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Electroanalytical overview: The detection of chromium

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ABSTRACT

Chromium exerts serious damage to human beings and to aquatic life and is one of the most common environmental contaminant and possess toxicity when present above threshold limits. In comparison with the traditional quantification methods such as atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry, UV-Vis or high-performance liquid chromatography, electrochemical methods towards monitoring chromium ions have the advantages of being portable, rapid, cost effective, simple, sensitive and selective enough to meet regulatory limits. This review presents the recent progress in the field of electroanalysis using different electrode platforms such as solid or screen-printed electrode (SPE) and various functional materials towards chromium determination. The fabrication strategy and the analytical performance of carbon nanomaterials (such as carbon nanotubes and graphene), metal and metal oxide nanomaterials enabled sensors for electrochemical determination of chromium (III) and chromium (VI) ions are summarized systematically. In addition, method validation and the application of these sensors in real samples for the analysis of chromium ions is discussed and future developments in this domain are provided.

1. Introduction

Chromium (Cr) is a d-block transition metal that can exist in various oxidation states, ranging from (0) up to (+6). Despite this plethora of oxidation states, it is predominantly only the trivalent (+3) and hexavalent (+6) forms of chromium that are stable enough to be routinely found in the environment [1]. The physiological effect on human life that these two species have could not be more different. Chromium (III) is classed as an essential micronutrient for living organisms, with the UK's National Health Service recommending approximately 25 mg per day for adults [2]. Additionally, studies have shown reduced risk of type 2 diabetes for adults taking chromium containing supplements [3]. On the other hand, chromium (VI) is highly toxic [4] and classed as group 1 carcinogen [5]. It has been shown to penetrate cell walls, followed by a reduction to chromium (III), forming reactive oxygen species (ROS) as a by-product. This process exerts an oxidative potential on the cell, leading to inhibition of the metallo-enzyme system [5,6]. As such, in 2003 the World Health Organisation (WHO) set a guideline value for chromium within drinking water at 50 μg/L, which has been upheld as valid in 2020 [7]. The presence of Cr in the environment is attributed to the rapid industrialization of cities and urban areas due to chromium's wide usage in a variety of industrial advancements such as electroplating, tanning of leather, in wood polishing and preservation and use as a pigment in the manufacturing of artificial gems and jewels. The effluent released from these metal plating industries further adds up to the increased content of chromium in biosystems. Due to the potential consequences of ingestion, and varied exposure limits set out by different countries worldwide [8], monitoring of the concentration levels of Cr (VI) present in natural waters is vital for global human health. Due to the critical health implications of Cr (VI), the majority of work found throughout the literature is aimed toward detecting and quantifying the presence of this species.

In this review we focus on the electrochemical approaches for the detection of chromium using various modified electrodes. We highlight detection strategies for Cr(III) and Cr(VI) species from various sample matrices and recent advances in fabrication of diverse modified electrodes towards chromium sensing are discussed.

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2. Detection of chromium

Work on the identification of chromium using diphenylcarbazide can be traced back to the early 1900's where Brandt [9] took the earlier observations from Cazeneuve [10] and used the violet to green colour change as an indicator for the end-point of the bichromate iron titration. This turned out to have significantly greater sensitivity compared to other methods at the time such as the ether-hydrogen peroxide method [11]. Diphenylcarbazide has been utilised for the detection of chromium ions ever since in conjunction with various methodologies, such as spot tests [12] and solid-phase spectrophotometry [13]. The latter is an example of conventional laboratory-based analytical methodologies commonly used for chromium detection, among many other analytes, throughout the world. Numerous analytical techniques considered as fundamental analytical methods are accessible for analysing chromium in variety of samples such as high performance liquid chromatography (HPLC) [14], capillary electrophoresis, capillary chromatography, atomic adsorption spectrophotometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), spectro-fluorimetry, spectrophotometry and chemiluminescence (CL) [15–17].

To enhance detection capabilities, the combination of two or more analytical techniques has been utilised in various sectors aimed at speciation and trace element analysis [18]. These conventional hyphenated techniques are powerful tools in solving various problems encountered in qualitative and quantitative elemental analysis and offer an attractive method to investigate oxidation and reduction processes. In this regard, Spanu et al. proposed a highly selective method by coupling frontal chromatography (FC) with Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) for the fast determination of Cr(VI) ultra-traces in a minute. However, a common disadvantage of ICP-MS methods is the requirement of acidifying the sample prior Cr(VI) measurement [19]. Pechancová et al. proposed the foremost study which focusses on soluble Cr(III), total Cr(VI) and total bound Cr species in living tissues. Herein alkaline EDTA extraction was followed by their separation using ion-exchange high-performance liquid chromatography inductively coupled plasma mass spectrometry (IE-HPLC-ICP-MS) was used towards the determination of total Cr(VI) and soluble Cr(III) species [20]. Monika et al. reported the use of hyphenation for elemental speciation analysis of mixture of metals such as arsenite – As(III), arsenate – As(V) and hexavalent chromium – Cr(VI) in water using high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC/ICP-MS). The method was successfully applied to real water samples with limit of detection (LODs) below the ppb levels [21]. Zou and co-workers developed a method for the non-chromatographic speciation of Cr(VI) and Cr(III) and selective determination of Cr(VI) which involves chemical vapor generation (CVG) in KBH_4-acid system for introduction sample into an inductively coupled plasma mass spectrometer (ICP-MS) for Cr(VI) detection. Non-chromatographic speciation analysis of Cr(III) and Cr(VI) can be achieved *via* the oxidation of Cr(III) to Cr(VI) supported by $KMnO_4$. The CVG of Cr(VI), rather than Cr(III), was reported to be enhanced in the presence of sodium diethylaminodithioformate. Under optimal conditions, the LOD of Cr(VI) was found to be 0.2 ng/mL and their method was successfully applied to the determination of Cr(VI) in real water samples [22]. Saraiva et al. reported a new analytical approach for the real-time speciation analysis of both Cr(III) and Cr(VI) by coupling high-performance liquid chromatography (HPLC) to inductively coupled plasma mass spectrometry (ICP-MS) and double spike species specific-isotope dilution (SS-ID) [23]. The selective extraction was achieved by sequential complexation of Cr(III) with ethylenediamine tetraacetic acid (EDTA) and of Cr(VI) with 1,5-diphenylcarbazide (DPC) in the same analytical run. The quantification limit was 0.013 µg/kg for Cr(III) and 0.049 µg/kg for Cr(VI), respectively. The authors concluded that the developed method is a powerful analytical tool for precise and specific quantification of Cr(III) and Cr(VI) at trace levels. The method was successfully applied to the analysis of meat and dairy products such as baby and semi-skimmed milk and steak beef samples.

Electrochemical techniques have also been used in hyphenated setups as the detection methodology, commonly alongside HPLC. [24] In 1982 Bond [25] reported the simultaneous detection of Cu, Ni, Co, Cr (III) and Cr (VI) using HPLC to separate metal dithiocarbamate complexes, followed by well-defined oxidations to detect below nanogram levels for the target metal ions. However, these methods are time consuming, require sample pretreatment prior to analysis, experienced experimentalists, are highly sophisticated and require expensive equipment maintenance. Environmental monitoring of Cr (VI) is one of the most pressing reasons for the development of suitable analytical techniques. The majority of environmental contamination for industrial applications will be in water sources, without easy access to the laboratory setting required to use these analytical techniques. Hence the drive for the development of rapid, portable, low-cost, simple to use sensing platforms that be performed on-site to obtain immediate results; electrochemical sensors can meet these specific criteria and that is where our focus of this review turns to.

3. Electrochemistry of chromium (III) and (VI)

When designing electrochemical sensing platforms, it is important for researchers to consider the different species that could be present and stable at their specific conditions. This can be obtained by consulting the Pourbaix diagrams specific for that element, in this case chromium as shown in Fig. 1. Pourbaix diagrams plot the potential (E) against the pH of the solution for a certain temperature and indicate the thermodynamically stable phases that are possible in an aqueous electrochemical system. The lines forming boundaries between species represent the 50/50 boundaries, where the two species will be in equilibrium. The electrochemical oxidation of Cr(III) has been studied at platinum [26], metal oxide electrode [27], glassy carbon electrode (GCE), boron-doped diamond electrode (BDDE) and gold electrodes [28]. In this latter study combining GCE, BDDE and gold (Au) electrodes, it was seen that trivalent Cr was electroactive in only very alkaline media (pH > 12) at an Au electrode surface, due to the formation of an oxide film. The oxidation occurs through a multi-step mechanism, where the first step is an electrochemically irreversible electron transfer and is rate determining. The full mechanism was proposed to be:

$$Cr^{(III)}O_2^- + OH^- \xrightarrow{RDS} e^- + H^+ + Cr^{(IV)}O_3^{2-}$$

$$Cr^{(IV)}O_3^{2-} \xrightarrow{\text{fast}} e^- + Cr^{(V)}O_3^-$$

$$Cr^{(V)}O_3^- + OH^- \xrightarrow{\text{fast}} e^- + H^+ + Cr^{(VI)}O_4^{2-}$$

where RDS is “rate-determining step”, the second and third steps represent two fast electron transfer steps or disproportionation steps. Key to the rate determining step is the transfer of a hydroxide anion, highlighted by the fact that at a KOH supporting electrolyte concentration of 1 M compared to 0.1 M, the oxidation potential of Cr(III) shifts by approximately 88 mV toward more negative values.

There are predominantly five Cr (VI) species that exist in equilibrium and impact the electrochemical detection: H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ according to the following equilibrium [31];

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+, k_1 = 1.58 \times 10^{-1} \tag{1}$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+, k_2 = 3.16 \times 10^{-7} \tag{2}$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O, k_3 = 1.01 \times 10^{1} \tag{3}$$

$$HCr_2O_7^- \rightleftharpoons Cr_2O_7^{2-} + H^+, k_4 = 1.17 \tag{4}$$

The speciation of Cr (VI) is dependent upon pH and concentration of the different forms of species, an indication in aqueous media is

