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Metal and metal oxide nanoparticles in the voltammetric detection of heavy metals: A review

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ABSTRACT

Most heavy metal ions are known to be toxic and carcinogenic when present in high amounts. Thus, rapid and reliable on-site detection of these ions is crucial. Voltammetry is a highly sensitive electrochemical method that has been widely used for heavy metal detection offering the advantages of sensitivity and rapidity. On the other hand, nanoparticles offer the advantages of high surface area and high selectivity. Thus, this review aims to highlight the application of metallic and metallic oxide nanoparticles for the voltammetric detection of heavy metals. The nanoparticles used were either applied solely on the electrode or as modifiers with various materials. In all cases, the synthesized devices showed an enhanced analytical performance, such that the limits of detection were lowered and the sensitivities were increased as compared to voltammetric systems not using nanoparticles. Moreover, the applicability of some of these systems was investigated in real samples.

1. Introduction

Heavy metals are defined as naturally occurring elements having a density or specific gravity greater than 5 g.cm^{-3} and atomic weights between 63.5 and 200.6 g.mol^{-1} [1]. Ions of heavy metals, even at trace levels, have been detected in different sources including food, beverages, soil, plants, natural waters, etc. The use of pesticides and fertilizers, burning of fossil fuels, mining, smelting and leaching from eating utensils and cookware are all sources of heavy metal contamination [2,3]. In addition to human activities, natural sources of heavy metals include: weathering of metal-bearing rocks, volcanic eruptions and forest fires.

Upon their release into the environment, whether through natural or anthropogenic sources, and since they are non-biodegradable, heavy metals accumulate and become toxic when present at high concentrations [4]. They are also known to hinder the developmental activity, yielding capacity and growth of plants. Moreover, heavy metals cause soil pollution and continuous exposure is very harmful to aquatic and terrestrial plants and animals [5]. In addition to their adverse impact on the environment, heavy metals are dangerous to the human health. They enter natural waters and start accumulating in sediments and living organisms, until they reach the final consumers in the food chain, which are human beings [6]. Continued exposure to heavy metals over a prolonged period of time can cause chronic poisoning, growth and developmental abnormalities, nephrotoxicity, encephalopathy, cardiovascular diseases and cancer.

For this reason, for each heavy metal, especially those considered as toxic, several agencies including the World Health Organization (WHO), Environmental Protection Agency (EPA) and Food and Drug Administration (FDA) [7,8] have set guideline values for the allowable intake and exposure of humans to these heavy metals. Some of these limits are summarized in Table 1.

Conventional methods that have been used so far for the detection of heavy metals include Inductively Coupled Plasma- Mass Spectrometry (ICP-MS), Liquid Chromatography (LC) [9], UV–vis Spectrometry [10], Atomic Absorption Spectroscopy (AAS), Atomic Emission Spectrometry (AES) [11], Atomic Fluorescence Spectrometry (AFS) [12], Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS) [13], Capillary Electrophoresis (CE) and Laser-Induced Breakdown Spectroscopy (LIBS) [14]. Even though these techniques are highly sensitive and selective, there still exists several challenges for their use in heavy metal detection [15]. These include high cost, complex operational procedures, long detection time and difficulty in achieving the detection in real environments [14].

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Table 1
Comparison between the allowable levels of some heavy metals in drinking water following the EPA, WHO and EU guidelines.

Heavy metal	EPA Guideline value in drinkable water (μg/L)	WHO Guideline value in drinkable water (μg/L)	EU Guideline value in foodstuff (μg/Kg)
Antimony	20	5	40
Arsenic	10	10	2
Cadmium	3	3	50
Chromium	50	50	250
Copper	2000	2000	36
Lead	10	10	20
Mercury	6	1	1.6
Nickel	70	20	n/a

On the other hand, electrochemical methods are gaining wide recognition in heavy metal detection. These methods offer the same sensitivity with a lower cost, less complex operational procedures and fast on-site detection. Different electrochemical platforms have been developed for heavy metal detection. Specifically, nanomaterials have brought several advantages in this area due to their unique electronic, chemical and mechanical properties. Accordingly, different electrochemical sensors using nanoparticles have been constructed for the detection of heavy metals [16,17].

To the best of our knowledge, recent reviews focus on the detection of heavy metals using either a specific technique, or a specific type of nanoparticles [15,17]. This review mainly discusses the use of voltammetry in the past fifteen years for heavy metal detection that can be applied to water samples using metal or metal oxide nanoparticles.

2. Voltammetric techniques

Among the different known electrochemical methods, voltammetry is the most used in the detection of heavy metal ions. Voltammetry in general describes all electrochemical systems which are based on potential-dependent current measurements. A three-electrode electrochemical set-up typically consists of a working electrode, a counter electrode and a reference electrode. The potential is applied between the working and the reference electrodes, while the current is measured between the working and the counter electrodes. Upon varying the method of potential change, one ends up with different techniques. Linear sweep voltammetry (LSV) is the simplest technique such that the potential is swept linearly with time [15]. Cyclic voltammetry (CV) consists of linearly scanning the potential in one direction followed by reversing the potential of a working electrode [17]. In other words, a single or multiple triangular potential waveform [18] are involved.

The use of a pulse of voltage signal is the main concept behind pulsed voltammetry. By varying the shape and amplitude of the pulses, different types of pulsed voltammetry exist [17]. Differential pulse voltammetry (DPV) uses fixed magnitude pulses superimposed on a linear potential ramp [18]. Square wave voltammetry (SWV) is when a waveform of a symmetrical square wave is superimposed on a base staircase potential and applied to the working electrode [18].

Stripping voltammetry, and more specifically, anodic stripping voltammetry (ASV) is based on a two-step process. The first step is a pre-concentration or electrodeposition of the heavy metal at the electrode surface through the reduction of the metal ions. The second step is the stripping step, where the metal is oxidized back to give the ion. Having taken the 2 steps into consideration, several factors are known to influence the analysis, such as electrode material, deposition potential, deposition time [19] … When the pre-concentration step is non-electrolytic, the analyte accumulates at the surface of the electrode by physical adsorption, a different method is obtained: Adsorptive Stripping Voltammetry (AdSV) [20]. Fig. 1 summarizes how the potential is varied with time for CV, LSV, DPV, SWV and ASV to produce a signal.

A combination of some of these techniques results in increased sensitivities and limits of detection. The combinations include differential pulse anodic stripping voltammetry (DPASV), square wave anodic stripping voltammetry (SWASV) and linear sweep anodic stripping voltammetry (LSASV).

3. Metal nanoparticles

Nanoparticles, specifically metal nanoparticles, present several advantages in the electrochemical sensing field. Due to their small sizes, nanoparticles can increase the surface area of the electrode being used. Moreover, metallic nanoparticles can increase the mass-transport rate and offer a fast electron transfer, both increasing the sensitivity of the used electrodes [16]. In this section, we will present the use of different types of metallic nanoparticles for the detection of the majority of heavy metals.

3.1. Silver nanoparticles

Silver nanoparticles (Ag NPs) are one of the most well-developed nanoparticles because they are relatively inexpensive and they have unique chemical and physical properties that make them useful in different catalytic, optical and chemical applications. Silver nanoparticles have been combined with different materials for the detection of Cd^{2+}, Cr^{6+}, Cu^{2+}, Hg^{2+} and Sb^{3+}. Two different ways have been employed for the synthesis of spherical Ag NPs: reduction and electrodeposition. When the NPs were used along with graphene oxide, reduction of silver nitrate ($AgNO_3$) was employed, either hydrothermally to produce Ag NPs with an average size of 10–20 nm [21] or using hydrogen iodide HI as a reducing agent to yield Ag NPs with an average particle size of 9.7 nm [22]. The resultant nanoparticles in both reports were homogenously distributed on the reduced graphene oxide network. On the other hand, the electrodeposition of silver nanoparticles [23,24] produced larger particles with sizes ranging between 30 and 50 nm.

Most recently, Cheng et al. synthesized reduced graphene oxide/silver nanoparticles composites for the simultaneous detection of several ions. Trace levels of Cu^{2+}, Cd^{2+} and Hg^{2+}, using cyclic voltammetry were detected with detection limits of 10^{-15} M, 10^{-21} M and 10^{-29} M respectively [21]. Although reporting exceptionally low LODs not reported elsewhere, specifically for mercury, this method could detect 1 atom in 166 m^3 of water! The detection mechanism is different than all other papers such that it relies on the area of the entirety of the CV curve instead of using that of a peak. Moreover, the paper lacks important data on the analytical performance such as the linear range, sensitivity and reproducibility. Han et al. also used silver nanoparticles with reduced graphene oxide to detect Hg^{2+} ions by differential square wave anodic stripping voltammetry. The synthesized nanoparticles were spherical and uniformly distributed on the graphene sheet. The signal and analytical performance were compared with and without the nanoparticles, and it was shown that the presence of nanoparticles enhanced the signal significantly (Fig. 2). A linear concentration range was obtained between 0.1 and 1.8 μM, the limit of detection was calculated to be 0.11 μM and the sensitivity was 8 μA/μM. Moreover, no interferences were detected from Cd (II) and Cu (II) [22].

