



Improved Bi film wrapped single walled carbon nanotubes for ultrasensitive electrochemical detection of trace Cr(VI)



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ABSTRACT

We report here the successful fabrication of an improved Bi film wrapped single walled carbon nanotubes modified glassy carbon electrode (Bi/SWNTs/GCE) as a highly sensitive platform for ultratrace Cr(VI) detection through catalytic adsorptive cathodic stripping voltammetry (AdCSV). The introduction of negatively charged SWNTs extraordinarily decreased the size of Bi particles to nanoscale due to electrostatic interaction which made Bi(III) cations easily attracted onto the surface of SWNTs in good order, leading to higher quality of Bi film deposition. The obtained Bi/SWNTs composite was well characterized with electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), the static water contact angle and the voltammetric measurements. The results demonstrate the improvements in the quality of Bi film deposited on the surface of SWNTs such as faster speed of electron transfer, more uniform and smoother morphology, better hydrophilicity and higher stripping signal. Using diethylene triaminepentaacetic acid (DTPA) as complexing ligand, the fabricated electrode displays a well-defined and highly sensitive peak for the reduction of Cr(III)–DTPA complex at -1.06 V (vs. Ag/AgCl) with a linear concentration range of 0–25 nM and a fairly low detection limit of 0.036 nM. No interference was found in the presence of coexisting ions, and good recoveries were achieved for the analysis of a river sample. In comparison to previous approaches using Bi film modified GCE, the newly designed electrode exhibits better reproducibility and repeatability toward aqueous detection of trace Cr(VI) and appears to be very promising as the basis of a highly sensitive and selective voltammetric procedure for Cr(VI) detection at trace level in real samples.

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1. Introduction

Chromium (Cr), a heavy metallic element, is usually found in waters, soils, rocks and gases [1]. However, the contamination of ecosystems with Cr is primarily as a result of human activities through the discharges of waste and effluent from a variety of industries, such as the production of steel, metal electroplating, spray painting, leather tanning, and other industries where Cr is currently used [2,3]. So Cr contaminated samples are mainly present in aqueous systems where both Cr(III) and Cr(VI) are the most abundant oxidation states on which the toxicity of Cr mainly depends [4]. Trace Cr(III) in cation forms of $\text{Cr}(\text{OH})_2^+$ or $\text{Cr}(\text{OH})^{2+}$

is considered an essential nutrient for human life, while Cr(VI), depending on the pH value and concentration of solution, can be available in anion forms such as CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ or their protonized forms reported as being 1000 times more toxic than Cr(III), highly mutagenic and potentially responsible for carcinogenic effects in humans as well [5,6]. This fact leads to the high and strict control of Cr(VI) content in the environmental samples [7]. The provisional guideline value for Cr(VI) in ground water has been set as 50 ppb by World Health Organization (WHO) [8]. Therefore, the determination of Cr(VI) is much more important than Cr(III), and the design of precise, accurate and highly sensitive analytical methods for Cr speciation and determination at trace level in aqueous systems is of great importance and significance.

Hence, in recent years, the development of analytical methods for the detection of Cr(VI) has been a topic of significant interest [9,10]. The conventional analytical methods for the determination of Cr(VI) include atomic absorption spectrometry [11,12], chromatographic methods [13], X-ray fluorescence spectrometry [14], inductively coupled plasma mass spectrometry (ICP-MS) [15], and

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electrospray ionization mass spectrometry (EIS-MS) [16]. However, these methods are not profitable enough to be adapted to routine analysis, since they are somewhat complicated and time-consuming, and usually involve expensive instrumentation and sample pretreatment [4,17]. Even more, the selective detection of Cr(VI) is a challenging task for these methods because of the suffer from Cr(III) interference [9,18].

Electrochemical methods are simple, reliable, sensitive and require less expensive equipment [19,20] and, for Cr particularly, allow direct redox speciation with no separation step [4,21–27]. So the selective detection of Cr(VI) is relatively easier based on electrochemical techniques due to the different reduction potentials of Cr(VI) and Cr(III) [28]. There are many studies on voltammetric methods for the detection of Cr(VI) [3,4,22,23,25,27–31] and some of them successfully determined Cr(VI) with detection limits below nanomolar. Among them, AdCSV is a significant sensitive and effective technique for the determination of trace Cr(VI) [21]. In this procedure, the determination of Cr was based on the adsorptive accumulation of a Cr complex on the electrode surface using DTPA [22,23], cupferron [30], ethylenediaminetetra acetic acid (EDTA) [31], etc. as complexing ligands. The hanging mercury drop electrode (HMDE) or the mercury film electrode (MFE) has been preferred to conduct these AdCSV procedures for many years [22,32–38]. Whereas the well-known toxicity and the handling inconvenience of mercury are responsible for the considerably declined popularity as electrode material. Therefore, many efforts have been made to develop less toxic alternative electrodes to replace the mercury electrode [21–27].

