPs/SWCNTs greatly enhance the total amount of effective imprinted sites. Moreover, the excellent conductivity of AuNP/SWCNT substrates also facilitates electron transfer through the electrode. Even a 20-fold excess of Ag(I), and a 100-fold excess of Cd(II), Zn(II), Pb(II) and Cu(II) over Hg(II) hardly cause significant interference (the peak current ratio only slightly varied from 0.91 to 1.03), which indicated that this imprinted electrode possessed a good selectivity to Hg(II). Importantly, the resulting imprinted electrode can also be readily renewed and shows a long life time, so that over 80% of the original responses were retained after 30 days.

5.3. Graphene-based modification

Graphene, as a novel "star" material, has led to an explosion of interest in the field of electrochemistry, due to its extraordinary electronic transport properties, large surface area and high electrocatalytic activity. In the past three years, several reviews with particular emphasis on graphene-based electrochemical applications have been published [64–68].

Similar to CNTs, graphene can also be employed as support materials for dispersion and stabilization of various materials, and the incorporated material can also prevent the aggregation problem of graphene. Recently, several graphene-based composites were employed for voltammetric determination of Hg(II). In these systems, graphene usually served as an advanced substrate and provided conducting pathways to improve electron transport.

Gong and Zhang et al. demonstrated a new highly sensitive and selective Hg(II) sensor based on graphene-based nanocomposite film constructed by homogenously distributing monodispersed AuNPs onto the two-dimensional graphene-nanosheet matrix [69]. The as-prepared composite matrix combines the advantages of the graphene nanosheets together with those of AuNPs, leading to a remarkably improved sensitivity of 708.3 µA ppb^{-1}, which is the highest reported value for Hg(II) detection to date. In addition, cysteamine-functionalized graphene with a terminal mercapto group modified the Au-electrode surface for determination of Hg(II) by SWASV [70]. The mercapto groups on the graphene nanosheet could selectively interact with Hg(II), which offered the strategy a high selectivity so that 200-fold excesses of Cu(II), Zn(II), Co(II), Fe(II) and Mn(II) over Hg(II) caused no interference.

Recently, a simple, sensitive strategy for voltammetric determination of Hg(II) was based on the synergistic effect between ionic liquid (IL)-functionalized graphene oxide (GO-IL) and AuNPs [71]. ILs have attracted intense interest in electrochemistry due to their excellent properties, and ILs here can improve the dispersion of GO. By electrodeposition, AuNPs are monodispersed on the GO-IL, resulting in a greatly enhanced electron-conductive nanostructured membrane and a large electroactive surface area. With the combination of the specific features of GO, IL and AuNPs, the developed AuNP-GO-IL-modified GCE showed good selectivity. A 50-fold variety of common coexistent ions in water samples, such as Na$^+$, K$^+$, Ca^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, Cl$^-$ and I$^-$, were investigated, and showed no obvious interferences with the Hg(II) detection.

Many excellent results have been obtained in the efforts to improve the selectivity for Hg(II). However, these surface-functionalization-based methods usually suffer from complexity in manufacturing the electrodes and/or the modification process or synthesis of specific receptors. Considering how to improve selectivity with simple, practical methods, our group recently developed a new detection strategy based on the selective adsorption behavior of nanomaterials toward Hg(II) [72] (Fig. 3). Inspired by the result that polypyrrole-reduced graphene oxide nanocomposite (PPy-RGO) shows a highly selective Hg(II) removal capacity, we demonstrated for the first time that Hg(II) can be selectively identified using a PPy-RGO-nancomposite-modified GCE. The simplicity in manufacturing and the practical utility of this sensor are superior to biotechniques and surface-functionalization-based methods. We also found that selective adsorption toward toxic metal ions can result in selective response. This finding gives a new route to improve the selectivity of electrochemical sensing of toxic metal ions.

5.4. Mesoporous silica-based modification

Mesoporous silica, especially those exhibiting ordered pore structure and uniform pore size, was investigated extensively for sensing applications in recent years [73]. The prefix "meso" refers to the range 2–50 nm. The main motivation for preparing such a nanostructure is to enhance the surface area/volume ratio for the immobilization of huge amounts of organic or biological receptors, while ensuring fast mass-transport properties due to the three-dimensional network being mechanically stable. Also, the silanol groups on the surface of mesoporous silica help to incorporate a wide range of functional groups.