Xing et al. modified a glassy carbon electrode with Nafion and electrodeposited silver nanoparticles on its surface for the direct detection of Cr (VI) using linear sweep voltammetry. A linear range

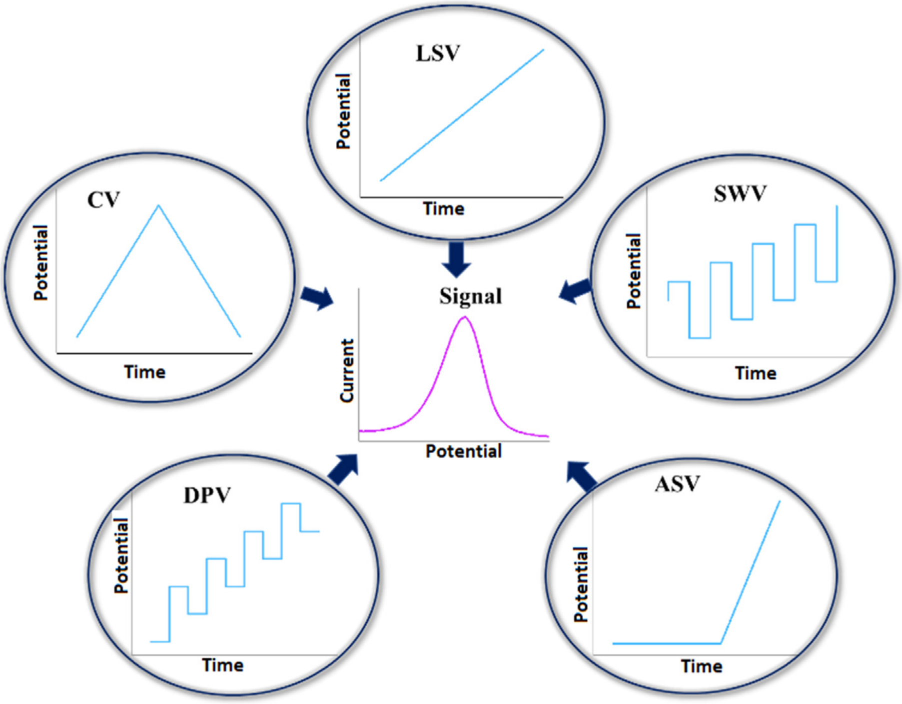

Fig. 1. The graphs of potential vs time for some voltammetry techniques to produce a signal.

was obtained between 2 and 230 ppb and the limit of detection was 0.67 ppb with no interference from different ions. The applicability of this sensor was studied using wastewater from a textile factory and the concentration of Cr (VI) was found to be 6.58 ± 0.04 μg/L with a recovery of 99 ± 5% for spiked samples [23]. Renedo et al. also conducted a study using silver nanoparticles modified screen printed electrodes for the detection of Sb by anodic stripping voltammetry. Differential pulse anodic stripping voltammetry was used and the linear concentration range was between 9.9×10^{-8} M and 9.09×10^{-7} M, whereas the LOD in case of silver nanoparticles was 6.79×10^{-10} M. Three different seawater samples were analyzed, and the amount of Sb (III) in all cases was below the detection limit and hence was not detected [24].

3.2. Gold nanoparticles

The most used nanoparticles for the electrochemical detection of heavy metals are gold nanoparticles (Au NPs). Their properties vary depending on their size, but whatever the size, gold nanoparticles are known to be biocompatible and of low toxicity [25]. Table 2 summarizes the different voltammetric studies done to detect heavy metals using gold nanoparticles. Only a few reports focus on the use of gold nanoparticles alone; nonetheless, different materials have been associated with gold nanoparticles for the detection of heavy metals, and especially mercury and lead.

Similar to Ag NPs, the most common methods utilized for the synthesis of Au NPs are either electrodeposition or reduction. However, different synthesis conditions lead to different shapes and sizes of the gold nanoparticles. The most common shape used in the electrochemical detection of heavy metals is spherical. Most groups have successfully synthesized spherical Au NPs of sizes ranging between 4 and 298 nm. Hassan et al. reported the synthesis and use of different gold nanostructures for the detection of As (III). The synthesis involved the reduction of chloroauric acid using ibuprofen in a basic medium. They investigated the effect of different heating times on the shape of the produced nanoparticles, and the results indicated that with increased heating time, nanoflowers formed along with other structures [26]. Ouyang et al. used a more complex method for the synthesis of nanoflowers. In brief, they modified a glassy carbon electrode with a layer of gold nanoparticles, followed by a layer of 3-mercaptopropyl-trimethoxysilane. Then, the electrode was immersed in a solution containing Au NPs to form a second layer of nanoparticles and pyridinium was attached to the NPs after dipping in 4-pyridineethanethiol hydrochloride solution [27]. Dutta et al. synthesized gold nanostars and spherical gold nanoparticles and compared their performances in the detection of As (III), Hg (II) and Pb (II). The nanostars were prepared by mixing an auric chloride solution with 4-(2-hydroxyethyl)-l-piperazineethanesulfonic acid (HEPES) without stirring or shaking. Boiling the resultant nanostars for 5 min yielded spherical nanoparticles. Using these 2 structures, they modified a screen-printed electrode and optimized some conditions to conclude that the gold nanostar shape improved the detection of arsenic compared to the spherical shape (Fig. 3) [28]. Later on, different studies used the same procedure for the gold nanostars synthesis to detect Cr (II), Cd (II), As (III) and Se (IV) [29,30].

It is worthy to note that the use of gold nanoparticles associated with different sensors is gaining wide recognition. Even though the inhibition of enzymatic activity by heavy metals has been extensively studied, only one study uses enzyme-based biosensors with gold nanoparticles to detect mercury ions. The presence of gold nanoparticles considerably increased the analytical response [31]. Some researchers focus on the use of gold nanoparticles with amino acid-based biosensors. Amino acids and peptides (amino acid chains) have a high affinity towards some heavy metals which can be tuned by altering the peptide sequence [32]. Amino acids are known to bind heavy metal ions through cooperative metal-ligand interactions [33]. The use of gold nanoparticles with these biosensors amplifies the signal, improving the analytical performance [34]. The majority of authors focus on DNA-based biosensors with an emphasis on certain interactions between the DNA bases and

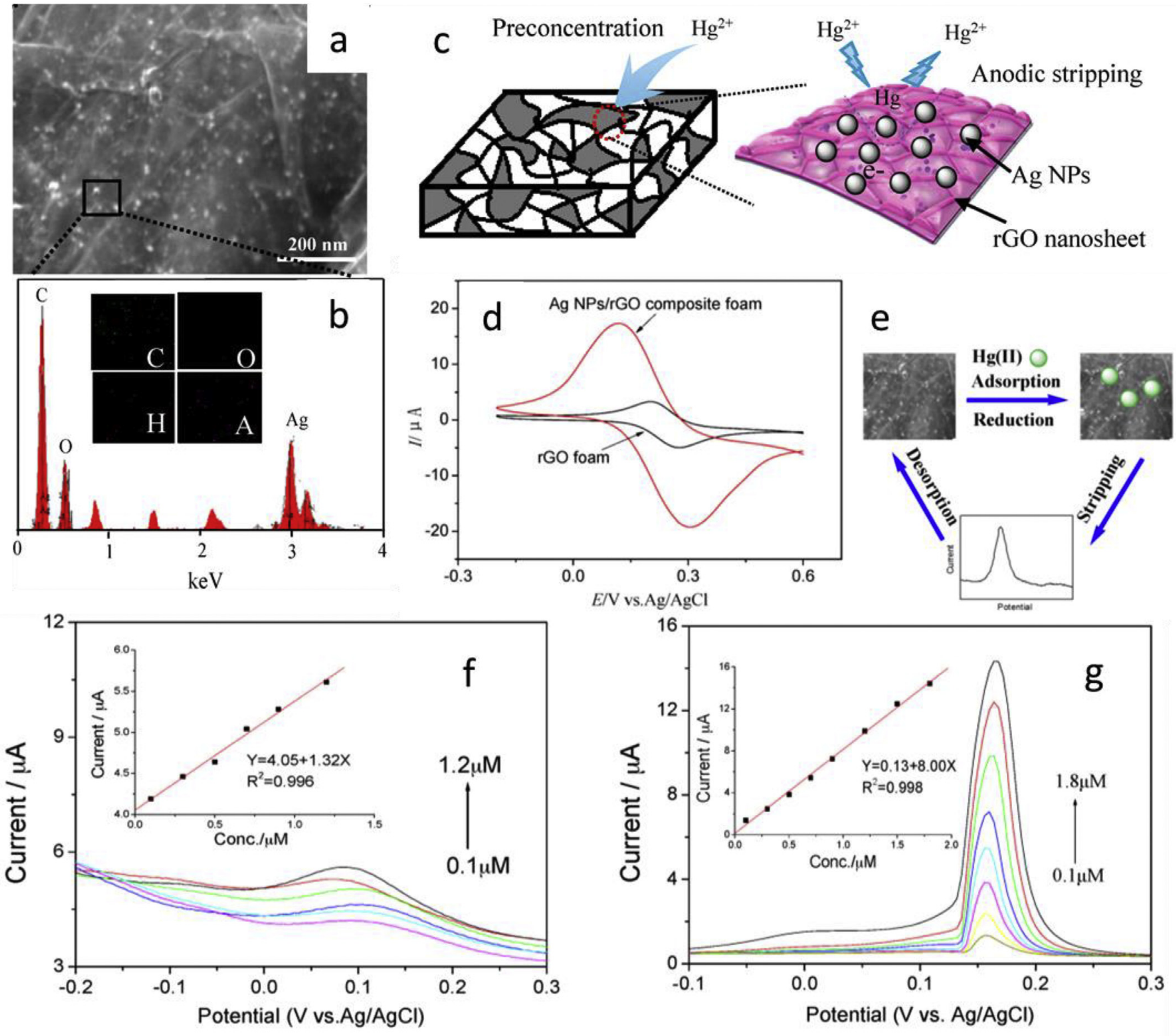

Fig. 2. (a) Scanning electron microscopy (SEM) image and (b) energy dispersive spectroscopy (EDS) spectrum with elemental mapping of Ag NPs/reduced graphene oxide. (c) Schematic diagram of the Ag NPs/reduced graphene oxide structure. (d) Cyclic voltammetry of pure reduced graphene oxide and Ag NPs/reduced graphene oxide. (e) Schematic representation of the electrochemical detection towards Hg (II) ions. (f) and (g) SWASV response of pure reduced graphene oxide and Ag NPs/reduced graphene oxide towards Hg (II) at different concentrations in a 0.1 M NH_3 solution; the insets correspond to the calibration plots, respectively [22].

certain heavy metal ions. Specifically, silver ion and mercury ion are well known to interact with cytosine-cytosine mismatch and thymine-thymine mismatch, respectively, to form stable base pairs [35–39].