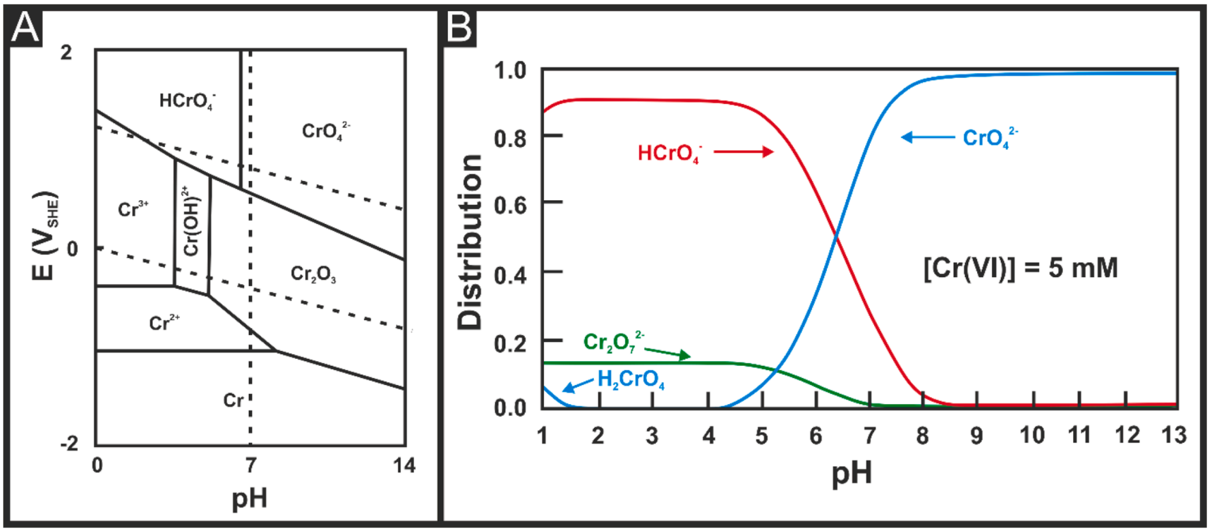

Fig. 1. A) Pourbaix diagram for chromium and $[Cr_{(aq)}]_{tot} = 10^{-6}$ M at 25 °C. Reproduced and adapted with permission from reference [29]. Copyright Elsevier 1997. B) The distribution diagram for Cr (VI) at different pH values, corresponding to a Cr (VI) concentration of 5 mM. Reproduced and adapted with permission from reference [30]. Copyright Elsevier 2013.

presented in Fig. 1B. At alkaline pH values, the major species in solution are chromates, CrO_4^{2-} and as the pH shifts to more acidic range, protonation is expected which results in the formation of $HCrO_4$ $^-$ and H_2CrO_4 species in aqueous solution. It has been reported that at low pH values, $HCrO_4^-$ is the dominant and electrochemically active species whereas H_2CrO_4 and complex species present no significant voltammetry [32]. It is important to note that the concentrations of the specific species in acidic media can vary depending on the concentration of Cr. At low Cr concentrations (< 50 μM), H_2CrO_4 is expected to be present in larger quantities than $Cr_2O_7^{2-}$ [33].

The electrochemical detection of Cr (VI) is commonly achieved through the reduction at the electrode's surface and, as with a vast majority of electrochemical work, this was first noted using polarography. In 1953, McElroy and Laitinen reported a two-step reduction using a mercury dropping electrode with tetrabutylammonium iodide or ammonium iodide as the supporting electrolyte [34]. More recently, Welch et al. [32] have extensively explored the electrochemical reduction of hexavalent chromium at gold, glassy carbon and boron-doped diamond electrodes in acidic media. At a glassy carbon electrode (GCE), an electrochemically irreversible single reduction peak was observed, confirmed through Tafel analysis of approximately 300 mV/decade. The authors rationalised this as the one-step reduction of Cr (VI) to Cr(III) at low concentrations (< 200 μM), with a pre-shoulder occurring above this concentration, thought to be due to the reduction of Cr(VI) to Cr(V). Due to the poor reproducibility using a GCE and the corrosive environment, they recommend not using a GCE for analytical purposes. For the boron-doped diamond (BDD) electrode, a single diffusion-controlled irreversible reduction peak at ~ -0.27 V (*vs.* SCE) shifting to more negative values with scan rate was observed, indicating a highly electrochemically irreversible reaction. They report the significantly improved voltammetric profile for the reduction of Cr(VI) at a solid Au macroelectrode compared to that seen at a GCE or BDD electrode. It was observed that a 1 mM solution of Cr(VI) exhibited a well-defined, diffusion-controlled reduction peak at +0.27 V (*vs.* SCE) that does not change significantly with scan rate, indicating an electrochemically reversible system, with the absence of a corresponding oxidative peak signalling toward a chemically irreversible reaction. Upon analysis in solutions of different pH they suggest the following proton-dependant mechanism for the reduction of the Cr(VI) monochromate species:

$$Cr^{(VI)} + e^- + H^+ \overset{slow}{\rightleftharpoons} Cr^{(V)}$$

followed by:

$$2Cr^{(V)} \overset{fast}{\rightleftharpoons} Cr^{(IV)} + Cr^{(VI)}$$

$$Cr^{(IV)} + Cr^{((VI)} \overset{fast}{\rightleftharpoons} Cr^{(III)} + Cr^{(VI)}$$

or

$$2Cr^{(IV)} \overset{fast}{\rightleftharpoons} Cr^{(III)}Cr^{(V)}$$

where the monochromate species undergoes a one-electron reduction, one-proton reaction, followed by disproportionation. At high concentrations of H^+, disproportionation from Cr(V) to Cr(III) can occur rapidly, whilst in dilute solutions further direct electrochemical reduction is most likely observed. Compton and co-workers used this understanding of the two species to explore the basis of Cr(III) and Cr(VI) electroanalytical sensing in this, and future work. Examples of how they and other groups have achieved this is where our attention turns next.

4. Electroanalytical detection of chromium (III) and (VI)

Table 1 chronologically summarizes the various accomplishments directed toward the sensing of chromium III and VI; consequently, below we explore this history, current electroanalytical approaches and offer insights into possible future trends in the field.

The first report of polarography for the determination of chromium was in 1954 of the insoluble residue remaining from dissolving calcium metal in hydrochloric acid, with a detection limit of 0.25 μg/mL [195, 35]. In 1975, differential pulse polarography and a hanging mercury drop electrode (HDME) were used to determine the concentration of Cr (VI) in natural water by buffering the water to a pH of 7 using ammonium acetate and ethylenediamine [36]. This achieved detection in the range of 0.035 – 2.0 μg/mL, a LOD of 0.01 μg/mL and showed no interference from the presence of Cu (III) or Fe (III). As can be seen from Table 1, this was the beginning of a plethora of publications using mercury electrodes for the detection of Cr in different mediums, from specific natural waters [65] to plants [49,50,57], coolant [44], concrete [46,52] and wine [67]. Most of these works then deviated away from

Table 1
A comprehensive summary of the electroanalytical methods reported in the literature for the detection of Cr (III) and (VI); highlighting the electrode used alongside any electrode modifications, the key analytical parameters of dynamic range and limit of detection, and the real sample composition tested.

Cr Ion	Electrode Material	Electrode Modification	Electroanalytical Technique	Dynamic Range	Limit of Detection	Real Sample Composition	Reference
-	MDE	N/A	Polarography	-	0.25 μg/mL	Calcium Metal	[35]
VI	MDE	N/A	Polarography	0.035-2 μg/mL	0.01 μg/mL	Natural Waters	[36]
VI	GCE	N/A	HPLC-EC	-	< 1ng	Wastewater	[25]
VI	MDE	DTPA complex	Polarography	-	100 ng/g	Gallium Arsenide	[37]
VI	Pt	Iodine	ISE	0.006-2 mM	2 μM	-	[38]
VI	Pt	Poly(4-vinylpyridine)	CV	0.01-1 μM	10 nM	-	[39]
VI	MDE	N/A	Polarography	0.06-1.2 μM	16 nM	Lake Water	[40]
III VI	MDE	DTPA complex	DPAdSV	20-2000 ng/L	20 ng/L	River, Lake, Sea Water	[41]
VI	MDE	Diphenylcarbazide complex	Polarography	0.2-60 μM	200 nM	Waste Solids	[42]
VI	Pd	N/A	FI-AMP	-	-	-	[43]
III	MDE	DTPA complex	AdSV	-	23 ng/L	PWR Coolant	[44]
VI	Pt	N/A	Polarography	0.05-17.2 ppm	0.02 ppm	Wastewater	[45]
VI	MFE	N/A	Polarography	1-10 ppb	0.3 ppm	Cement	[46]
VI	Pt	Poly-3-methylthiophene	LSV	-	100 ppb	Acidic Media	[47]
III	MDE	TTHA complex	DPAdSV	-	0.3 ng/L	Aluminium Samples	[48]
VI	MDE	NaPipDTC	Polarography	-	0.01 ppm	*Ocimum sanctum*, stainless steel	[49]
III	MDE	5-Br-PADAP complex	LSV	3-90 nM	0.9 nM	Millet, Rice	[50]
VI	CFE	DTPA complex	AdSV	-	10 nM	-	[51]
VI	MDE	N/A	Polarography	-	1 μM	Concrete	[52]
VI	MDE	Diphenylcarbazide complex	AdSV	0-10 nM	0.02 μg/L	Mineral Water	[53]
III VI	CPE	Diphenylcarbazide	LSV	0.013-100 μM	13 nM	Soil Samples	[54]
III	MDE	EDTA complex	DPV	-	-	Plating Bath Water	[55]
III	MDE	DTPA complex	AdSV	-	5 μM	-	[56]
III	MDE	BPY complex	CSV	0.02-50 nM	20 pM	Natural Water, Soil, Plants	[57]
VI	MDE	N/A	DPAdSV	1-100 nM	1 nM	Aqueous Samples	[58]
III	MDE	Surfactant additions	Polarography	-	-	-	[59]
VI	MDE	DTPA complex	AdSV	-	0.51 nM	Estuarine Waters	[60]
III VI	MDE	Pyrocatechol Violet complex	AdSV	15-100 nM	3 nM	Lake Water	[61]
III VI	MDE	Xylenol Orange complex	CSV	-	1.2 ng/L 1.8 ng/L	Sea Water	[62]
VI	MDE	TTHA complex	AdSV	-	0.3 ng/mL	Gallium	[63]
III	MFM	DTPA complex	CSV	9.62-170 nM	0.28 nM	Cell Culture	[64]
VI	MDE	N/A	DPV	-	-	Louisiana Water	[65]
VI	MDE	DTPA complex	DPAdSV	0.1-10 nM	30 pM	Natural Water	[66]
III	MDE	DTPA complex	DPAdSV	-	0.47 nM	Wine	[67]
VI	MDE	N/A	DPV	0.1-100 μM	0.3 μM	Alkaline solutions	[68]
III VI	MDE	HEDTA, PCV complexes	DPAdSV	4.85-105 nM 4.76-99.6 nM	30 nM 8.72 nM	Mineral, Tap Water	[69]
VI	GCE	Hg Film	SWAdSV	0.01-0.6 μM	32.3 nM	Drinking Water	[70]
VI	DPE	Natural or synthetic diamond	DPV	10^{-11}-10^{-9} 10^{-10}-10^{-7} 10^{-6}-10^{-3}	10^{-12} 10^{-11} 10^{-8}	Vitamin Tablets	[71]
III	DPE	Natural or synthetic diamond	DPV	10^{-10}-10^{-8}	10^{-12}	Vitamin Tablets	[72]
VI	Pt	PANI/Glucose Oxidase	Amp	0.49-95.73 μg/L, 0.096-8.05 mg/L	0.49 μg/L	Soil Samples	[73]
VI	GCE	PPy/tyrosinase	Amp	0.5-100 μM	0.5 μM	Urine, Waste and River Water	[74]
VI	Hg	N/A	DPCAdSV	0.10 nM	40 pM	Tap, River Water	[75]
III	BFE	N/A	AdSV	0.5-40 μg/L	100 ng/L	Soil/Tobacco	[76]
VI	CPE	N/A	DPCSV	0.5-50 μM	50 nM	Tea	[77]
VI	Gold	N/A	CV	20-200 μM	4.3 μM	N/A	[32]
VI	CPE	Bentonite/DPCI	DPV	0.03-0.5 mg/L	17 μg/L	Sea Water	[78]
VI	GCE	Bi	CAdSV	0-50 nM	0.3 nM	River Water	[79]
VI	GCE	Pyridine-Sol Gel Films	SWV	0-400 ppb	4.6 ppb	N/A	[80]
III	GCE	N/A	FIA-SPS	-	14 ng/L	River Water	[81]
III	Hg	N/A	CAdSV	0.5-50 nM	80 pM	Tea Leaves, Mixed Herbs, Rain/ Estuarine Water	[82]
VI	SPCE	AuNPs	SWV	10-5000 μg/L	5 μg/L	River Water	[83]
III	GCE	Stannum film	DPASV	10-110 μg/L	2 μg/L	Tap Water	[84]
VI	GCE	Porous	CT	5-500 μg/L	1.9 μg/L	Tap, Mineral, River Water	[85]
VI	SPCE	Poly-L-histidine	LSV	0.1-150 μM	0.046 μM	Waste Water	[86]
III	Ni-BPE	N/A	FIA	0.3-1000 μM	0.3 μM	Water	[87]
VI	GCE	Au_{nano}	SWV	0.13-45 μg/L	0.01 μg/L	Tap/Sewage Water	[88]
VI	SPCE	AuNP AgNP	DPV	0.4-30 μM 0.5-38 μM	0.4 μM 0.85 μM	Tap/Sea Water	[89]
VI	ITO	AuNPs	Amp	0.5-50 μM	0.1 μM	Tap, Stream, Sea Water	[90]
VI	Gold	silicate/nanoAuNPs	Amp	0.2-3 ppb	0.1 ppb	River Water	[91]
VI	GCE	Bi Film	SWASV	10-70 ppb	5.27 ppb	Polypropylene	[92]
VI	GCE	Prussian Blue	Amp	0.5-200 ppb	0.15 ppb	Waste Water	[93]
VI	CPE	Trioctylamine	CSV	500 nM-1 mM	3.4 nM	Electronic Materials	[94]