Bismuth-film electrode (BiFE) [39–41] has been approved as a good alternative due to the similar performance to mercury electrodes, the negligible toxicity as well as the property of being environmentally friendly [4,21–23,41]. Wang et al. and Xue et al. reported better catalytic AdCSV measurements of Cr(VI) at sub nanomolar level with BiFE by comparison with the MFE [22,23]. Unfortunately, it is not easy to obtain a Bi film with satisfactory morphology and reproducibility for AdCSV measurement of Cr(VI) by electrodeposition on GCE surface, hindering the practical applications of BiFE in analytical chemistry to some extent. Thus, Neto et al. presented an AdCSV protocol coupled with a rotating-disk Bi film electrode for the determination and speciation of Cr(III) and Cr(VI), where the thickness of Bi film was easily controlled and well optimized to allow the simultaneous determination of Cr(III) and Cr(VI) with low detection limits of nanomolar [4]. In Nunes et al.'s and Zhang et al.'s report, the analytical performance of Bi film electrode was significantly improved by adding citrate ions to the hydrochloric acid electrodeposition solution which helped to form a homogeneous structure by aggregates of spherical Bi particles with a few nanometers in diameter [27,42]. Consequently, the quality of Bi film is supposed to have significant effect on its stripping performance toward Cr(VI).

Therefore, in the present work, the main purpose is to explore a simple way to improve the quality of Bi film electrodeposited on GCE for the AdCSV measurement of Cr(VI) using DTPA as complexing ligand. The carboxylic-group functionalized SWNTs were introduced here to facilitate the deposition of Bi film. The existence of electrostatic interaction between negatively charged SWNTs and Bi(III) cations provided Bi(III) cation a driving force to be attracted onto the surface of the carboxylic-group functionalized SWNTs in good order, which is more favorable for high-quality Bi film deposition than the commonly used Bi film formation by reducing the randomly adsorbed Bi(III) cations on bare GCE surface for the analysis of Cr(VI). Accordingly, the well-deposited Bi film wrapped SWNTs were prepared as illustrated in [Scheme 1](#) and their properties were characterized with electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), the static water contact angle and the voltammetric measurements. The

obtained results demonstrate the improvements in the quality of Bi film deposited on the surface of SWNTs such as faster speed of electron transfer, more uniform and smoother morphology, better hydrophilicity and higher stripping signal which are profitable for efficient aqueous analysis of Cr(VI). The proposed method offers benefits such as wide linear calibration range, very good limit of detection, good reproducibility, low cost, simple preparation and the potential applications in the electroanalysis of other toxic metals in the environmental samples.

2. Experimental

2.1. Chemicals and apparatus

2.1.1. Chemicals

Acetic acid (HAc, glacial, Aladdin), sodium acetate (NaAc, anhydrous, Aladdin), potassium nitrate (KNO_3 , J&K chemicals) and chromium nitrate ($\text{Cr}(\text{NO}_3)_3$, Aladdin) were used as received. Cr(VI) and Bi(III) AA standard solutions ($1000 \mu\text{g L}^{-1}$, J&K chemicals) were diluted prior to use. SWNTs (<2 nm diameter) were purchased from Shenzhen Nanotech Port Ltd. Co. (China). DTPA (J&K chemicals) was dissolved in deionized water and adjusted to pH 6.0 with ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$). The buffer solution (pH 6.0) contained 0.25 M KNO_3 and 0.1 M NaAc/HAc. The buffer solution (pH 4.5) was prepared by mixing 0.1 M NaAc and 0.1 M HAc. A stock aqueous solution of cupferron (analytical-reagent grade, Aldrich) was freshly prepared. A 0.01 mol L^{-1} piperazine-N,N'-bis-(ethanesulfonic acid) (PIPES, Aldrich) solution (pH = 7.0) containing 0.2 mol L^{-1} of KCl served as the supporting electrolyte. Cr(VI) standards with different concentrations were prepared by diluting the appropriate amount of stock solution in supporting electrolytes. All aqueous solutions were prepared in ultrapurewater ($\geq 18 \text{ M}\Omega$). All other chemicals used are of analytical grade.

SWNTs of a certain mass were dispersed in 30% HNO_3 and then refluxed for 24 h at 140°C to obtain the carboxylic group-functionalized SWNTs. The resulting suspension was centrifuged, and the sediment was washed with deionized water until neutral pH. Then, the oxidized SWNTs were dispersed in deionized water to a concentration of 0.5 mg mL^{-1} for subsequent use.

2.1.2. Apparatus

All voltammetric measurements were performed using a modulated potentiostat (CHI 660D, CH Instruments, Inc.) at room temperature. A three-electrode configuration consisted of a Bi/SWNTs modified GCE, Ag/AgCl, and a platinum wire (CH Instruments, Inc.) as working, reference and counter electrodes, respectively. The morphologies of differently modified electrodes were examined with a SEM515 scanning electron microscope (Philip). The static water contact angle was measured at 25°C by a contact angle meter (OCA15 pro) employing drops of pure deionized water.

2.2. Electrode modification with Bi film wrapped SWNTs

A GCE (3 mm diameter, CH, Inc.) was polished to a mirror like surface using a standard electrode polishing kit (CH, Inc.) including a 1200 grit Carbimet disk, 1.0 and $0.3 \mu\text{m}$ alumina slurry on a nylon cloth, and $0.05 \mu\text{m}$ alumina slurry on a microcloth polishing pad. After successive sonication in diluted HNO_3 , ethanol (95%, Aladdin), and deionized water, $6.0 \mu\text{L}$ of 0.5 mg mL^{-1} carboxylic group-functionalized SWNTs solution was dropped on the pretreated GCE and dried in N_2 flow. Before the formation of the Bi film, the SWNTs-coated GCE was immersed in 0.1 M NaAc/HAc (pH 4.5) solution containing 100 mg L^{-1} of Bi solution for 5 min under stirring. Then, the *ex situ* deposition of Bi was performed at -1.0 V for 2 min under stirring. After being carefully rinsed with deionized

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