From the above table, it can be concluded that the best analytical performance for the detection of As (III) is obtained using gold nanoparticles modified carbon nanotubes [41]. The process of electrode modification and arsenic detection using square wave voltammetry can be achieved within minutes producing a very high sensitivity and low LOD compared to similar studies. Although the authors claim that this sensor can be used for the detection of arsenic in natural waters, to the best of our knowledge, the study has not been conducted. The modification of a glassy carbon electrode with gold nanoparticles, L-cysteine and reduced graphene oxide showed a superior performance in the detection of Cd (II) by square wave voltammetry (Fig. 4). The modified electrode was used to assess the concentrations of cadmium in different water sources (lake, sewage, tap and ground water) and the obtained results were comparable with those of AAS [57]. The same electrode exhibited the highest reported sensitivity for the detection of Pb (II) as well; however, a better LOD was obtained by Zhu et al. [83] using differential pulse voltammetry. The latter team modified a glassy carbon electrode with gold nanoparticles, cysteine, graphene and bismuth film which exhibited a low LOD and good repeatability and reproducibility along with the possible usage in real water samples such as spring water. However, the preparation procedure was too complex compared with other studies. The modification of a GCE with graphene quantum dots and Au NPs is the method of choice for the detection of Cu (II) using anodic stripping voltammetry. Both the LOD and sensitivity are better than those obtained with different modifications, unfortunately the electrode was not tested with real samples [67]. This same electrode showed the highest

Table 2
Comparison between the different studies using gold nanoparticles for heavy metal detection.

HM	Technique	Electrode	LOD (μM)	Sensitivity (μA/μM)	Linear range (μM)	Addition to Au NPs	Real sample	Ref
Ag^{+}	DPV	Au	3×10^{-5}	124.6	$10^{-4} - 0.12$	Oligonucleotide sequences		[35]
As^{3+}	SWV	GCE	10^{-3}	71.7			River water	[40]
	SWV	GCE	8.89×10^{-4}	1985		Multiwalled Carbon nanotubes		[41]
	ASV	CμF	67.43	1318	0.067–0.8		Tap, well water	[42]
	SWASV	GNEE	1.78×10^{-4}	0.7492	0–0.2	3-(mercaptopropyl)trimethoxy silane		[43]
	SWASV	SPE	6.53×10^{-3}				River water	[30]
	SWASV	GCE	1.06×10^{-3}	113.9	0.01–0.67			[44]
	SWASV	SPE	0.01		0.03–10.2		Ground water	[28]
	LSV	GCE	0.024		0–1.2			[46]
	LSV	GCE	5.34×10^{-3}	32.8		Multiwalled Carbon nanotubes		[41]
	LSV	GCE	2×10^{-3}	14.2			River water	[40]
	LSASV	GCME	0.01		0.01–10.01	Carbon nanotube		[47]
	LSASV	GCE	3.7×10^{-3}	940	0.005–3	Pt NPs	Tap, spring, river water	[48]
	LSASV	GCE	2.9×10^{-3}	230	0.005–1	Porous graphitic carbon nitride	Tap, spring, river water	[49]
	DPV	GCE	0.2	0.8075	4–40	Crystal violet	Drinking water	[50]
	DPSV	SPCE	8.01×10^{-4}		Up to 53.4	Poly (L-lactide)	Ground, surface water	[51]
	CV	Basal-plane pyrolytic graphite	0.8			Glassy carbon microsphere		[52]
	CV	SPCE	2.4×10^{-4}		$1.3 \times 10^{-3} - 24$	Ibuprofen	Drinking, tap, river, ground water	[26]
Cd^{2+}	DPV	SPCE	0.023	26.19	0.07–4448		River, tap water	[53]
	DPV	GCE	0.022		0.05–300	Reduced graphene oxide, Tetraphenylporphyrin	Lake water	[54]
	DPASV	GCE	0.3	3.24	0–1.4			[55]
	SWV	GCE	8.89×10^{-4}		$4.4 \times 10^{-3} - 0.35$	Graphene, cysteine	Spring water	[34]
	SWASV	GCE	0.1	1.88	0.1–1	Carbon nanofibers		[56]
	SWASV	SPE	0.015				River water	[30]
	SWASV	GCE	6×10^{-5}	2.2×10^{3}	$10^{-3} - 0.01$	L-cysteine, reduced graphene oxide	Lake, tap, sewage, ground water	[57]
Cr^{3+}	SWV	GCE			100–400			[58]
Cr^{6+}	SWV	SPE	0.096		0.19–96		River water	[59]
	SWV	GCE	1.92×10^{-4}	5.98	$2.5 \times 10^{-3} - 0.86$		Sewage, tap water	[60]
	SWCSV	GCE	5.58×10^{-5}		$1.9 \times 10^{-4} - 23$	3-mercaptopropyl-trimethoxysilane		[27]
	AdSV	Graphene	0.02	1.94×10^{-4}	0.48–5.77	Reduced graphene oxide, 4-pyridylethylmercaptan hydrochloride	Waste water	[71]
	DPV	SPCE	0.4	2.01×10^{-8}	0.4–30		Tap, sea water	[72]
	CV	Indium tin oxide	2	0.3025	5–100		Tap, sea, stream water	[73]
	LSV	SPE	0.067		0.19–1442		Ground water	[29]
	LSV	SPCE	0.1	0.0572	0.38–3.8		River water	[74]
Cu^{2+}	DPV	SPCE	0.126		0.79–157	L-cysteine		[32]
	DPASV	GCE	0.3	4.18	0–1.4			[55]
	ASV	GCE	5×10^{-5}	3690	Logarithmic	Graphene quantum dots, cysteamine		[67]
	SWV	Au	10^{-7}	0.29435×10^{-6}	$10^{-4} - 10$	4-aminothiophenol, DNAzymes	Lake, tap water	[36]
	SWASV	SPE	0.025	4.368	0.31–4.72			[69]
	SWASV	GNEE	2.22×10^{-3}		$6.67 \times 10^{-3} - 0.2$	3-(mercaptopropyl)trimethoxy silane		[43]
	SWASV	GCE	0.1	4.41	0.1–1	Carbon nanofibers		[56]
Hg^{2+}	SWASV	GNEE	9.97×10^{-5}	2.006	0–0.07	3-(mercaptopropyl)trimethoxy silane		[43]
	SWASV	SPE	2.49×10^{-3}		$7.5 \times 10^{-3} - 2.69$		Ground water	[28]

(*continued on next page*)

Table 2 (*continued*)

HM	Technique	Electrode	LOD (μM)	Sensitivity (μA/μM)	Linear range (μM)	Addition to Au NPs	Real sample	Ref
	SWASV	GCE	2.99×10^{-5}	708.3 7.37	$3.99 \times 10^{-5} - 2.49 \times 10^{-4}$ $4.98 \times 10^{-4} - 0.3$	Chitosan graphene	River water	[75]
	SWASV	SPCE	3.99×10^{-3}		$2.49 \times 10^{-5} - 10^{-4}$		Rain, river water	[76]
	SWASV	GCE	4.2×10^{-4}	1370	$0.64 \times 10^{-3} - 4 \times 10^{-3}$			[77]
	SWASV	Pencil graphite	4×10^{-15}		$10^{-13} - 10^{-4}$	DNA, L-methionine	Sea water, fish	[78]
	SWV	Au	5×10^{-4}		0.09–1.99	MSO, linker probes		[79]
	SWV	Carbon ionic liquid	2.3×10^{-3}		0.01–20	Thiolated amino acids	Waste, tap water	[33]
	SWV	SPE	9.97×10^{-4}	47.54	$2.5 \times 10^{-3} - 0.25$	Carbon nanotubes	Tap, river water	[70]
	DPV	GCE	3×10^{-5}	35.88	$10^{-4} - 0.02$	Multi-walled C nanotubes, DNA	Tap, lake water	[38]
	DPV	GCE	7.48×10^{-6}	1603.6	$4.98 \times 10^{-5} - 4.98 \times 10^{-3}$	Reduced graphene oxide, thymine-1-acetic acid, cysteamine	Tap water	[61]
	DPV	Au	5×10^{-4}		$10^{-3} - 0.1$	DNA, methylene blue	Tap, river water	[37]
	DPV	Indium tin oxide	7.8×10^{-4}		$5 \times 10^{-3} - 0.11$	Graphene oxide, 5-methyl-2-thiouracil	Tap, lake, bottled water	[62]
	DPV	Au	7.38×10^{-6}	333	$5 \times 10^{-5} - 2.5 \times 10^{-3}$	Thiolated probe DNA	Tap water	[39]
	DPASV	GCE	8×10^{-5}	749	$4 \times 10^{-4} - 0.096$	Single walled C nanotubes, poly (2-mercaptobenzothiazole)	River, tap water	[64]
	DPASV	GCE	0.3	3.39	0–1.4			[55]
	DPASV	GCE	10^{-4}	0.09	$5 \times 10^{-4} - 1.25$	Carbon nanotubes		[80]
	DPASV	Indium tin oxide	1.49×10^{-4}		$4.98 \times 10^{-4} - 0.05$		Tap, lake water, milk, soil	[65]
	ASV	GCE	0.16		0.79–3.15		River water	[75]
	ASV	GCE	7.48×10^{-7}		Up to 0.25		Drinking water	[66]
	ASV	GCE	2×10^{-5}	2470	$2 \times 10^{-5} - 0.1$	Graphene quantum dots, cysteamine		[67]
	CV	Au	0.01			MSO, ss-DNA		[68]
Pb^{2+}	SWASV	GCE	4×10^{-5}	3.2×10^{3}	$10^{-3} - 0.01$	L-cysteine, reduced graphene oxide	Lake, tap, sewage, ground water	[57]
	SWASV	SPE	0.02		0.06–1.56		Ground water	[28]
	SWASV	SPE	0.0106	31.91	0.096–0.96			[69]
	SWASV	GCE	0.1	19.08	0.1–1	Carbon nanofibers		[56]
	SWV	SPE	4.34×10^{-4}	17.612	0.01–1.2		Tap, river water	[70]
	SWV	GCE	2.4×10^{-4}		$2.41 \times 10^{-3} - 0.19$	Graphene, cysteine	Spring water	[34]
	SWV	GCE	800	455.83	0.01–0.15	Graphene oxide	Tap water	[81]
	CV	Au	2.8×10^{-5}			DNA		[31]
	DPASV	GCE	0.3	17.63	0–1.4			[55]
	DPASV	CGE	4.83×10^{-5}	24.86	$2.41 \times 10^{-3} - 0.48$	Graphene oxide, chitosan	River water	[82]
	DPV	Au	10^{-3}		$5 \times 10^{-3} - 0.1$	DNAzymes		[63]
	DPV	GCE	4.3×10^{-9}		$10^{-8} - 5 \times 10^{-5}$	Multi-walled carbon nanotubes, DNA	Tap, river, spring water	[83]
Sb^{3+}	DPASV	SPE	9.44×10^{-4}		$9.9 \times 10^{-2} - 0.909$		Sea water, drugs	[84]
Se^{4+}	SWASV	SPE	0.01				River water	[30]