(*continued on next page*)

Table 1 (*continued*)

Cr Ion	Electrode Material	Electrode Modification	Electroanalytical Technique	Dynamic Range	Limit of Detection	Real Sample Composition	Reference
III	SPCE	Hg	DPV	30-300 μM	39 μM	Waste Water	[95]
VI		AuNPs		4.9-40 μM	0.5 μM		
III	Bi Film	Rotating Disc Electrode/DTPA	SWAdSV	1-10 nM	0.336 nM	River Water	[96]
VI					0.414 nM		
VI	SPCE	N/A	Amp	100-1000 μg/L	19 μg/L	Canal Water	[16]
III	SPCE	L-DOPA	Amp	10-125 μg/L	6.01 μg/L	Wastewater	[97]
III	GCE	Polycarbonate/IrO_2 nanotubes	DPV	1-10 μM	0.2 μM	N/A	[98]
VI	GCE	Al_2O_3/μNP-Bi Film	AdSV	50-300 ng/L	0.12 ng/L	N/A	[99]
VI	Gold	AgNPs	Amp	2-370 ppb	0.65 ppb	Wastewater	[100]
VI	GCE	AgNPs/Nafion film	Amp	2-230 ppb	0.67 ppb	Wastewater	[101]
VI	GCE	AuNPs/MPTS/AuNP/PET	SWCSV	10-1200 ng/L	2.9 ng/L	Blood	[102]
III	GCE	Fe_3O_4/rGO	CV	0.2-2 nM	N/A	N/A	[103]
VI	BDD	-	LSV	0.01-5 ppm	3 ppb	N/A	[104]
VI	GCE	Bi Film/SWCNT/DTPA	AdCSV	0-25 nM	0.036 nM	River Water	[105]
VI	Gold	-	ASV	2-200 μM	0.9 μM	Tap/Sewage/Industrial Water	[106]
VI	GCE	TiO_2/quercetin	PEC	1-10, 20-140 nM	0.24 nM	Drinking Water	[107]
VI	SPCE	quercetin	ASV	1-200 μM	0.3 μM	Drinking Water	[108]
VI	Ti	TiO_2NT/AuNP	Amp	0.1-105 μM	0.03 μM	Tap/Lake Water	[109]
VI	Gold	Graphene/AuNPs/chitosan	CV	5-800 μM	N/A	N/A	[110]
VI	SPCE	DTPA	Amp	0.003-40 mM	1 μM	N/A	[111]
III	CFE	Poly(natural red)/HRP	Amp	0.2-5.1 μM	0.27 μM	N/A	[112]
VI				0.05-0.35 μM	0.09 μM		
III	SPCE	Tetrathiafulvalene	Amp	1.8-15.8 μM	2 μM	Wastewater	[113]
VI	$SPC_{Pt}E$	Glucose oxidase	Amp	89-769 nM	90.5 nM		
VI	BD-Si	SWCNT/PA	Amp	0.01-10 ppb	0.01 ppb	Wastewater	[114]
VI	SPCE	DTPA	Amp	3-3000 μM	1 μM	N/A	[115]
VI	GCE	Ag@TiO_2NPs	Amp	0.1-3.1 μM	0.01 μM	Tap/Lake Water	[116]
VI	Gold	6-mercapto-1-hexanol/methylene blue	CV	0.5-10 μM	500 nM	Synthetic Aquifier	[117]
III	GCE	CNT/chitosan/MnO nanoflakes	Amp	3-200 μM	0.3 μM	Drinking Water	[118]
VI	MCE	Bi Film	ASV	1-25 μg/l	0.05 μg/L	N/A	[119]
VI	SPCE	AuNPs	LSASV	0.7-3.5, 3.5-35 ng/mL	1.6 pg/mL	Tap/Sea Water	[120]
VI	ITO	Agar/PANI	CV	2.48-50 μM	2.48 μM	N/A	[121]
VI	GCE	rGO	DPSV	0.2-1000 μM	150 nM	Tap Water	[122]
VI	FTO	TiO_2/AuNPs	PEC	0.01-100 μM	4 nM	Tap/River Water	[123]
VI	Gold	Azacrown Monolayer	EIS	1-100 ppb	1.4 ppt	River Water	[124]
III	GCE	AuNPs	DPSV	0.5-75 ppb	10 ppt	Wastewater	[125]
VI	Pt	GQD/$S_2O_8^{2-}$	ECL	0.05-60 μM	20 nM	River Water	[126]
VI	ITO	PVS/PANI	SWV	14.6-60 μM	4.83 μM	Tap Water	[127]
VI	GCE	MWCNTs/PEI	Amp	0.002-20 μM	0.6 nM	Tap/Lake/Wastewater	[128]
VI	Gold	B-galactosidase	EIS	10^{-10}-10^{-4} M	0.312 nM	River Water	[129]
VI	GCE	SWCNTs/pyridine-solgel	SWV	5-300 μg/L	0.8 μg/L	Swine Blood	[130]
VI	GCE	Fe_3O_4/MoS_2	Amp	1-2360 μM	0.5 μM	N/A	[131]
VI	CTE	Gold	Amp	1-50 μg/L	0.7 μg/L	Tap/Lake Water, Plastics	[132]
III	GCE	Electrochemical Activation	DPV	0.05-6 μM	0.015 μM	N/A	[133]
VI				0.4-250 μM	0.12 μM		
VI	SPCE	CNT	Amp	20-1000 ppb	5 ppb	Power Plant Water	[134]
VI	GCE	POT/PVC	ASV	30-1300 nM	12 nM	Tap Water	[135]
III	SPCE	Chitosan/Au	DPSV	1-100 μM	0.4 μM	Industrial Wastewater	[136]
VI	FTO	IIP/F-g-C_3N_4	PEC	0.01-100 ppb	0.006 ppb	River Water	[137]
VI	SPCE	PANI/GQD	FIA-LSV	0.1-10 mg/L	0.097 mg/L	Drinking Water	[138]
VI	GCE	Au/TiO_2	Amp	0.1-3.1 μM	0.01 μM	Tap/Wastewater	[139]
VI	PET	Gold	CAdSV	0.5-100 μg/L	0.5 μg/L	Textile/River Water	[140]
III	CPE	IIP (itaconic acid based)	DPV	0.1-10 μM	17.6 nM	River/Sea Water, Urine	[141]
III	CPE	*C. freundii*	DPCSV	10^{-6}-10^{-2} M	100 nM	Mine Water	[142]
VI				10^{-7}-10^{-4} M	1 nM		
VI	GCE	CB	Amp	0.025-483 μM	10 nM	N/A	[143]
VI	GCE	NiFeNPs	Amp	0.025-98.3 μM	10 nM	Ground Water	[144]
VI	SPCE	AuNPs	LSV	20-200 μg/L	5.4 μg/L	River Water	[145]
VI	GCE	AuNPs/Graphene	CV	0-20 μM	10 nM	River Water	[146]
VI	Ni Foam	PANI	DPV	0-4528 nM	0.396 pM	N/A	[147]
III	GCE	CNF/chitosan/AuNPs	FIA-DECD	0.1-100 ppm	0.69 ppb	Industrial Waste Water	[148]
VI				0.1-100 ppm	0.32 ppb		
VI	Gold	IIP-S	DPV	0.009-10 μM	0.64 nM	Tap/River Water	[147]
VI	CPE	AuNPs	DPV	40-3000 μg/L	7 μg/L	Tap Water	[149]
VI	GCE	Ag plating	ASV	0.35-40 μM	0.1 μM	Tap Water	[150]
VI	GCE	AuPdNPs/rGO	DPV	0.05-5, 5-1000 μM	13 nM	Lake/River Water	[151]
III	Pt	AgNP-LE	DPV	10-90 μM	0.804 μM	Lake/Waste Water	[152]
VI	GCE	Bi Film/Zn	CAdSV	0.2-1.25 pM	5.8 fM	Sea/Estuarine/Rain Water	[153]
VI	GCE	AuNPs/rGO	SWV	0.1-30 μM	46 nM	Lake/River Water	[154]
VI	Gold	AuNPs/PANI-co-PoT/GO	SWV	5-500 μM	21.5 nM	Tap Water	[155]

(*continued on next page*)

Table 1 (*continued*)