In the past five years, several electrode modifiers based on organic-receptor-functionalized mesoporous silica were reported for voltammetric determination of Hg(II). Cesarino et al. did a lot in this field [74–76]. First, they reported a 2-benzothiazolethiol functionalized mesoporous SBA-15 silica-modified CPE for simultaneous determination of Pb(II), Cu(II) and Hg(II) ions in natural water and sugar cane [74]. Later, they reported a thin thiol-functionalized mesoporous silica film-modified GCE for the determination of Hg(II) [75]. Recently, they reported a 2-benzothiazolethiol-functionalized mesoporous SBA-15 silica-modified graphite-polyurethane composite electrode for simultaneous determination of Cd(II), Pb(II), Cu(II) and Hg(II) in natural waters [76]. Compared to their first work using CPE, the main advantage of the latest work was the robustness of the graphite-polyurethane composite electrode.

5.5. Other nanomaterial-based modifications

Although metal-oxide nanostructures have been widely fabricated for electrochemical sensors, they are rarely explored for voltammetric determination of Hg(II). Inspired by the new detection strategy based on the selective adsorption behavior of nanomaterials, our group recently tried to explore the potential of metal-oxide nanomaterials for determination of Hg(II). Because of the high adsorption capacity toward heavy-metal ions, AlOOH@SiO$_2$/Fe$_3$O$_4$ porous magnetic microspheres were found to be useful for the
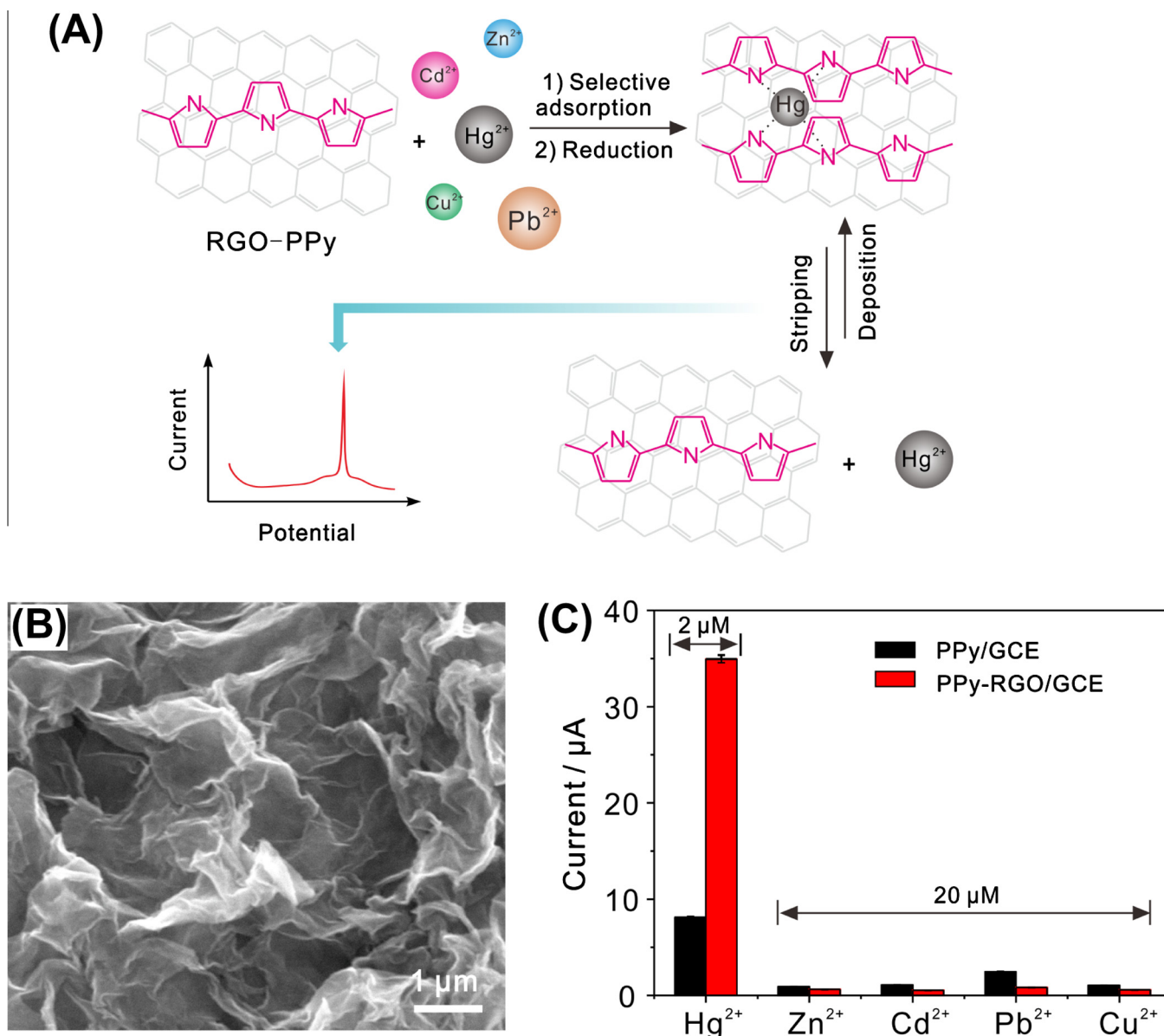
Fig. 3. (A) Hg^{2+} electrochemically-selective detection by the PPy–RGO nanocomposite. (B) Typical SEM image of the PPy-RGO nanocomposite. (C) The voltammetric peak current of Hg^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+} ions, respectively, at the PPy/GCE (black) and PPy–RGO/GCE (red), showing the high selectivity toward Hg(II). (From [72], ©2012 the Royal Society of Chemistry).