Abbreviations: Au gold, GCE glassy carbon electrode, CμF carbon ultra-microfiber, GNEE gold nanoelectrode ensembles, SPE screen printed electrode, GCME carbon nanotube flow-through membrane electrode, SPCE screen printed carbon electrode.

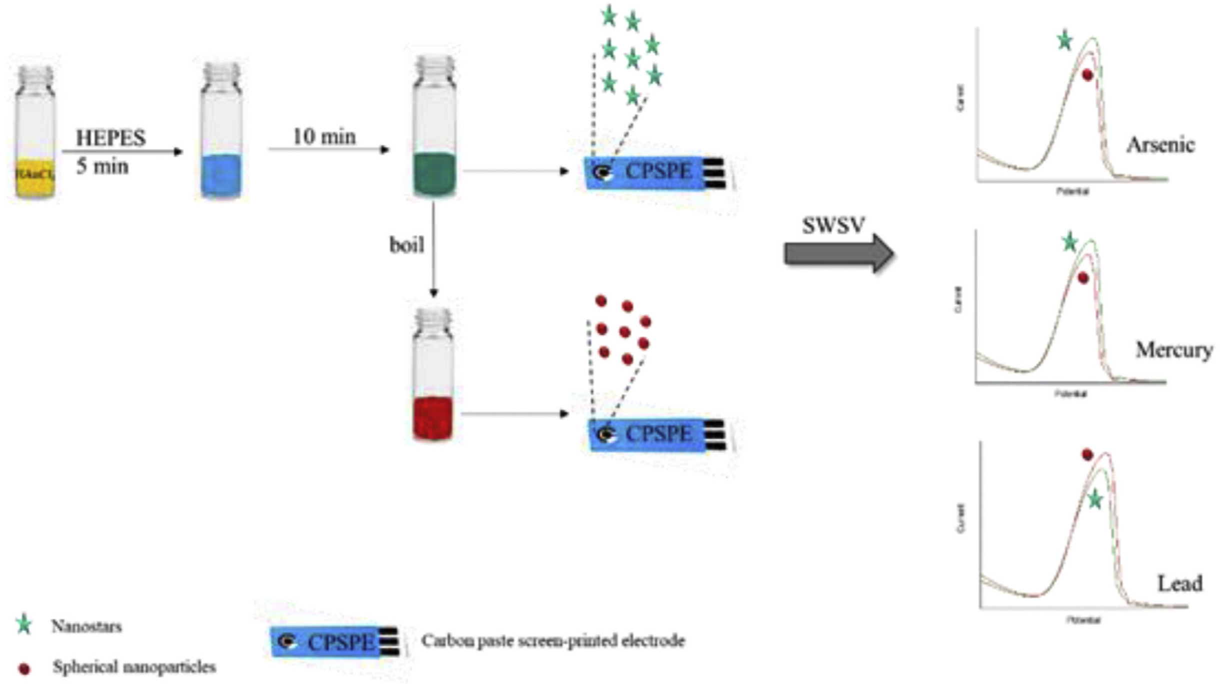

Fig. 3. Modification of carbon paste screen-printed electrodes by Au NPs for the detection of As^{3+}, Hg^{2+} and Pb^{2+} [28].

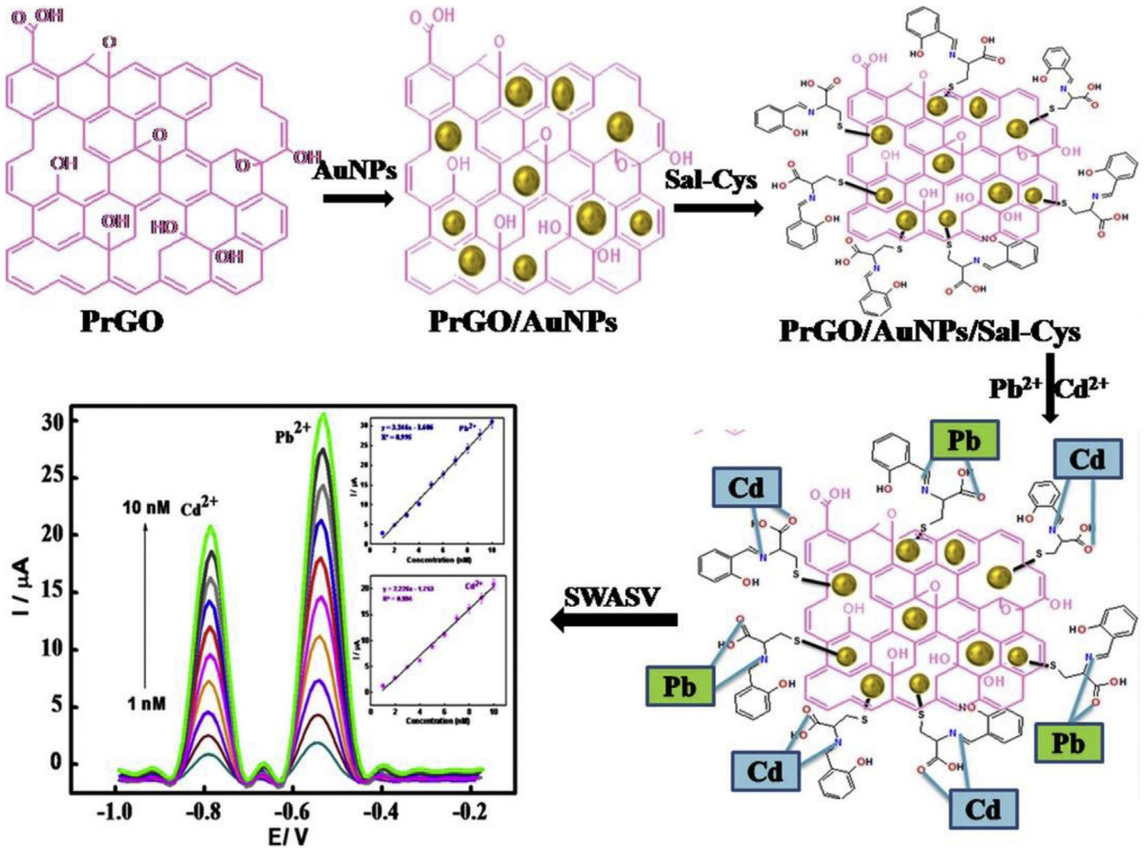

Fig. 4. Schematic diagram of the possible interactions of Cd (II) and Pb (II) with gold nanoparticles, L-cysteine and reduced graphene oxide modified GCE electrode leading to the simultaneous analysis of the heavy metals [57]. Reproduced with permission from Elsevier.

sensitivity for the detection of Hg (II), while an outstanding LOD was obtained by Hasanjani et al. [78] who used DNA and L-methionine along with Au NPs for the modification of a pencil graphite electrode. Interestingly, for the detection of Cr (VI), the sensitivities are either not reported, or are very small, with the best limit of detection obtained by Ouyang et al. [27] who modified a glassy carbon electrode with Au NPs and 3-mercaptopropyltrimethoxysilane. It should be noted that the focus of most of the papers using gold nanoparticles was on the synthesis of the nanoparticles and not on testing the applicability of the sensor in real samples. However, it was implied in some of the studies that their fabricated sensors can be used in real samples.

3.3. *Bismuth nanoparticles*

The use of bismuth in different areas of chemistry (catalysis, organic synthesis, clusters…) has grown in the past decade. In electroanalytical chemistry, bismuth is used as an electrode coating, replacing the mercury electrode, because of its low toxicity and excellent peak resolution.