Cr Ion	Electrode Material	Electrode Modification	Electroanalytical Technique	Dynamic Range	Limit of Detection	Real Sample Composition	Reference
VI	FTO	NiO	CV	N/A	N/A	N/A	[156]
III	SPCE	AuNPs	LSV	0.5–10 μM	0.01 μM	Tea, coffee and mineral water	[157]
VI	Gold	*Ox*-MWCNT/Au_{nano}	AMP/RDE	0-0.2 mM	720 nM	"Real Water"	[158]
III	Gold	Nick-HCR nanostructure	I-V	200 fM-20 nM	200 fM	N/A	[159]
VI	SPCE	α-Fe_2O_3	LSV	5-3000 μg/L	1.17 μg/L	Tap Water	[160]
III	GCE	Bi film	FSV	10^{-12}-10^{-7} M	0.3 pM	Tap Water	[161]
VI	SPCE	$BiVO_4$	AMP	0.01-264.5 μM	3.5 nM	N/A	[162]
VI	GCE	Pyridine/AuNPs/rGO	ASV	25-300 μg/L	1.16 μg/L	Wastewater	[163]
VI	ITO	Bi/BiOI-3	PEC	1-230 μM	0.3 μM	Tap/Lake Water	[164]
VI	Gold	Mn_3O_4/Nafion	CV	50-400 ppb	9.5 ppb	Canal/Sewage Water	[165]
VI	GCE	Ni-dealloyed AuNi/pPAT	SWV	1 ppb – 10 ppm	0.25 ppb	Hard/Soft/Waste Water	[166]
VI	GPE	AgNPs/BP/BPQ NRs	DPV	0.08-10 nM, 0.01-1 μM, 1-100 μM	2 pM	Tap/River/Waste Water	[167]
VI	GCE	PcIrCl	Amp	50-2500 nM	18 nM	Tap/Bore Well Water	[168]
VI	SPCE	MWCNT/Neutral red/AuNPs	LSV	0.4-80 μM	25 nM	Tea/Milk Mineral Water	[169]
VI	GCE	Nafion/AgM/g-C_3N_4	Amp	0.1-0.7 μM	1.6 nM	Drinking/Tap/ River/Industrial Water	[170]
VI	GCE	$[HC_5H_6N_2]_6(Co[Mo_6O_{12}(OH)_3(HPO_4)]_2).3H_2O$	Amp	0.5-378 μM	26 nM	Lake Water	[171]
VI	BDD	AuNPs	CSV	10-1000 μg/L	1.19 μg/L	Tap Water	[172]
VI	GCE	$(H_2bpp)_2[Na_4Fe(H_2O)_7][Fe(P_4Mo_6O_{31}H_6)_2].2H_2O$/CB	Amp	2-2610 μM	0.174 μM	Lake Water	[173]
III VI	CPE	*S. macrogoltabida*	DPCSV	0.1-1 mM 0.01-10 μm	100 nM 1 nM	Sukinda Valley Water	[174]
VI	GCE	N/A	CV	25 μM-1 mM	N/A	Tap/Lake/River Water	[175]
VI	GCE	$(H_2bpp)_6[GdMo^{V}_2Mo^{VI}_{16}O_{49}(HPO_4)(PO_4)_5]_2.11H_2O$	Amp	5-510 μM	0.202 μM	Lake Water	[173]
III	GCE	4-BBBSH	I-V	100 pM-100 mM	95.5 pM	Coal/Red Sea/Tap/Well Water, Industrial Effluent	[176]
III	ITO	AuNPs/MSA/MSA/AgNPs	ASV	0.1-10 nM	0.05 nM	Tap/Pond/Lake Water	[177]
VI	ITO	MoS_2/BiOI	PEC	0.05-160 μM	0.01 μM	Tap/Lake Water	[178]
VI	ITO	0.05-Bi-$BiPO_4$/BiOI-6%	PEC	0.5-180 μM	0.3 μM	Tap/Lake Water	[179]
VI	GCE	TPBS-C	ECL	10^{-12}-10^{-4} M	0.83 pM	Lake Water	[180]
VI	SPCE	Melanin NPs	Amp	0.1-5 μM	0.03 μM	Tap/Lake Water	[179]
VI	gold	PDDA/Graphene/TiO_2	PEC	1.4-2592.3 ppb	0.44 ppb	N/A	[181]
VI	CPE	chitosan@Fe_3O_4	SWV	0.01-0.3 μg/L 0.5-30 μg/L	6.1 ng/L 78 ng/L	Drinking/Sea Water	[182]
VI	ITO	BiOI/CN-34%	PEC	0.5-190 μM	0.1 μM	Tap/Lake Water	[183]
VI	ITO	5%-CuS/BW	PEC	0.5-230 μM	0.12 μM	Tap/Lake water	[184]
III VI	SPCE	AuAgNPs	DPV	0.05-1 ppm 0.05-5 ppm	0.1 ppb 0.1 ppb	Artificial saliva/sweat, tap water, wastewater	[185]
III	ITO	AuNP/3-mpa/Cr(III)/3-mpa/ AuNP	SWV	200-500 ppb	278 ppb	Pond Water	[186]
III VI	CPE	MNPZ	EIS	1 nM-1 μM 1 nM-50 μM	69 pM 0.45 nM	N/A	[187]
VI	GCE	Au/mpg-C_3N_4	LSV	100-1000 ppb	14.7 ppb	Tannery Wastewater	[188]
VI	CPE	$[Co_2(4\text{-dptb})_2(1,3\text{-BDC})_2].2H_2O$	Amp	10-1000 μM	6.51 μM	Tap Water	[189]
VI	PL	Au	CV	5-100 μM	2.3 μM	N/A	[190]
VI	GCE	rGO/NiS/AuNCs	SWASV	2-14 μg/L	0.09 μg/L	Ground Water	[191]
VI	MGCE	PANI/Hep/MTA	DPV	10^{-7}-10^{-4} ppm	0.0358 ppm	Whole Blood	[192]
VI	GCE	PANI@ZrO_2-SO_4^{2-}@MWCNT	DPV	0.55-39.5 μM	64.3 nM	Industrial Wastewater	[193]
VI	GCE	$[Cu^{I}(BBTZ)]_4[Mn^{II}(H_2O)_3]_2[Cu^{II}(P_4Mo^{V}_6O_{31}H_7)_2].H_3PO_4.3H_2O$	DPV	0.1-1 μM	1.59 nM	Lake Water	[194]

Key: MDE: mercury dropping electrode; MFM: mercury film microelectrode; MGCE: magnetic glassy carbon electrode; MCE: mesoporous carbon electrode; GCE: glassy carbon electrode; DPE: diamond paste electrode; Ni-BPE: Nickel barrel plating electrode; CTE: carbon tape electrode; CPE: carbon paste electrode; BDD: boron-doped diamond; PL: pencil lead; SPCE: screen-printed carbon electrode; GPE: graphite paste electrode; PET: poly(ethylene terephthalate); ITO: indium-doped tin oxide; FTO: fluorine-doped tin oxide; BD-Si: boron doped silicon; NaPipDTC: sodium pentamethylenedithiocarbamate; 5-Br-PADAP: 2-(5'-bromo-2'-pyridylazo)-5-diethylaminophenol; BPY: 2,3-bipyridine; TTHA: triethylene tetramine-N,N,N',N'',N''',N'''-hexaacetic acid; HEDTA: N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid; PCV: pyrocatechol violet; TiO_2NT: titania nanotubes; SWCNT-PA: single walled carbon nanotubes – bis(2,4,4-trimethylpentyl)phosphinic acid; AuNP: gold nanoparticles; MPTS: 3-mercaptopropyltrimethoxysilane; DPCI: 1,5-diphenylcarbizide; DTPA: diethylenetriamine-pentaacetic acid; GQD: graphene quantum dots; CNT: carbon nanotube; CNF: carbon nanofibers; PVS: poly(vinyl sulfonic acid); POT: poly(3-octylthiophene); PVC: poly(vinyl chloride); F-g-C_3N_4: formate anion incorporated graphitic carbon nitride; IIP: ion-imprinted polymer; IIP-S: ion-imprinted chitosan-graphene nanocomposite; pPAT: poly[3'-(2-aminopyrimidyl)-2,2':5',2''-tertiophene]; AgNPs: silver nanoparticles; AgNPs-LE: silver nanoparticles from *Lycopersicon esculentum*; PANI-co-PoT: poly(aniline)-co-poly(*o*-toluidine); Nick-HCR: nick hybridization chain reaction; BP: biphenol; BPQ NRs: biphenoquinone nanoribbons; PcIrCl: iridium phthalocyanine; AgM: silver molybdate; g-C_3N_4: graphitic carbon nitride; CB: carbon black; 4-BBBSH: (E)-N'-(4-bromobenzyledene)-4-benzenesulfonohydrazine; MSA: mercapto succinic acid; TPBS-C: 2,3-bis(4-cyanophenyl)-1,1-diphenyl-benzosilole; PDDA: poly(diallyldiamine chloride); BiOI: bismuth oxyiodide; CN: carbon nitride; BW: Bi_2WO_6 (180 °C); 3-mpa: 3-mercaptopropionic acid;

MNPZ: ZnO_2 modified-Fe_3O_4 magnetic nanoparticles; mgp-C_3N_4: mesoporous graphitic carbon nitride; rGO: reduced graphene oxide; AuNCs: gold nanocubes; Hep: heparin; MTA: magnetic tannin-modified adsorbent; PANI: poly(aniline); MWCNT: multi-walled carbon nanotube; BBTZ: bis(1,2,4-triazol-1-ylmethyl)benzene); CV: cyclic voltammetry; PEC: photoelectrochemistry; LSV: linear sweep voltammetry; DPV: differential pulse voltammetry; EIS: electrochemical impedance spectroscopy; AMP: amperometric; ECL: electrochemiluminescence; SPS: Solid-Phase Spectrophotometry; FSV: fast scan voltammetry; FIA: flow-injection analysis; RDE: rotating disc electrode; SWASV: square-wave adsorptive stripping voltammetry; CT: coulometric titration; CSV: cathodic stripping voltammetry; CAdSV: catalytic adsorptive stripping voltammetry; LSASV: linear sweep anodic stripping voltammetry; ASV: anodic stripping voltammetry; FIA-DECD: flow injection analysis coupled dual-electrochemical detectors; DPSV: differential pulse stripping voltammetry; DPCSV: differential pulse cathodic stripping voltammetry; I-V: current voltage.

differential pulse polarography toward stripping voltammetry, whilst still using a mercury electrode.

Adsorptive cathodic stripping voltammetry (AdCSV), when applied to chromium detection, exhibits the benefit of allowing direct redox speciation with no separation step. This process has been widely reported within the last four decades of literature for the determination of chromium in water samples at trace levels [32,44,41,196–200]. Fig. 2 shows the principles of voltammetric (A) and amperometric (B) techniques and, although stripping voltammetry is the most common electrochemical method for heavy metal sensing, differential pulse voltammetry (DPV), square wave voltammetry (SWV) and chronoamperometry (CA) are often applied as well. As shown in Fig. 2C, stripping analysis starts with a pre-concentration method that accumulates the heavy metal in question onto the working electrode's surface, followed by a stripping step that allows the direct quantification of the analyte (by measuring the directly proportional associated current) [201]. Stripping analysis is generally expressed by $i = KCt_{pre-concentration}$ [202]; where K, is a constant that includes the electrode (geometric) area (A), scan rate (ν), diffusion coefficient (D), number of electrons transferred in the electrochemical process (n) and convection rate (usually applied using the deposition step). Electroanalytical metal stripping offers ppb-grade detection limits, multi-elemental determination and *in-situ* analysis of the free heavy metal at the pH of the sample (unlike other techniques that require the ions to be forced into free-state) [202,203].