simultaneous detection of Hg(II), Cu(II), Pb(II), Cd(II) and Zn(II) [77].

To realize a truly nanoelectrochemical architecture, our group recently designed a three-dimensional (3D) Au micro-/nanopore array containing as receptor, 2-mercaptobenzothiazole (MBT), to improve the performance for voltammetric determination of Hg(II) [78]. The incorporation of MBT molecules as receptor was to eliminate the interference of other metal ions, and the use of an array of layered micro/nano pores was to improve sensitivity. With an active surface area larger than two-dimensional (2D) bowl-like structured microarrays, 3D Au-micro-/nano-pore arrays provide a much higher sensitivity (Fig. 4).

6. The limitations of present work

To date, great achievements have been made in voltammetric determination of Hg(II), with exciting sensitivity and selectivity.

However, the embarrassing question is "How many approaches can be really well applied in complex real samples with long-term stability and how many of them can be transferred to commercial products with good selectivity?"

There is no clear answer. On the one hand, the presence of surface-fouling matter (e.g., surfactants, proteins, and humic acid) in many natural samples provides a challenge for the voltammetric determination of trace Hg(II). The fouling content can adsorb on the electrode and foul it partly or even totally. On the other hand, the interference from other heavy-metal ions, such as the formation of amalgam, is specific and relates to the nature of the stripping measurement. And this problem is still a challenging task in stripping voltammetry detection of Hg(II). Thus, extensive sample preparation is frequently required to eliminate the interferences of organic and inorganic species, and that is an impediment to routine measurement and in-situ monitoring.

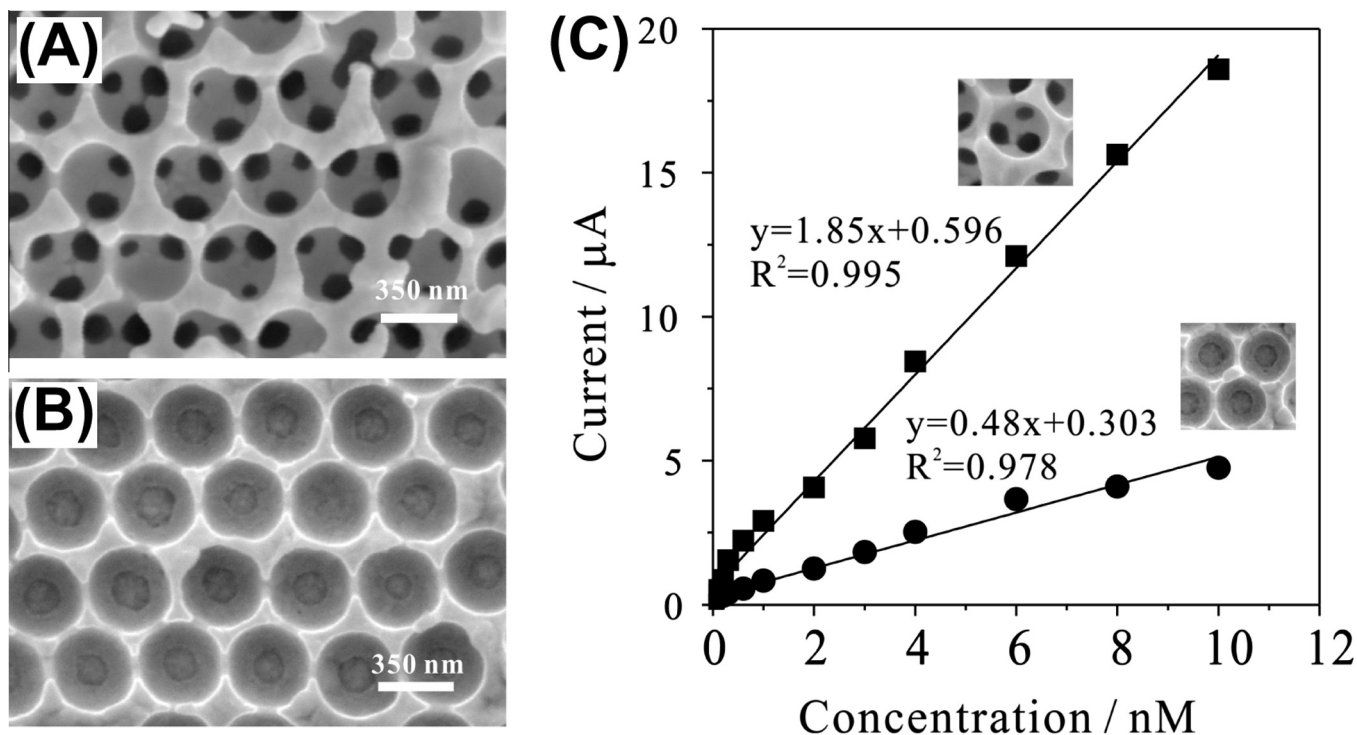Furthermore, how to improve the selectivity remains a challenge, because the excellent results are commonly obtained