Lee et al. used bismuth nanopowder modified electrode to detect Zn, Cd and Pb ions using square wave anodic stripping voltammetry. Spherical bismuth was prepared with different particle size distribution in order to investigate its effect on the sensitivity and limit of detection of the studied metals. It was concluded that as the particle size decreases from 406 to 166 nm, both the sensitivity and the limit of detection are improved [85]. In another work, the same group modified a thick-film graphite electrode with bismuth nanopowder for the detection of thallium (Tl). Applying the same procedure, a limit of detection of 0.03 μg/L was obtained with the possibility to overcome any interference from divalent ions through the addition of EDTA [86]. Rico et al. [87] adopted the method of Lee et al. [85], to modify a screen-printed carbon electrode and detect the heavy metals. Optimization of the method included the accumulation configuration; both convective and flow configurations were tested. The limits of detection that were obtained at the flow cell for Zn (II), Cd (II) and Pb (II) were better than those at the convective cell. Those limits were 2.6, 1.3 and 0.9 ng/mL, respectively. Moreover, the reproducibility and sensitivity of the method were good after analyzing a certified reference sample and tap water, but further tests showed that high concentrations of Cu (II) interfered with the results. Saturno et al. modified a glassy carbon electrode with micro-nanoparticles/bismuth film for the determination of cadmium and lead by differential pulse voltammetry. The shape and size of the nanoparticles were irregular, but they still obtained LODs of 11 μg/L for Cd (II) and 18 μg/L for Pb (II) with the response being highly reproducible [88]. Sahoo et al. modified a carbon paste electrode with graphene oxide and bismuth nanoparticles of diameter between 40 and 100 nm for the determination of zinc, cadmium, lead and copper ions using differential pulse anodic stripping voltammetry. A linear concentration range was obtained from 20 to 120 μg/L with limits of detection of 2.8, 0.55, 17 and 26 μg/L for Cd^{2+}, Pb^{2+}, Zn^{2+} and Cu^{2+}, respectively. The performance of the electrode was tested in two different water samples, ground and lake water, and the concentrations of the divalent metals were determined [89]. The obtained LODs were comparable in the different studies for lead and cadmium ions. However, the problem of Cu (II) interference was faced in more than one study.

3.4. *Platinum nanoparticles*

Platinum metal has received a lot of attention in the catalysis industry. Platinum nanoparticles (Pt NPs) have also found a lot of applications in electrochemical analyses due to their stability and conductivity [90]. Hrapovic et al. electrodeposited spherical platinum nanoparticles on a glassy carbon electrode and on a boron doped diamond electrode for the detection of Arsenite (As (III)). The electrodeposition resulted in a non-homogenous and non-uniform distribution of the Pt NPs. Using linear sweep voltammetry, the boron-doped electrode was proven to have a superior performance with a limit of detection of 0.5 ppb without interference from copper (II) ions. Moreover, the analysis of drinking water and river water from Montreal confirmed that As (III) concentrations can be determined without any interference [91]. Spherical platinum nanoparticles of diameters between 105 and 180 nm were also electrodeposited on a glassy carbon electrode by Dai et al. for the detection of Arsenic (III) ions. Cyclic voltammetry was applied and the measured limit of detection was 35 ppb. The performance of this electrode was compared using different techniques (square wave voltammetry and differential pulse voltammetry) all giving the same results. Moreover, possible interfering ions were investigated and the results still showed a clear peak for arsenic [92]. Both studies rely on the oxidation of As (III) to As (V) electrocatalyzed by Pt on a BDD electrode. Dai et al. obtained a LOD that is higher than recommended guidelines for water. Moreover, even though Hrapovic et al. obtained a lower LOD, the electrodeposited Pt NPs were not uniform in size.

3.5. *Other metal nanoparticles*

Owing to the advantages of nanoparticles in the modification of electrodes in electrochemical analysis, different metal nanoparticles have been used for the electrochemical detection of cadmium, copper, mercury and lead.

Two groups have reported the use of palladium nanoparticles (Pd NPs) for the detection of heavy metals. Both groups synthesized porous activated carbon (PAC), followed by the decoration of PAC with palladium nanoparticles via a one-step thermal reduction method (with slightly different conditions). Spherical 20–30 nm Pd NPs were used by Zhang et al. for the simultaneous and individual determination of Cd^{2+}, Pb^{2+} and Cu^{2+} by applying square wave anodic stripping voltammetry (Fig. 5). The obtained limits of detection for individual determinations were 13.33, 6.6 and 11.92 nM for Cd^{2+}, Pb^{2+} and Cu^{2+}, while for simultaneous determinations the values were 20.9, 9.19 and 14.78 nM, respectively. The applicability of the sensor was successfully tested in practical water, without specifying what this water is [93]. Veerakumar et al. were able to obtain smaller crystals with an average size of 4–5 nm. They used differential pulse voltammetry for the detection of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}. Results showed superior performance for both individual and simultaneous detections. For simultaneous detection of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}, a linear response in the ion concentration ranges of 0.5–5.5, 0.5–8.9, 0.5–5.0 and 0.24–7.5 μM, with sensitivities of 66.7, 53.8, 41.1 and 50.3 $\mu A\ \mu M^{-1}.cm^{-2}$, and detection limits of 41, 50, 66 and 54 nM, respectively, were observed [94].

Lee et al. have used tin nanoparticles (Sn NPs) with reduced graphene oxide on glassy carbon electrode for the determination of Cd^{2+}, Pb^{2+} and Cu^{2+}. The Sn NPs of 50 nm diameter were synthesized using the electrochemical reduction of Sn^{2+} with graphene oxide solution. Individual analysis of metal ions using square wave anodic stripping voltammetry showed a high stability and detection limits of 0.63 nM, 0.60 nM and 0.52 nM, respectively. However, simultaneous analysis of the heavy metal increased the detection limits to 7.56 nM, 6.77 nM and 5.62 nM, respectively due to the possible formation of intermetallic compounds. The feasibility of the sensor was tested in tap water samples with and without spiking. No peaks were observed before spiking, while recoveries ranged between 97 and 102% after spiking [95].

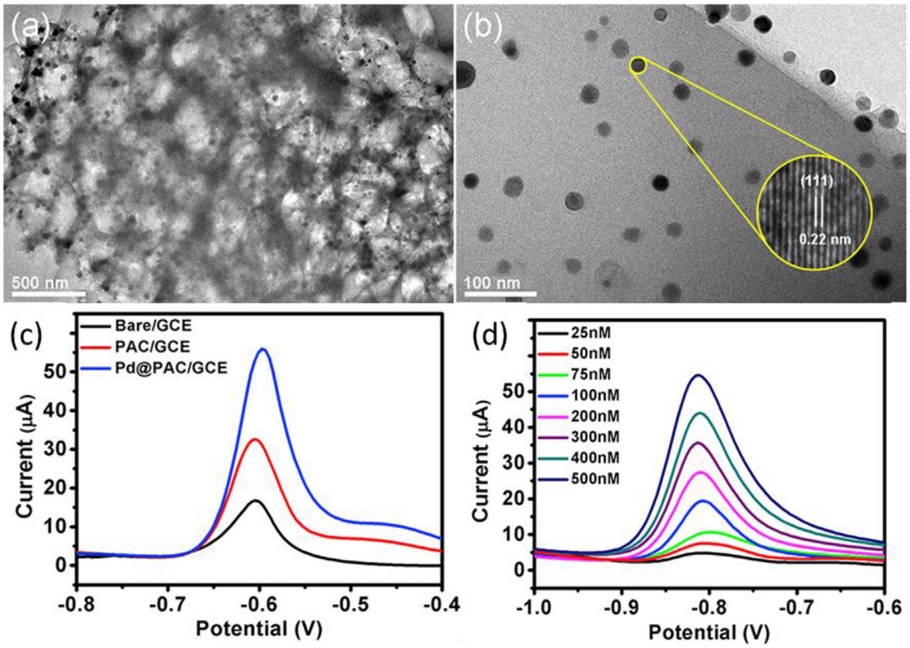

Fig. 5. (a) and (b) TEM and HR-TEM images of Pd@Pac. (c) SWASV curves for 500 nM each of Cd2+, Pb2+ and Cu2+ on the bare, PAC-modified and Pd@PAC-modified GCEs in 0.1 M acetate buffer solution (pH 4.8). Conditions: deposition potential: 2.1 V; deposition time: 210 s; room temperature; amplitude: 50 mV; increment potential: 4 mV; and frequency: 15 Hz. (d) SWASV curves of the Pd@PAC/GCE for the individual analysis of Cd^{2+} [93]. Reproduced with permission from Elsevier.

Toghill et al. modified a BDD electrode with Sb nanoparticles for the detection of Cd^{2+} and Pb^{2+} using linear sweep anodic stripping voltammetry. The nanoparticles were electrochemically deposited on the electrode, with an average size of 108 ± 70 nm, but due to the toxicity of Sb, the team tried to use the smallest possible concentration of antimony. Based on this study, the addition of Sb nanoparticles didn't improve the individual detection of each analyte as compared to the bare BDD. On the other hand, simultaneous detection of cadmium and lead was improved and Pb did not inhibit Cd from nucleating on the electrode surface like previous works [96].

4. Metal oxide nanoparticles

Metal oxide nanoparticles are being extensively studied in electrochemical detection these past few years. They have been synthesized using different methods to obtain different sizes, stability, and morphology. These differences allow them to exhibit various electrical and photochemical properties resulting in different applications [97]. Various oxides of metals, mainly transition metals, have been used in the modification of electrodes for the detection of different analytes including heavy metals. Even though these oxides have been synthesized using almost all transition metals, only a few were used for the detection of heavy metals.

4.1. Iron oxide nanoparticles

The most common metal oxide used for the detection of heavy metals is iron oxide in different forms ($MnFe_2O_4$, Fe_2O_3 and Fe_3O_4). While iron in the first 2 species is found as Fe^{3+}, both Fe^{2+} and Fe^{3+} are present in Fe_3O_4, which permits an electron hopping process between the 2 ions, and thus increasing the electrical conductivity compared to $MnFe_2O_4$ and Fe_2O_3.