For the ideal electroanalytical determination of heavy metals, the working electrode should be highly reproducible, exhibit low background currents and exhibit large potential ranges [202]. Jin and collaborators elegantly summarised the chronological use of different types of mercury electrodes (dropping mercury electrode (DME), hanging dropping mercury electrode (HDME), solid and mercury film electrode (MFE) with potentiostatic techniques towards chromium sensing [204, 205]. Clearly due to the potential dangers of working with mercury electrodes [202], these have been replaced by solid substrates such as precious metals (Au, Ag and Pt) and carbon electrodes, which exhibit low background current, wide potential range and chemical inertness [206,207]. It is because of the advances in electrode materials and progress replacing these classic solid electrodes, a plethora of electrode materials and modification strategies have been reported since and this is where our focus turns for the majority of this review.

5. Working electrode composition

The electrochemical signature of analytes is critically influenced by the working electrode material. Usually, electrochemistry and material science go hand-in-hand to achieve a material that exhibits good

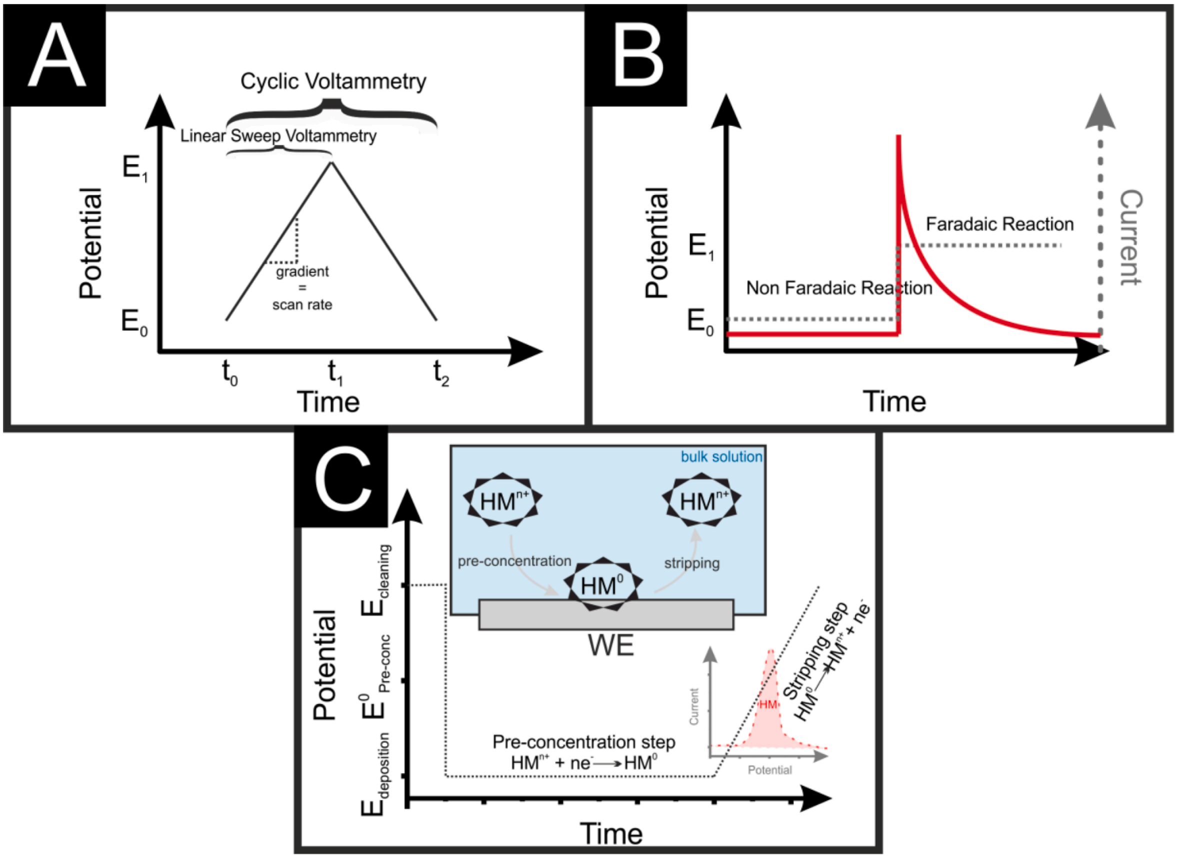

Fig. 2. Schematic diagram of voltammetric (A), amperometric (B) and stripping voltammetric (C) methods. C is reproduced and adapted with permission from reference [201] and with permission of Royal Society of Chemistry 2020.

electron transport, large electrochemically active surface area and offers a wide stable potential window with low background currents and chemical stability [208,209]. Conventional solid electrodes have been reported, extensively, towards the direct oxidation of trivalent chromium, with examples such as platinised platinum microelectrodes [210], metal oxide electrodes [211], synthetic diamond paste electrodes [212], boron doped diamond, glassy carbon and gold electrodes [28]. Brett and collaborators applied their batch injection analysis (BIA) with adsorptive stripping voltammetry (AdSV) for the detection and quantification of chromium [213]. BIA allows the injection of a small sample volume (<mL) of analyte to be added directly perpendicular to the working electrode, while all is immersed within the electrolyte. They reported the use of a mercury thin film electrode in conjunction with DTPA and cupferron as ligands for their BIA-SWAdSV, achieving an optimal LOD of 32.3 nM using cupferron complexes and a mercury electrode. O'Mahony and collaborators reported the transfer of Cr(VI) across two immiscible electrolyte solutions (ITIES) when NeoTT ionophore was used in the organic phase, achieving a LOD of 0.25 ppm Cr (VI) when using square wave voltammetry (SWV) [214].

Platinum (Pt) and Gold (Au) electrodes are often used within electroanalysis due to their excellent potential stability and electrolyte compatibility while exhibiting fast electron transfer kinetics [215,216]. Gold solid electrodes were initially used as a substitute to mercury ones due to their wide polarization range [28,217], and are still widely reported nowadays in the form of gold nanoparticles (AuNPs), thin films and other types of decorations. However, it is well known that Au(I/III) oxides are unstable, which can be easily reduced to elemental gold by electrode treatments (such as heat, UV light or reducing agents) [218–220]. It is because of this that obtaining stable Au(I/III) is considered a priority for sensor developers, and often experimentalists design combinations of several forms of gold with other metals (such as Ag-Au NPs [218] or other Au alloys such as AuCu, AuCo, and AuNi) [166], graphitic materials (graphene oxide (GO) [163], nanotubes (CNTs) [158,169]) and others forms of gold [221] towards chromium determination. Burke et al. published a comprehensive study comparing the electrochemical reduction behaviour of Cr(VI) between platinum and gold disk electrodes, reporting that the reduction of Cr(VI) occurred rapidly at lower overpotentials when using gold electrodes, compared to platinum [222]. The authors rationalised this on the basis of the pre-monolayer Cr(VI) oxidation or the hydrous oxide electrochemistry of both gold and platinum. Later on, Welch reported the direct detection of Cr(VI) at polycrystalline gold disk electrode by cyclic voltammetry, reporting good interference resistance when Cr^{3+}, Ni^{2+}, Cu^{2+}, Fe^{3+} and other surfactants were present [28]. In more recent times, and with the trend of applying the attractive physicochemical and electroanalytical properties of noble metal nanoparticles (NPs), gold NPs (AuNPs) have been widely applied to Cr(VI) determination [223]. Jin et al. [224], as shown in Fig. 3, combined the use of TiO_2 nanotubes (TiO_2NTs) with AuNPs reporting a 23-fold improvement in the electrochemical performance towards Cr(VI) detection due to the enhanced electron conductivity and increased surface-to-volume ratio of the AuNPs-TiO_2NTs. Their system achieved a LOD of 0.03 μM *via* chronoamperometry and exhibited good anti-interference resistance against Cr(III) and Fe(III). Stefan et al. [212] reported the use of monocrystalline (natural and synthetic) diamond paste electrodes for the determination of Cr(III) and (VI) in pharmaceutical compounds in the 2000s. They reported excellent analytical performance when interfering species (Fe^{2+}, Mg^{2+}, Cr^{6+}, Mn^{2+}, Cu^{2+} and Zn^{2+}) were present, being the natural diamond-based electrode the one exhibiting the highest sensitivity due to its higher conductivity when compared to synthetic diamonds. This was assumed to be due to the uncontrolled development of the monocrystals, causing more structural defects that hinder the electron transfer.

Following the use of solid precious metals, glassy carbon became apparent as a graphitic alternative for electrochemists. A simple

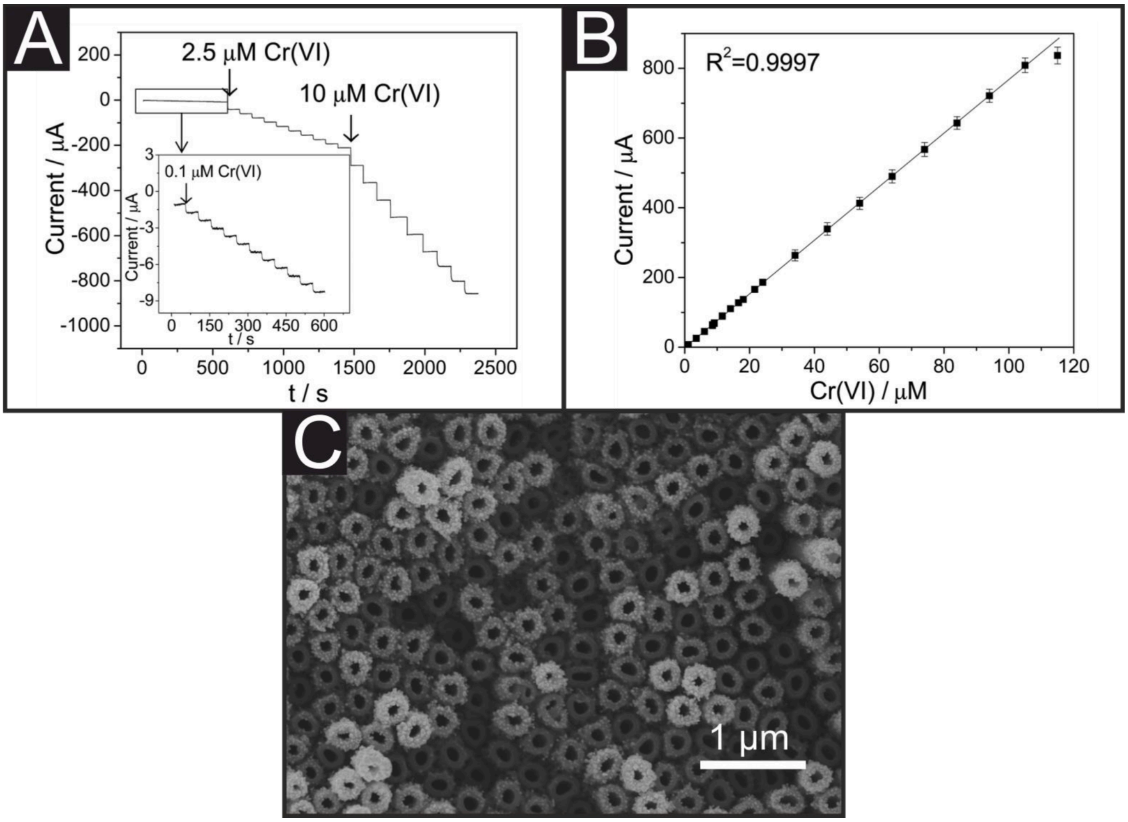

Fig. 3. (A) Amperometric current signals of the TiO_2NT-AuNPs electrodes with the addition of Cr(VI) at a fixed 0.28 V potential. (B) Calibration plot of the current responses from (A) against the Cr(VI) concentration (n=3). (C) SEM image of the as prepared Au NPs decorated TiO_2 nanotube electrode. Reproduced and adapted with permission from reference [224].