Fig. 4. (A) SEM image of 3D micro-/nanopore array, face-on view, showing a representative section of the array. Layered micro- and nano-pores are clearly seen. (B) SEM image of 2D microarray, clearly showing a 2D bowl-like feature. (C) Calibration plots of the SWASV peak current *versus* the concentration of Hg(II) on a 3D micro-/nano-pore array and 2D bow-like microarray electrode. (From [78], ©2010 Elsevier Ltd.).

through an approach suffering from complexity in manufacturing the electrodes and/or the modification process or synthesis of modifiers. With the prerequisites of portability, high sensitivity and good selectivity, the overall approach should be as simple as possible, because the more construction steps an approach comprises, the more difficult it is to perform *in situ* and the greater the risk of contamination in complex real samples.

Finally, the depth and the scope are still inadequate for the present studies. With respect to depth, in-depth theoretical study is not enough, although Compton's group has contributed a lot to this field [45].

Here, we highlight a recent *Analytical Chemistry* editorial by Murray [79], who pointed out that, in many studies, the modifiers are usually claimed to give the modified electrode "special" properties, but most often these properties remain to be proved. Murray [79] considered many of these works "empiricism", which improved results but without scientific understanding.

As another example, we find that, in most works, the supporting electrolytes are always optimized. However, why different supporting electrolytes result in different electrochemical responses remains unclear.

As for scope, although this article focuses on determination of inorganic Hg(II) ions, we found that another main Hg species in nature waters, organic Hg [generally more toxic than inorganic Hg(II) ions], is relatively unexplored by voltammetric determination. And the interference of organic Hg in determination of Hg(II) ions is not evaluated. Also, in many works, the interference of other common heavy-metal ions in natural water has been assessed. However, the interferences of humic matter (e.g., humic acid) are unexplored in spite of most Hg(II) ions in natural water being complexed by dissolved humic matter [80]. And last, the application of microelectrode arrays and nanoelectrodes for Hg(II) analysis has been developing slowly in recent years.

7. Conclusions and outlook on future work

The present review focuses on recent trends in voltammetric determination of Hg(II). There have emerged a great many inspiring, promising approaches in the past five years, and voltammetric determination of Hg(II) by stripping voltammetry will remain an active research field. We should note that all approaches have their own specificity and potential, which in many cases do not cover all the application needs. There is a promising future for chemically-modified electrodes and many areas remain open for exploration. As there is a long way to go towards commercialization, development of a commercially-available electrode for field use is still in progress. Further work continues on searching for simple, sensitive, selective, rapid and cost-effective strategies for detection of trace Hg(II) under real field conditions, and ensuring that the *in-situ* results are comparable with those of laboratory instruments. Also, incorporating sample pre-treatment onto the electrode surface to construct a lab-on-a-chip device would be beneficial for *in-situ* detection.

Nanomaterials have made significant contributions to voltammetric determination of Hg(II). There are still a lot of opportunities in modification with various nanomaterials. Whereas considerable progress has been made with metal NPs, CNTs, graphene and mesoporous silica, there is potential for research with metal-oxide nanomaterials, which is rare at present. Also, constructing the electrode on the nanoscale or with a single NP could yield unique information for better understanding heterogeneous electrode/ solution interfaces. To improve selectivity, a strategy using the highly selective adsorption of new nanomaterials toward Hg(II) would be of great interest and significance.

Finally, we believe that theoretical studies need to be strengthened to guide the experiments, and, in return, the experiments would enrich the theory. Only in this way can this field develop.

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