Lee et al. were the first group to report the use of iron oxide in the form of Fe_2O_3. Briefly, graphene oxide was prepared and reduced, after which Fe_2O_3/graphene composites were prepared using a solvent-less method by mixing iron (III) acetylacetonate and oleic acid with the prepared graphene. The synthesized spherical maghemite nanoparticles had an average size of 30 nm and uniformly decorated the graphene sheets. Prior to be used in the detection of Pb^{2+}, Zn^{2+} and Cd^{2+} in tap water, the nanoparticles with graphene oxide were deposited on a cleaned glassy carbon electrode and dried under infrared heat lamp, and the electrode was modified with bismuth. Differential pulse anodic stripping voltammetry was applied and the analysis showed a linear range of detection between 1 and 100 $\mu g.L^{-1}$ for all the ions, and limits of detection of 0.11 $\mu g.L^{-1}$ for Zn (II), 0.08 $\mu g.L^{-1}$ for Cd (II) and 0.07 $\mu g.L^{-1}$ for Pb (II) [98]. Li et al. later reported the synthesis of 2 different morphologies (nanorods and nanocubes) of Fe_2O_3 for the electroanalysis of Pb (II) by anodic stripping voltammetry. The limit of detection of Pb (II) by nanorods was much smaller (0.0034 μM) than that with nanocubes (0.083 μM). Moreover, Fe_2O_3 nanorods proved to be much more sensitive (109.67 $\mu A.\mu M^{-1}$) compared to nanocubes (17.68 $\mu A.\mu M^{-1}$). The practicability of the proposed sensor was evaluated in drinking water, and good recoveries were observed with a slightly decreased sensitivity for lead that could be the result of interfering ions [99].

On the other hand, Fe_3O_4 is the most common form of iron oxide used to detect heavy metals. Most recently, Fe_3O_4 nanoparticles have been investigated for heavy metal detection. Fe_3O_4 is known for having a high affinity for heavy metal ions, but only a few reports that use iron oxide alone are available. This is due to the fact that iron oxide nanoparticles have the tendency to aggregate and become non-conductive units [100]. Most studies use either functionalized Fe_3O_4 or Fe_3O_4 combined with other materials. Table 3 summarizes the different studies done using Fe_3O_4 to detect heavy metals. Most of the magnetic nanoparticles used in heavy metal detection were spherical or quasi-spherical with sizes ranging between 5.8 nm and 200 nm. Sun el al. synthesized different Fe_3O_4 shapes by varying the ratio of Fe^{2+} to Fe^{3+} ions. They used a one-step coprecipitation method with the following

Table 3
Comparison between the different studies using Fe_3O_4 to detect heavy metals.

HM	Technique	Electrode	LOD (μM)	Sensitivity (μA/μM)	Linear range (μM)	Addition to iron oxide NPs	Real sample	Ref
Pb^{2+}	SWV	GCE	2.41×10^{-4}		0–0.24	DMSA	Urine	[102]
Ag^{+}	SWV	GCE	3.4×10^{-3}		0.01–0.15	Au NPs, DNA	Natural water, orange juice, wine	[103]
Hg^{2+}			1.7×10^{-3}		0.01–0.1			
As^{3+}	SWASV	GCE	1.29×10^{-4}	1015	$1.33 \times 10^{-3} - 0.27$	Au NPs	Natural water	[104]
Pb^{2+}	SWASV	GCE	0.15	10.07	0.5–8	Amine	Waste water	[105]
Pb^{2+}	SWASV	GCE	1.4×10^{-5}	235	$5 \times 10^{-3} - 0.6$	polydopamine	Aqueous effluent	[106]
Cd^{2+}			9.2×10^{-5}	196	0.02–0.59			
Cd^{2+}	SWASV	GCE	0.056	14.82	0–0.8	Reduced graphene oxide		[107]
Pb^{2+}	SWASV	GCE	0.17	13.6	0.4–1.5	Reduced graphene oxide		[101]
Cu^{2+}			0.073	7.4	0.7–1.2			
Cd^{2+}			0.033	2.4	0.8–1.2			
			0.05	10.1	0.5–1.5			
			0.04	4.35	0.4–1.1			
Cd^{2+}	SWASV	CPE	1.78×10^{-3}			Macrocyclic Schiff-base ligand	Carrot, fish, rice, different waters	[115]
Cu^{2+}			0.014					
Hg^{2+}			4.98×10^{-3}					
Pb^{2+}	SWASV	GCE	0.119	14.9	0.3–1.3		River water	[108]
Cd^{2+}			0.154	3.18	0.3–1.3			
Hg^{2+}			0.0839	7.67	1.3–1.8			
Cu^{2+}			0.0765	4.73	0.3–1.7			
Pb^{2+}	SWASV	GCE	0.0422	50.6	1.1–1.3	Chitosan	River water	[109]
Hg^{2+}			0.0957	9.65	0.4–1.1			
$Cu^{2+}Cd^{2+}$			0.0967	4.24	0.3–1.2			
			0.0392	8.11	1.2–1.7			
Cd^{2+}	SWASV	GCE	0.2	12.15	0.4–1.1	Terephthalic acid	River water	[100]
Pb^{2+}			0.04	8.56	0.4–1.1			
Hg^{2+}			0.3	13.81	0.4–1.1			
Cd^{2+}	SWASV	GCE	1.52×10^{-3}	8.4	$4.4 \times 10^{-3} - 0.89$	Glutathione	Natural water	[110]
Pb^{2+}			8.78×10^{-4}	27.37	$2.41 \times 10^{-3} - 0.48$			
Ni^{2+}	LSV	Pt	3.5×10^{-3}		$5 \times 10^{-2} - 1$	Chitosan	Sewage water, urine	[111]
					3–100			
Cr^{6+}	LSV	SPCE	0.01		0.5–10	Au NPs, Sephadex G-150	Lake water	[112]
Ag^{+}	DPV	GCE	0.059		0.117–17.7	Au NPs	Lake, tap, synthesized water	[113]
Cu^{2+}	DPV	GCE	0.5×10^{-3}			Multi-walled carbon nanotubes, poly-3-nitroaniline		[114]

Abbreviations: CPE carbon paste electrode.

molar ratios of Fe^{2+}/Fe^{3+}: 2/5 to obtain spherical nanoparticles, 4/0 to get rod Fe_3O_4 (20−50 nm in width and 200−300 nm in length) and 5/4 to obtain band Fe_3O_4 (80−120 nm in width and 300−400 nm in length) (Fig. 6). Along with reduced graphene oxide, the iron oxide nanoparticles were used for the detection of Pb (II) and it was shown that the sensitivity is best with the band nanoparticles followed by spherical nanoparticles and then rod nanoparticles (the results are shown in decreasing order in Table 3). On the other hand, the limit of detection did not differ much between the three structures. Band NPs were also used for the detection of Cu (II) and Cd (II) [101].

Lead and cadmium are the most studied heavy metal ions with Fe_3O_4 NPs. The lowest LODs and highest sensitivities for both ions were detected by Song et al. who coated the magnetic nanoparticles with polydopamine. Additionally, the proposed method that uses SWASV was applied for the determination of lead in aqueous effluents of a factory. The method proved to be successful and comparable with ICP-AES [106]. Moreover, it is worthy to note that square wave voltammetry and glassy carbon électrodes are the most commonly used when working with Fe_3O_4 NPs.

Recent studies have reported that the addition of another metal to iron oxide to produce spinel ferrites can enhance its electrochemical behavior towards some heavy metals. All the groups relied on a solvothermal method for the synthesis of $MnFe_2O_4$ along with surface modifications when applicable. The ferrite nanoparticles prepared had a spherical morphology with sizes ranging between 200 and 400 nm.

In this regard, one group has done different studies on $MnFe_2O_4$ to detect different heavy metals. Zhou et al. successfully synthesized $MnFe_2O_4$ nanocrystals and used them to modify a gold electrode and detect As (III) using SWASV. A linear response was obtained at As concentrations between 10 and 100 ppb with a limit of detection of 1.95 ppb and a sensitivity of 0.295 μA/ppb. The sensor was successfully applied in tap water for the detection of arsenic in tap water with a recovery of 95.6% [116]. In another attempt to detect As (III), they modified a glassy carbon electrode with $MnFe_2O_4$ and gold nanoparticles. Using SWASV, the electrode showed a sensitivity of 0.315 μA/ppb and a LOD of 3.37 ppb with the sensor also being used to test tap water [117], proving that a similar sensitivity and lower LOD for the detection of As (III) were obtained without modification with gold nanoparticles. Then, the same group modified a glassy carbon electrode with these nanoparticles for the selective determination of Pb^{2+}. Using SWASV, a sensitivity of 19.9 μA.μM^{-1} and LOD of 0.054 μM were obtained under optimized conditions, while the response to Cd^{2+}, Hg^{2+}, $Cu^{2+}$and Zn^{2+} was poor. The modified electrode was successfully used to detect a spiked lead concentration in river water [118].

In a later study, and in attempt to obtain a better analytical performance, Zhou et al. also used $MnFe_2O_4$ and graphene oxide to modify a glassy carbon electrode for the detection of Pb (II), Cd (II), Cu (II) and Hg (II). Using square wave anodic stripping voltammetry, the best electrochemical response was obtained for Pb (II) with a sensitivity of 33.9 mA/mM and a LOD of 0.0883 mM. The sensitivities for Cd (II), Cu (II) and Hg (II) were 13.5 mA/mM, 13 mA/mM and 5.79 mA/mM, respectively. Moreover, the limits of detection were calculated to be 0.778 mM, 0.0997 mM and 1.16 mM, respectively, with a successful application in the analysis of river water [119]. They also tried modifying a glassy carbon electrode with L-cysteine functionalized $MnFe_2O_4$ to detect Pb (II), Hg (II), Cu (II) and Cd (II) by SWASV. The developed sensor was particularly selective towards lead, with sensitivities of 57 μA/μM and 35.3 μA/μM and LODs of 0.0843 μM and 0.0607 μM under individual and simultaneous conditions of detection. The sensor was also successfully used to monitor the concentration of lead in river water [120]. Thus, all attempts to modify $MnFe_2O_4$ nanoparticles to detect different heavy metal ions have showed a higher selectivity and preference for Pb (II). Moreover, although all studies have checked the practicability of the different modified sensors in real water samples,