approach was the one performed by Stern et al. [175] who reported the use of glassy carbon as an effective electrode material for the reduction and detection of hexavalent chromium in water. Fig. 4A shows their (200 μM) potassium chromate sensing with bare glassy carbon electrodes with increased concentrations of citric acid (0.05 mM (dark blue), 0.1 mM (light blue), 0.15 mM (cyan), 0.2 mM (green), 0.3 mM (yellow), 0.4 mM (orange), and 0.5 mM (red)). Fig. 4B summarises the changes in the oxidation peak of potassium chromate at different pHs. Ouyang et al., in a combined approach, reported the fabrication of a flower-like assembly of AuNPs on GC for the ultratrace detection of Cr(VI) [102]. They reported the use of two AuNP layers, where the first one is electroplated onto the GC surface as anchors, to which a thiol sol-gel film would bind to. The second AuNP layer was a self-assembled layer on top of the sol-gel, creating a flower-like AuNP nanoelectrode, expanding the electroactive area of the electrode. Finally, the surface was functionalised by a thiol pyridinium, which allowed for an enhanced preconcentration of the Cr(VI). Their proposed sensor exhibited a linear range between 10-1200 ng/L and a LOD of 2.9 ng/L towards the Cr(VI) determination.

A different electrochemical strategy of using glassy carbon (GC) was the one proposed and reported by Manova et al. [225], where they used an in-electrode coulometric titration with a porous GC electrodes. They reported the use of a coulometric method for the direct determination of Cr(VI) in water samples. The coulometry applied a constant current that will reduce the chromate ions to Cr(III) at the porous surface of the GC, where the potential of the electrode is monitored during the reduction process, indicating the end of the titration. The use of a porous GC electrodes allowed for in-electrode coulometric titration, which are based on the direct electrolysis of the chromium in the bulk of the porous electrode by the applied constant current. On the contrary to classical coulometric titrations, here the measurements were in a thin-layer solution around the three-dimensional area of the electrode. Herein, the analyte was titrated directly by electrical charge and the potential of the electrode was controlled by the oxidation-reduction couple engaged in the process. By using this clever approach, the authors reported a reproducible Cr(VI) sensor with 1.9 and 6.0 ppb as LOD and LOQ respectively. The authors also reported recoveries of around 100% for real tap, mineral and river water samples. It is important to note from their work that the use of porous electrodes might be clogged by complicated matrix samples with colloidal and solid particles. Also based on GC electrodes, Xing and collaborators reported the use of the Everitts/Prussian Blue (PB) redox couple as a mediator for the Cr(VI) reduction [226]. Under optimal conditions, their PB/GCE sensor provided a wide linear response for Cr(VI) from 0.5 to 200 ppb with a LOD of 0.15 ppb; testing it in real world waste water samples with satisfactory results. They applied an amperometric method for the Cr(VI) determination, with interference studies in the presence of metal ions (40 ppm Bi^{3+}, 2.5 ppm Co^{2+}, 1 ppm Cd^{2+}, 6 ppm Ni^{2+}, 2 ppm Sb^{2+}, 1 ppm Zn^{2+}) to solutions containing 10.0 ppb Cr(VI) which induced a less than 5.0% current deviation. Although Prussian Blue was reported as a redox mediator in catalysis and electroanalysis [227–230], the PB film was not reported until then as an electron-transfer mediator for Cr(VI).

Using a different approach, Domínguez Renedo and collaborators [231] reported the use of a Polypyrrole (PPy)-tyrosinase modified glassy carbon electrode for the indirect chromium determination in urine, waste and river waters. They used an enzymatic amperometric approach to measure Cr(III) based on the inhibitive action of this chromium on tyrosinase enzyme activity. They used electrodeposited PPy-tyrosinase membrane on the GC electrode, where the tyrosinase catalysed the oxidation of o-diphenoles to o-quinones. Afterwards, the o-quinones are reduced back to catechols, which is directly influenced by the presence of Cr(III) in the sample, where the tyrosinase activity is inhibited by the chromium presence. Sánchez-Fernández et al. [232] reported the use of a bentodine-modified carbon paste electrode towards the determination of Cr(III) as shown in Fig. 5. Their procedure was based on the electrochemical response of Cr(VI)/1,5-dyphenylcarbazide (DPCI) complex, measured by differential pulse voltammetry and cyclic voltammetry. The use of the DPCI complex avoided the usual interferences of other heavy metal reduction procedures and exhibited successful quantification of Cr(III) in spiked seawater. An interesting approach was the one reported by Svancara et al. [77] where they applied the synergistic pre-concentration effect of the chromate anion at the carbon paste electrode, which was *in-situ* modified with quaternary ammonium salts. They reported the successful determination of Cr(VI) in either certified reference materials and CRM black tea samples achieving a limit of detection of about 5×10^{-8} M CrO_4^{-2}. Interference studies were also explored and successful towards $TlCl_4^-$, $AuCl_4^-$, $PdCl_4^{2-}$, $PtCl_6^{2-}$, VO_4^{3-}, MnO_4^- and I^-.

More recently and following the miniaturisation trend, screen-printed electrodes (SPEs) have also been applied towards chromium detection. SPEs offer disposable and decentralised analysis with high specificity and little requirements to achieve tailored mass-producible sensors at low-cost [201,233]. Screen-printed technologies also offer the versatility of design, modification, and material composition such as graphite [111,234], carbon nanotubes (CNTs) [158,134] or gold macro-electrodes [15], which have all been successfully applied towards chromium electroanalytical determination. We note that recent work has shown that the connection length of graphitic SPEs can have a profound effect on the electrochemical and electroanalytical performance of the electrode, something which should be considered by experimentalists before undertaking work [235]. Hallam et al. demonstrated the successful use of graphite screen-printed macro-electrodes to Cr(VI) with LOD at the ppb level in canal water samples [234]. They reported that the underlying electrochemical mechanism follows an indirect process involving surface oxygenated species, suggesting that the use of HCl as a model solution might affect those species.

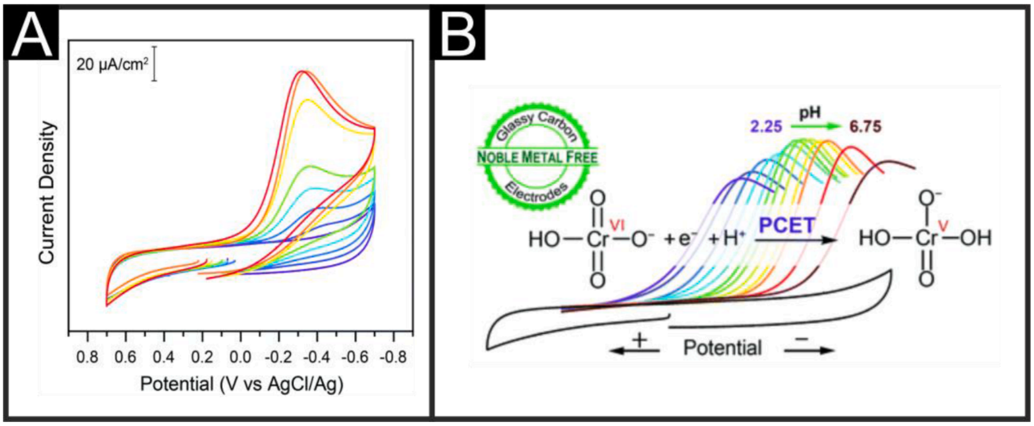

Fig. 4. (A) Cyclic voltammograms on glassy carbon electrodes of a 200 μM solution of potassium chromate in water in the absence (purple) and presence of increasing concentrations of citric acid: 0.05 mM (dark blue), 0.1 mM (light blue), 0.15 mM (cyan), 0.2 mM (green), 0.3 mM (yellow), 0.4 mM (orange), and 0.5 mM (red). Data recorded at 100 mV s^{-1}. (B) Peak current comparison of the potassium chromate oxidation at different pHs. Reproduced and adapted with permission from reference [175]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

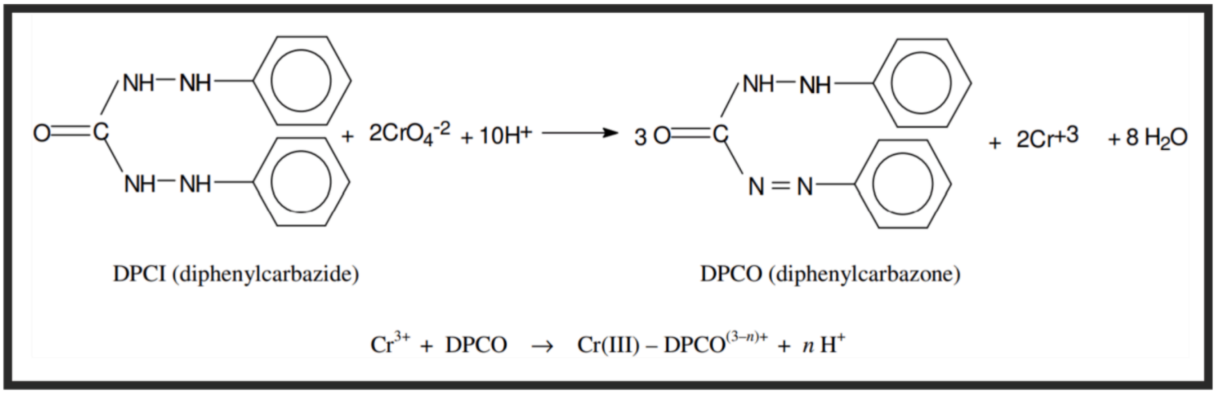

Fig. 5. Complexation of the DPCI and CrO_4^{-2} for the following electrochemical determination of Cr^{+3}. Reproduced and adapted with permission from reference [232].

Their system exhibited a simplified methodology capable of achieving a LOD of 19 ppb Cr(VI). Sánchez-Moreno et al. [236], reported the use of a BIA-SPE system targeting the chromium determination with a graphite-epoxy composite for the selective potentiometric response in batch and flow analysis, achieving LODs of 0.21 and 0.94 µM respectively. The authors also tested their sensor against Cr(VI) in mineral, tap, river waters and in leachates from municipal solid waste landfills with successful results. Metters and collaborators later explored the use of gold screen-printed macro-electrodes (AuSPEs), towards the speciation of Cr(III) and Cr(VI) [15]. They reported that the AuSPEs have electrode kinetics of at least one order of magnitude lower than polycrystalline gold macroelectrodes, however the AuSPEs mimic the analytical performance of the solid gold electrode towards sensing Cr(III) and Cr(VI). The AuSPEs however, are capable of disposable one-shot measurements and offer ease of manufacture. In terms of enhancing the electrochemical performance of working electrodes, surface modifications are a common solution that many experimentalists explore. Surface modifications such as adsorption (coatings such as dip coating or drop-casting), covalent bonding, electro-polymerisation and/or electrochemical depositions are often utilised towards electroanalytical applications [201,237].