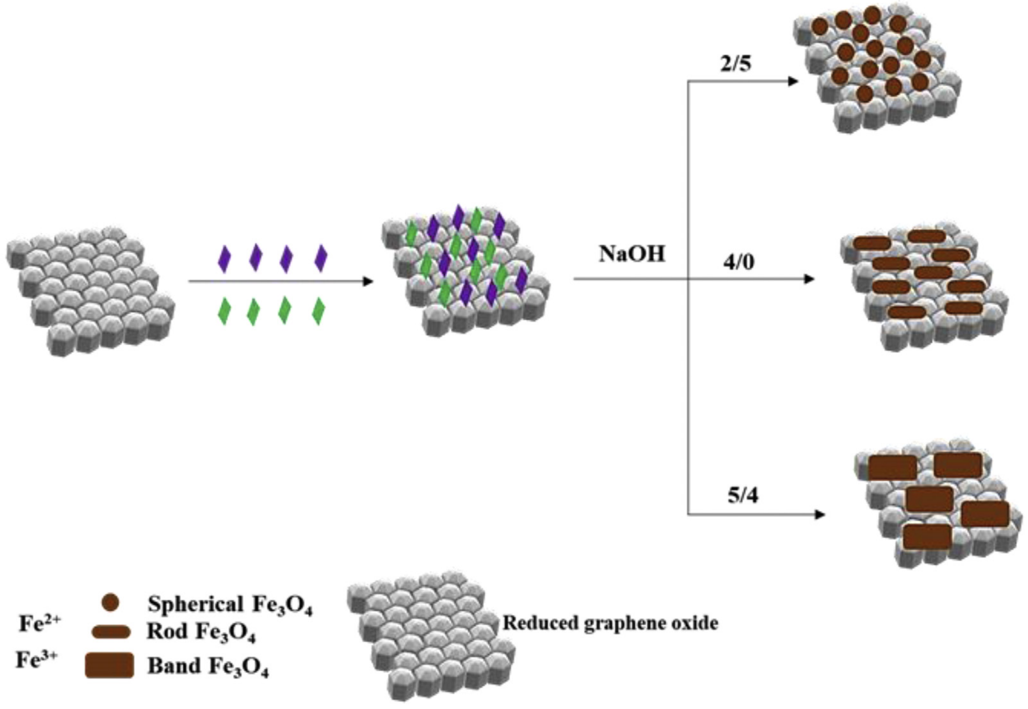

Fig. 6. Synthesis of Fe_3O_4 nanoparticles, nanorods and nanobands done by Sun et al. [101].

more experimentation should be done in this regard by monitoring the ions in water samples other than tap and river water.

4.2. Other metal oxide nanoparticles

Co_3O_4 nanoparticles are one of the most versatile transition metal oxides mainly because of their high reactivity, superior stability and excellent electrocatalytic activity. Salimi et al. electrodeposited cobalt oxide nanoparticles on a glassy carbon electrode in order to detect Arsenic (III) using cyclic voltammetry. The nanoparticles were small in size (100 nm) and uniformly distributed on the surface of the electrode. The results exhibited a detection limit of 0.6 μM and no interferences in presence of other heavy metal ions with a linear range of 10–50 μM. The possibility to use this sensor for the analysis of water samples was tested on drinking water from a village in Kurdistan and a concentration of 2.1 μM of As was found in water and confirmed by atomic absorption spectrometry [121].

On the other hand, titanium oxide nanoparticles have attracted attention due to their biocompatibility, high conductivity, stability and low cost. TiO_2 nanoparticles were used to detect Hg (II) by Zhou et al. Titanium oxide nanoparticles were prepared using sol-gel process. Briefly, tetrabutyl titanate was dissolved in ethanol and acetic acid, after which water was added dropwise with vigorous stirring until a white transparent sol was formed. The sol was transformed into a gel, dried and calcinated to obtain TiO_2 powder. The nanoparticles, along with gold nanoparticles, were used to modify a gold electrode with the help of chitosan as a binder. Characterization showed that TiO_2 nanoparticles had a size range between 5 and 15 nm, with gold nanoparticles on their surface. In a medium buffered at a pH of 5 and using differential pulse anodic stripping voltammetry, the sensor showed a wide linear concentration range of Hg (II) from 5 to 400 nM and a low detection limit of 1 nM with a sensitivity of 3.133 $\mu A.\mu M^{-1}$ and no interference from different ions. Moreover, the sensor was tested for Hg (II) in some water samples, and the recoveries were between 98 and 106% for all samples [122]. Zhang et al. used purchased titanium oxide nanoparticle to modify a gold strip electrode to detect As (III) by linear sweep voltammetry. The linear range of analysis was obtained between 10 μg/L and 80 μg/L with a limit of detection of 10 μg/L and the possibility to use it for arsenic determination in real samples. Moreover, the stability of the electrodes was investigated and 96% of the initial response current was retained after 15 days [123]. Mao et al. incorporated TiO_2 nanoparticles into multiwalled carbon nanotubes and a cationic surfactant to modify a glassy carbon electrode. LSASV was used for the determination of mercury (II) and a linear range of 0.1–100 μM with a limit of detection of 0.025 μM were obtained. The potential applicability of the sensor was evaluated in spiked and non-spiked samples of river and industrial wastewater, and the sensor was able to successfully detect mercury in the wastewater even before spiking [124]. Ramezani et al. constructed an electrochemical sensor using spherical TiO_2 nanoparticles intermixed with graphite powder and 1,2-bis-[o-aminophenyl thio] ethane. Using DPASV, and under optimum conditions, Cd (II) was detected in a linear concentration range of 2.9 nM–4.6 μM with a limit of detection of 2 nM. A spiked concentration of Cd (II) ions in tap water was successfully detected without requiring any treatment of the water [125]. Liu et al. used an Fe_3O_4–TiO_2 core-shell nanoparticles on a glassy carbon electrode for the detection of Pb (II). Using square wave voltammetry (SWV), the limit of detection of the proposed sensor was calculated to be 7.5×10^{-13} M with a linear range of 4×10^{-13} M – 2.5×10^{-8} M. Different concentrations of Pb (II) were evaluated in river and rain water samples with recoveries ranging between 99 and 110% [126]. Each one of these modifications with TiO_2 NPs presents its advantages, from outstanding limit of detection of 7.5×10^{-13} M for Pb (II) [126] to the wide linear range of detection of 2.9 nM–4.6 μM for Cd (II) [125]; nevertheless, more experimentation is required in order to be able to compare between the different methods.

Different forms of manganese oxide nanoparticles have been explored due to properties like low cost, non-toxicity and high activity (mainly in alkali media). Zhang et al. focused on investigating the difference between various MnO_2 structures, including nanoparticles, nanotubes and nanobowls on the mutual interference of Cd^{2+}, Pb^{2+} and Zn^{2+} (Fig. 7). The nanoparticles were prepared by dissolving potassium permanganate in ethanol, washing the product with water and drying it. The nanotubes were prepared by dissolving $MnSO_4.H_2O$ and $KMnO_4$ in water, heating the mixture for 12 h, washing the product with water and drying it. The nanobowls were hydrothermally prepared by dissolving $MnSO_4.H_2O$ and $(NH_4)_2S_2O_8$ in water, heating the mixture for 24 h, washing the product with water and drying it. The group modified a glassy carbon electrode with MnO_2 and square wave anodic stripping voltammetry was applied. The individual response was studied for Cd (II) and Zn (II) and the higher sensitivities were observed with Cd (II) (18.05 μA/μM for the nanoparticles, 12.36 μA/μM for the nanotubes and 18.69 μA/μM for the nanobowls). However, the interference mechanism was not clearly understood and demonstrated. Upon fixing the concentration of Zn (II), the trend in the mutual interference between Cd (II) and Zn (II) was similar on the three morphologies of MnO_2. On the other hand, when fixing the Cd (II) concentration, the interference between Cd (II) and Zn (II) on MnO_2 nanoparticles was different from that on the other structures. Similarly, the interference between Cd (II) and Pb (II) on MnO_2 nanotubes was different from the other morphologies [127]. Fayazi et al. used MnO_2 nanotubes for the detection of Hg (II) using differential pulse voltammetry. A simple chemical precipitation followed by a hydrothermal method were used for the fabrication of halloysite nanotubes – iron oxide – manganese oxide nanocomposite. The electrode displayed a limit of detection of 0.2 $\mu g.L^{-1}$ in a linear range of 0.5–150 $\mu g.L^{-1}$. The proposed sensor was validated for mercury determination in well and aqueduct water where the concentration of Hg (II) before spiking was below the detection limit and the recoveries after spiking were close to 100% [128]. Salimi et al. investigated the use of yet another form of manganese oxide nanoparticles: nanoflakes. A glassy carbon electrode was first modified with chitosan and multiwalled carbon nanotubes followed by the electrodeposition of manganese oxide. Using cyclic voltammetry, Cr (III) was detected in a linear range of 40–360 μM, and the electrode was used for the detection of chromium ions in drinking water samples such that the calculated Cr (III) concentration agreed with that measured by AAS [129]. All these studies were nicely elaborated, but at the same time each one of them still misses some important data on the analytical performance of each electrode.