Domínguez-Renedo et al. [238] also applied carbon screen-printed electrodes (CSPE) towards Cr(VI) sensing, but this time with metallic silver and gold nanoparticle surface electrodeposition. As shown in Fig. 6, their newly created silver (Fig. 6A) and gold (B) nanoparticles were deposited in aggregated forms on the graphite flakes. They report that the use of bare carbon screen-printed electrodes (CSPEs) exhibited no Cr(VI) electrochemical DPV signal, however the use of silver and gold nanoparticles produced a reduction peak of Cr(VI) to Cr(III) as shown in Fig. 6C and D respectively. Their system exhibited LODs of 8.5 and 4.0 × 10^{-7} M for the silver- and gold-modified CSPEs, with high selectivity towards the analysis of Cr(VI) in the presence of foreign ions, including Cr(III). The same group took their CSPE modification strategy one step forward, using a two-working electrode CSPE to be the base of a Hg film and AuNP-modified bi-CSPE for the determination of Cr(III) and Cr(VI) [239]. The determination of Cr(III) was carried out by DPV using the Hg-SPEs and analogously, the Cr(VI) analysis was performed using the AuNPs-CSPEs by DPV too. The choice of an array of two working

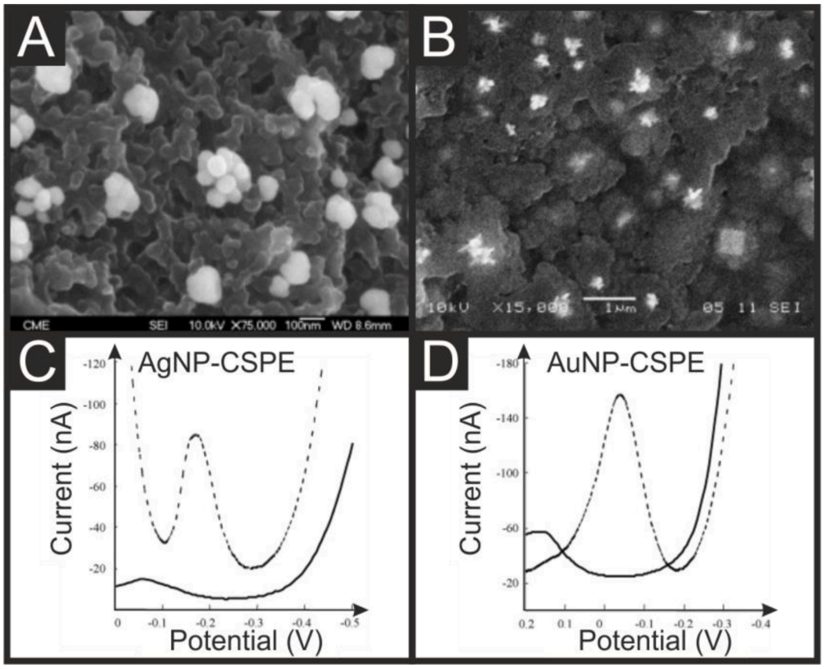

Fig. 6. SEM images of silver- (A) and gold-nanoparticle (B) modified CSPE modified by electrodeposition. Differential pulse voltammograms for Cr(VI) using silver- (A) and gold-nanoparticle (B) modified CSPEs, where solid lines represent the blank an the dotted lines are in presence of 1 µM Cr(VI); potentials vs Ag/AgCl. Reproduced and adapted with permission from reference [238].

electrodes allows for the simultaneous determination of Cr(III) and (VI) by DPV, exhibiting LODs of 1.4×10^{-4} and 4.8×10^{-6} M for Cr(III) and (VI) respectively (in the presence of each other). The authors also demonstrated its analytical application in sewage wastewater from tanning industries. Filik et al. reported the use of a neutral red interlinked AuNPs/MWCNT modified screen-printed carbon electrode for the successful simultaneous speciation of Cr(VI) and V(V), exhibiting high sensitivity for both due to the synergistic effect of AuNPs and graphite to facilitate electron transfer, reporting a 100 fold improvement over polycrystalline gold electrode when detecting Cr(VI) [169]. Filik and Avan [157] reported a new analytical approach for the speciation analysis of both Cr(III) and Cr(VI). A simple and fast solid phase microextraction method using magnetic dextran (Sephadex G-150) as a sorbent was developed for the extraction, separation and speciation analysis of chromium ions. The retained Cr(VI) ions on the magnetic dextran sorbents were eluted and detected by linear sweep voltammetry at the gold nanoparticles modified screen- printed carbon electrode.

Another example of using AuNPs and CNTs towards Cr(VI) electroanalysis was the one reported by Breslin et al. who functionalised a gold disc electrode with multi-walled carbon nanotubes, Ox-MWCNT-Au_{nano} [158]. Their sensor showed good selectivity for the detection of Cr(VI) in the presence of Cu(II), chloride and nitrates and in a real water sample, which was attributed to the electropositive reduction potentials of Cr (VI) and the acid (H_2SO_4) supporting electrolyte that provided a clean gold surface to deposit the AuNPs without agglomeration [158].

Another successful attempt of using gold nanoparticles on screen-printed carbon electrodes (AuNPs-CSPE) was the one reported by Tu et al. [240], where they developed an *in-situ* miniaturised system for Cr (VI) determination. Their electrochemical deposition of choloroauric acid on the CSPEs generated AuNPs, which were later activated by a voltammetric cycling step in sulfuric acid to expose more active sites. Fig. 7A shows a photograph of their CSPE before and after the gold decoration and Fig. 7B shows a series of SEM images before (above) and after (below) the gold decoration at different magnifications. Fig. 7C shows the recorded voltammograms for increasing concentrations of Cr (VI) and its corresponding calibration curve (Fig. 7D). Their disposable and portable solution exhibited reproducibility of around 5% RSD and the electrodes maintained a LOD of 5.4 ppb with long-term stability when vacuumed and tested their performance in river water samples from the Tiesha River in Hangzhou. The authors confirmed to achieve the development of a portable Cr(VI) sensor, capable of challenging AAS at a much lower cost ($2 for the AuNp-CSPE vs $350 for the AAS samples).

The use of Ag nanoparticles was also explored by Xu et al. [241], with the use of gold nanoporous films on gold substrates (AgGNF) towards the amperometric detection for trace Cr(VI). Their solid gold electrode (SGE) was directly anodized at +5 V to be then reduced to obtain the gold nanoporous film (AuNF) by freshly prepared ascorbic acid. Afterwards the AgNPs were grown via electrodeposition. Their multi-step AgGNF electrode exhibited higher electrocatalytic performance than those of AuNF and SGE, exhibiting a LOD of 0.65 ppb for Cr (VI) and successful anti-interference effects from other heavy metals (Cr^{3+}, Cu^{2+}, Pb^{2+}, As^{3+} and Hg^{2+}).

These are some examples of recent uses of SPEs towards chromium sensing, often with surface modifications. However, recently there is a new trend in electrode methodology, where the introduction of nanomaterials [242], composites and metal-organic frameworks (MOFs) into the field of electroanalysis has promoted the advances of environmental

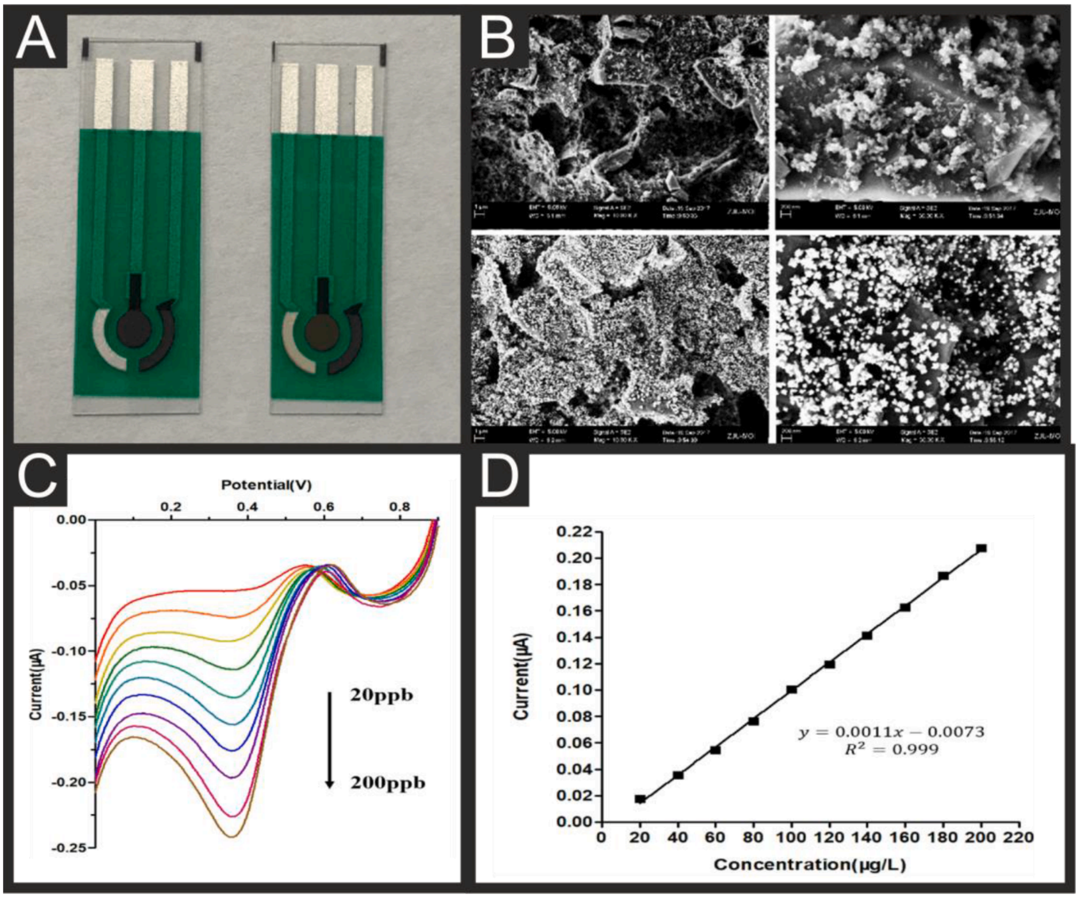

Fig. 7. Photograph of the CSPEs before (left) and after (right) the AuNPs decoration. SEM images of CSPEs before (above) and after (below) the decoration at 10K (left) and 50K (right) magnifications. C) Voltammograms for increasing Cr(VI) concentrations and D) its corresponding calibration curve. Reproduced and adapted with permission from reference [240].

monitoring solutions. Although recent, the application of MOFs to electroanalysis offers a precise and open-pore structure for surface functionalization, allowing the improvement of charge transfer and electron conductivity. One example of MOF surface modification of SPEs is by Fu et al. [160], who decorated α-Fe_2O_3 on SPEs. They produced iron nanostructures in the presence of glycerol by hydrothermal conditions, as shown in Fig. 8. Their urchin-like α-Fe_2O_3 with restricted (001) plane exposure was deposited onto SPEs, exhibiting a successful Cr(VI) sensor in tap water, with a LOD of *ca.* 1 ppb. The iron nanostructure had mostly exposed (001) planes, which have a higher density of coordinated hydroxyl groups that allowed a high Cr(VI) adsorption.

A graphene carbon nitride immobilisation using a nafion-modified glassy carbon electrode and coated with silver molybdate (g-C_3N_4/AgM/Nf/GCE) was proposed by Karthika et al. [170]. The nanocomposite was created *via* a sonochemical approach, as shown in Fig. 9, and showed high electrocatalytic activity towards the amperometric reduction of Cr(VI). The use of g-C_3N_4/AgM nanorods exhibited a large surface area and an enhanced electron transfer when immobilised with nafion. The use of an amperometric technique at fixed 0.29 V allowed the Cr(VI) determination in 3 seconds, which exhibited a limit of detection of 0.0016 μM. No interference effects were detected with Fe^{2+}, Ca^{2+}, Mg^{2+} and Mn^{2+} (at 4x the concentration against Cr(VI)). The authors also tested their systems in real tap, bottled, river and industrial waste waters, which averaged recovery percentages >95% among them. A functionalised three-dimensional graphene electrode with AuNPs was reported by Xu et al. [163] towards Cr(VI) sensing in water samples. The use of 3D graphene alleviated the self-aggregation issue of graphene, which often hinders electrochemical performance. The three-dimensional reduced graphene oxide structure offered a porous and interconnected framework for fast electron transfer, enhanced mass transfer and large surface area. This, when coupled with AuNPs, exhibited synergistic cooperation for Cr(VI) determination. In this work, the authors used a self-assembled pyridine groups on the AuNPs through a S-Au bond as shown in Fig. 10, which exhibited LOD of *ca.* 1 ppb and recoveries in the rage of 96-104%.

6. Future prospects

Numerous research groups have reported the use of additive manufacturing (AM) to achieve electrodes and microfluidic detection systems for heavy metal monitoring [243–247]. These are portable and cost-effective alternatives to conventional desktop detection methods, which can be fully printed modularly [248] or all-in-one [249] for their electrochemical application. However, these have their own challenges and have not been reported towards chromium detection in water yet. The use of 3D printed/additive manufactured electrodes towards electroanalytical applications depends on the effectiveness of the surface of the electrode to transport electrons, pre-accumulate the metal on its surface, and then to strip it back to the solution. Further research in material science and electrochemical detection methods is necessary to allow these AM electroanalytical devices to be fully developed. In addition, challenges such as the determination in complex water matrices and variable matrix conditions need to be addressed. Microfluidic-based systems are often used within the literature, however their use within the water industry is still limited due to biofouling, gas bubbles and irregular flow rates, although, current manufacturing techniques are advancing at a high pace, this might allow these issues to be sorted out in the near future. The introduction of filtration systems, highly selective recognition elements, multi-array electrode systems and internal standards might allow these challenges to be a thing of the past soon. Despite rapid advances and research outcomes towards on-site low-cost heavy metal analysis in water, these are often only applicable to laboratory conditions. Only a handful of systems that comply with water quality regulations, whilst being developed and proven as portable and mass-producible chromium devices.

7. Conclusions and outlook

In this review, we remind the reader the importance of Chromium contamination in drinking water. Herein, we have explored and analysed the historical use of electroanalytical methods towards Cr determination as an alternative robust, sensitive and rapid methodology to bench-top instruments. Due to the introduction of stricter limits for

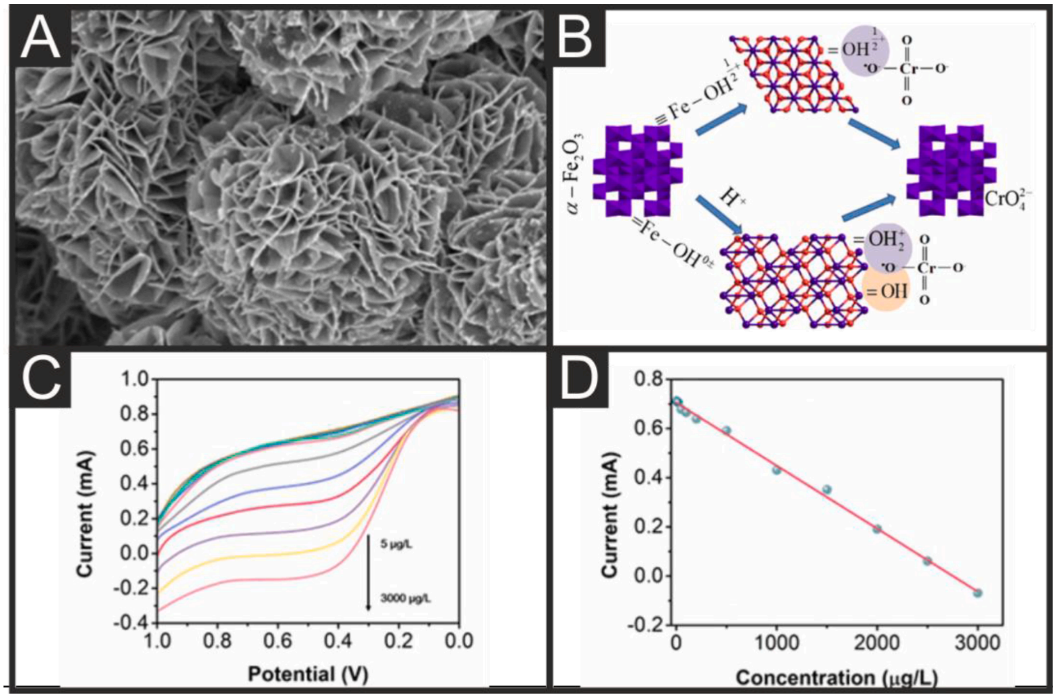

Fig. 8. SEM image of urchin-like α-Fe_2O_3, adsorption mechanism of Cr(VI) on α-Fe_2O_3 (B), linear sweep voltammetry of the α-Fe_2O_3/SPE electrochemical signals with increasing amounts of Cr(VI) were present (C) and its corresponding calibration curve (D). Reproduced and adapted with permission from reference [160].

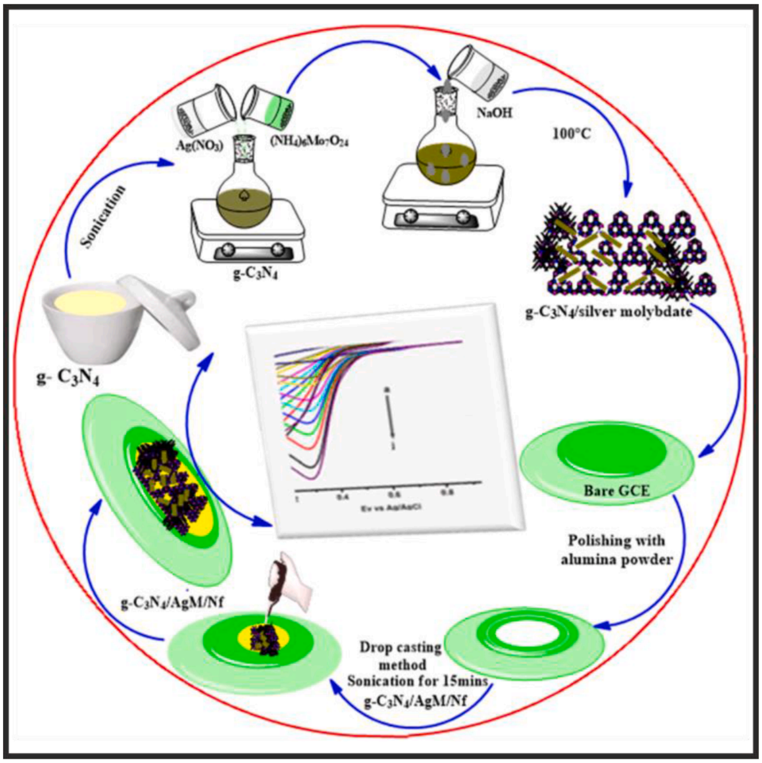

Fig. 9. Step-by-step schematic representation of the fabrication of g-C_3N_4/AgM/Nf modified glassy carbon electrode for Cr(VI) electrochemical determination. Reproduced and adapted with permission from reference [170].

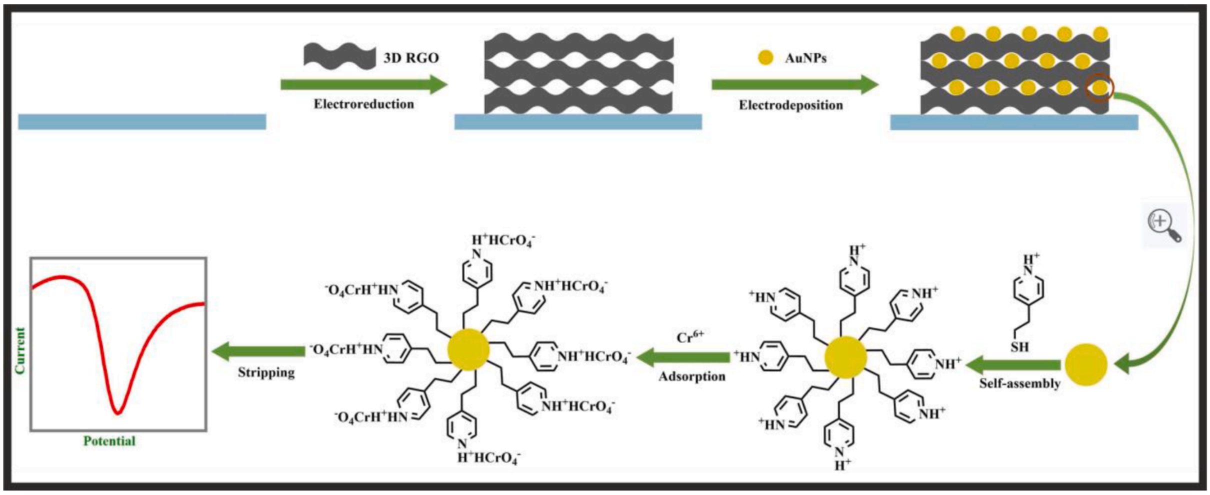

Fig. 10. Schematic illustration of the pyridine preparation and functionalisation on AuNPs/3D graphene/GCE and an analytical Cr(VI) response. Reproduced and adapted with permission from reference [163].

drinking water and environmental pollutants, there is a need for alternative solutions that can create large-scale environmental monitoring at an affordable cost. This review showcases and explains some of the recent advances in nanomaterials and electrochemistry and their application to Cr analysis, with particular attention to screen-printed electrochemical platforms, However, more efforts are needed to target multi-analyte speciation, unknown matrices or on-line sensors for screen-printed electrode platforms to become a dominant instrument in the environmental monitoring market. As material science grows, more materials will likely be reported towards electroanalytical purposes, however it is clear that this is an emerging and exciting field utilising previously well-known methodologies.

Declaration of Competing Interest

There are no conflict of interest to declare.

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