Wei et al. used tin oxide nanoparticles with reduced graphene oxide for the determination of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} by square wave anodic stripping voltammetry. SnO_2 nanoparticles are known to have a high electric conductivity and chemical sensitivity, along with the ability to adsorb heavy metal ions. The nanoparticles were prepared by a one-step wet chemical method after the preparation of reduced graphene oxide. This step involved mixing graphene oxide with $SnCl_4.5H_2O$ in water. After stirring and centrifuging, the product was heated to improve its crystallinity. The obtained nanoparticles were uniformly distributed on the graphene network, with an average diameter of 4–5 nm. Individual and simultaneous determination of these ions were done, and the limits of detection of the ions were 1.015×10^{-10} M, 1.839×10^{-10} M, 2.269×10^{-10} M and 2.789×10^{-10} M, respectively, with an

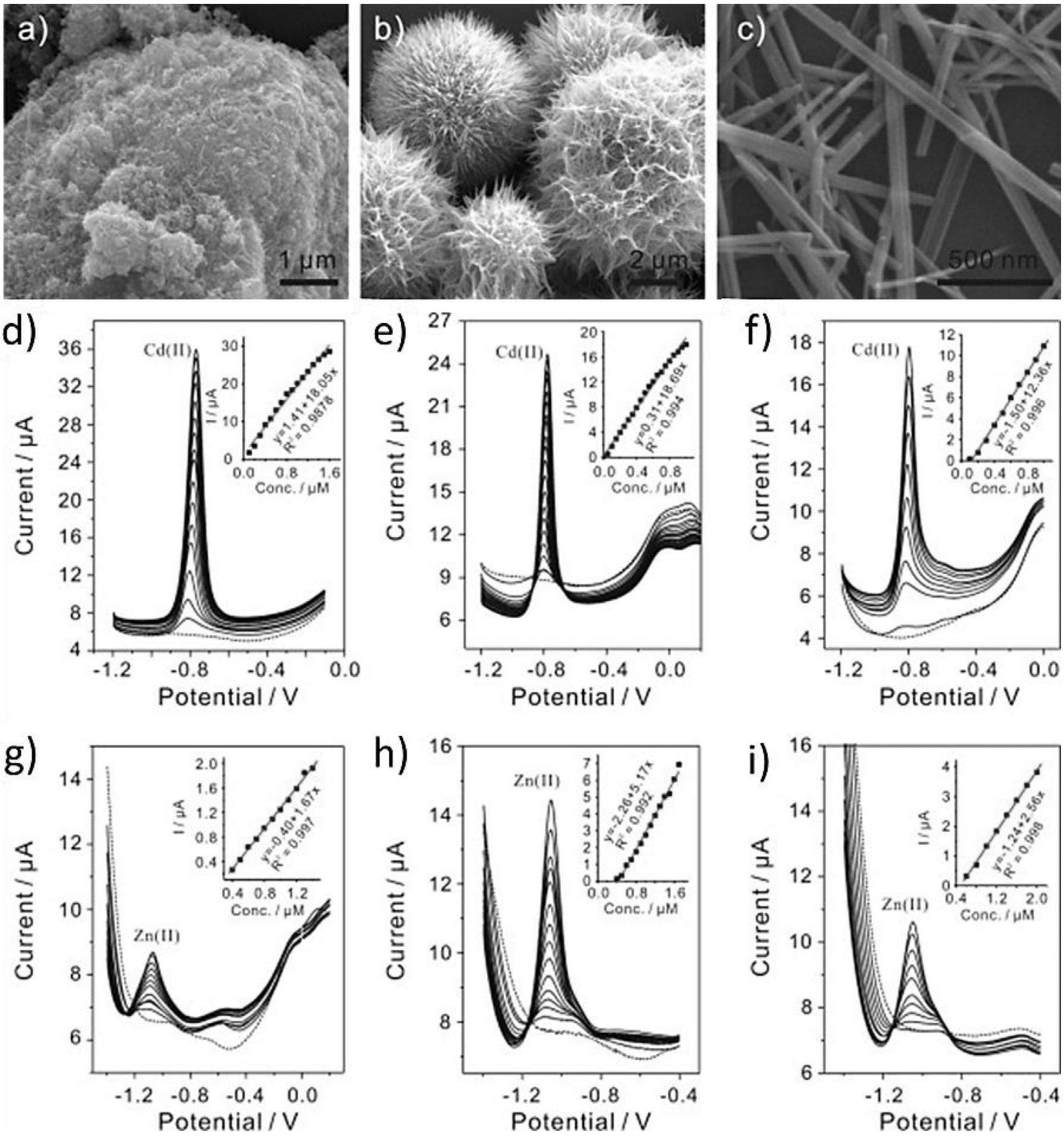

Fig. 7. SEM images of (a) MnO_2 nanoparticles, (b) MnO_2 nanobowls and (c) MnO_2 nanotubes. SWASV responses of MnO_2 (d and g) nanoparticles, (e and h) nanobowls and (f and i) nanotubes modified electrode towards Cd (II) and Zn (II) at different concentrations in 0.1 M NaAc–HAc (pH 5.0), respectively. The insets are plots of current vs concentration of Cd (II) and Zn (II), respectively [127]. Reproduced with permission from Elsevier.

enhanced sensitivity for Cu (II) and Hg (II) when analyzed simultaneously. The authors reported that even though the sensitivities and LODs are not the best, but the electrode can be used without needing regeneration [130]. Yang et al. synthesized an amino-based porous SnO_2 nanowires and modified a glassy carbon electrode for the detection of Cd (II) by means of SWASV. The sensor displayed a sensitivity of 124.03 μA.μM^{-1} and a limit of detection of 0.0054 μM, with an effective determination of cadmium ions in water samples [131]. Cui and coworkers synthesized a 2-amino benzothiazole and 2-amino-4-thiazoleacetic acid derivative graphene enhanced with fluorine, chlorine and iodine on SnO_2 nanoparticles for the detection of Cu (II), Cd (II) and Hg (II). The nanoparticles were nearly spherical and well distributed on the graphene sheet. Using cyclic voltammetry, it was shown that the fluorine-SnO_2 sensor is the best suited for the detection of Cu (II), and thus differential pulse voltammetry was used. A linear range from 2 to 1000 nM and a LOD of 0.3 nM were obtained. The electrode was later used for the simultaneous detection of Cd (II), Cu (II) and Hg (II) such that all the linear ranges were between 20 and 2000 nM and the LODs were 5 nM, 3 nM and 5 nM, respectively, and hence the electrode was successfully evaluated for these ions in lake water, with results in agreement with those of AAS [132].

In addition to the general properties of nanoparticles, CeO_2 has a strong adsorption ability. Li et al. used a glassy carbon electrode modified with cerium oxide (CeO_2) nanoparticles, multi-wall carbon nanotubes, 1-ethyl-3-methylimidazolium tetrafluoroborate

(EMIMBF$_4$) and DNA to detect Pb (II). Differential pulse voltammetry was applied and the linear range for Pb (II) was between 10^{-8} and 10^{-5} M with the detection limit being 5×10^{-9} M hardly exhibiting any interference from five different metal ions with a practical application for the detection of lead in tap water [133].

Yukrid et al. used thermal pyrolysis for the synthesis of ZnO nanorods mixed with graphene solution through colloidal coagulation for the modification of a screen-printed carbon electrode. Anodic stripping voltammetry was used for the concurrent determination of Cd^{2+} and Pb^{2+}. The limits of detection obtained were 0.6 μg.L^{-1} for Cd (II) and 0.8 μg.L^{-1} for Pb (II) in a linear range of 10–200 μg.L^{-1}, respectively. These heavy metal ions were simultaneously determined in wastewater samples, with measurements in accordance with those obtained by ICP-OES [134]. Yuan-Yuan et al. prepared a ZnO nanotubes/reduced graphene modified glassy carbon electrode via electrospinning and thermal decomposition of zinc acetate-polyacrylonitrile-polyvinyl pyrrolidone. SWASV was used for the analysis of Pb (II). A linear concentration range of 2.4×10^{-9}– 4.8×10^{-7} M and the limit of detection was 4.8×10^{-10} M [135].

MgO nanoflowers were also used for the detection of Pb (II) and Cd (II). Their synthesis involved mixing a magnesium precursor with potassium carbonate and heating the mixture to obtain a white precipitate that was later collected and calcinated. These nanoflowers along with Nafion® were used to modify a glassy carbon macroelectrode and SWASV was used under optimized conditions. The results for Pb (II) and Cd (II) detection showed linear ranges between 1 and 30 nM for lead and between 20 and 140 nM for cadmium, sensitivities of 0.706 and 0.077 μA.nM^{-1} and limits of detection of 2.1×10^{-12} M and 8.1×10^{-11} M, respectively. The sensor was successfully tested for Pb (II) in Reservoir water samples from China [136].

5. Summary and perspectives

Electrochemical methods have been extensively used for the detection of heavy metals. However, the use of metal and metal oxide nanoparticles for modifying electrochemical sensors, for the voltammetric detection of heavy metals, proves to be more promising. Taking advantage of the unique properties of nanoparticles along with the advantages of electrochemical detection over conventional detection techniques, the analytical performance of all the reported electrodes was enhanced. The result was a rapid response time, increased sensitivity, very low limits of detection, simplified operational procedures and enhanced reproducibility.

In this review, the emphasis was on electrochemical sensors that could be applied for water samples. However, different water systems exist, from sea water, river water, tap water, drinking water to wastewater. Thus, these matrices are considered complex, some more than others, with the presence of different heavy metals either free or complexed, cations and anions, organic and inorganic materials… Despite the claims that some of the fabricated sensors were tested in these complex matrices, transition to commercialization remains shy. Moreover, most of these sensors require significant improvements, especially in the selectivity and capability of simultaneous analysis, before they can be applied for commercial use. Besides, commercialization also presents the challenges of reusability and mass production, which question the simplicity and cost-effectiveness of some of the sensors. For example, great focus has been given to gold nanoparticles and some excellent electrochemical sensors have been developed for the detection of heavy metals with LODs much lower than those obtained with Fe_3O_4 NPs for instance. Nonetheless, noble metals such as gold and silver are known to be costly, and hence an alternative that presents high selectivity and can detect limits lower than the guidelines such as Fe_3O_4 NPs would be convenient. On the other hand, several materials were used along with the nanoparticles for the modification of the electrodes. However, with the use of all these nanoparticles, a few inconveniences, including toxicity and non-biocompatibility during the synthesis of the modified electrodes, still exist.

Recently, bimetallic nanoparticles are emerging as promising candidates that can overcome the challenges faced by mono-metallic nanoparticles. These materials are the result of combining two different metals, thus offering the advantages of each metal alone, along with new characteristics that arise from blending the two metals. Hence, we expect to see in the near future a major increase in research using bimetallic nanoparticles dedicated for the electrochemical detection of heavy metal ions.

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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