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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 demonstrates 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 towards 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.

Keywords

Bismuth; Single walled carbon nanotubes; Catalytic adsorptive cathodic stripping voltammetry; Chromium detection; Diethylene triaminepentaacetic acid

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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 $\text{Cr}(\text{OH})_2^{2+}$ 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 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) have been preferred to conduct these AdCSV procedures for many years[22,32-38]. Whereas the well-known toxicity and the handling inconvenience of mercury is 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 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-disc 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 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 towards 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 demonstrates 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

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 ($<2 \text{ nm}$ 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 KNO₃ 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 (18 MΩ). All other chemicals used are of analytical grade.

SWNTs of a certain mass were dispersed in 30% HNO₃ 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.

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 μm alumina slurry on a nylon cloth, and 0.05 μm alumina slurry on a microcloth polishing pad. After successive sonication in diluted HNO₃, ethanol (95%, Aladdin), and deionized water, 6.0 μL of 0.5 mg mL⁻¹ carboxylic group-functionalized SWNTs solution was dropped on the pretreated GCE and dried in N₂ 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 water, the obtained Bi/SWNTs/GCE was used for subsequent assays, and the electrode was used for many times. The process is simpler than the common *in-situ* Bi deposition followed by the removal and redeposition of Bi film after each measurement.

2.4 Sample analysis

River samples were collected in polypropylene bottles from the Huangpu River, in Shanghai, China, which was surrounded by a number of industrial factories. Prior to analysis, the river samples from three locations of the river were mixed and acidified by 3% nitric acid followed by filtration. Afterwards, the pretreated samples were stored in a freezer. The resulting river water was diluted using 0.1 M acetate buffer solution (pH 6.0) containing 0.25 M KNO₃ right before the determination of Cr(VI). Standard additions of 3 and 8 nM Cr(VI) were performed, individually, to the river water, to a total volume of 10 mL.

2.5 Catalytic adsorptive cathodic stripping measurements of Cr(VI)

Standard solutions of Cr(VI) ranging from 0 to 25 nM were analyzed by catalytic AdCSV with the obtained Bi/SWNTs/GCE in the acetate buffer solution (pH 6.0) containing 0.25 M KNO₃ and 0.1 M NaAc/HAc. Prior to the detection, the solution was first deaerated with pure N₂ for 5 min, followed by the addition of DTPA solution with a final concentration of 5 mM. Cr adsorption was carried out by holding the voltage at −0.8 V for 140 s while stirring. Square wave voltammetry (SWV) was subsequently performed in an unstirred solution by negatively scanning from −0.8 to −1.4 V with a potential step of 4 mV, an amplitude of 25 mV, a frequency of 20 Hz, and a quiet time of 10 s. A cleaning step was taken between each measurement by applying −1.2 V potential for 30 s in the electrolyte solution. With all other parameters same, SWV was performed in an unstirred solution by negatively scanning from −0.8 to −1.2 V while using cupferron as complexing ligand.

3. Results and discussion

3.1 EIS characterization

Fig. 1A shows the EIS measurements for bare GCE, Bi/GCE, SWNTs/GCE as well as Bi/SWNTs/GCE. The bare GCE showed the highest impedance, and Bi coated GCE dramatically decreased the impedance, indicating a favorable Bi coating for fast electron transfer. The presence of the carboxylic group-functionalized SWNTs further improved the electron transfer over the electrode surface, leading to much lower impedance, due to the good conductivity of SWNTs. After being wrapped by Bi film, the finally obtained Bi/SWNTs/GCE exhibited the lowest impedance as the synergistic effect of conductive Bi/SWNTs composite accelerated the speed of electron transfer to a great extent. In order to further verify this fact, regression plots were achieved for the IP spectra of both SWNTs and Bi/SWNTs modified electrodes (Fig. 1B). Clearly, Bi/SWNTs/GCE displayed a straightest IP curve, while a small arc in the real impedance range of 150-300 ohm were observed for SWNTs/GCE. By zooming in these two IP curves in the real impedance range of 100-200 ohm (Fig. 1B *inset*), most of data dots were easily seen stay right on the regression plot for Bi/SWNTs/GCE, but not for SWNTs/GCE, revealing the lowest impedance of Bi/SWNTs/GCE. This contributes to the remarkable increase in stripping signal towards Cr(VI) at Bi/SWNTs/GCE described below.

3.2 Surface morphological study

The morphologies of both Bi/GCE and Bi/SWNTs/GCE were examined in Fig. 2. Without SWNTs, the deposition of Bi formed rather coarse and inhomogeneous large Bi particles that were distributed on GCE surface without order (Fig. 2A). Even under the exact same deposition conditions, the morphology of the electrode surface coated by the produced Bi kept changing (Fig. 2C and D), revealing the poor reproducibility. As seen from the images taken with a regular optical microscope (zoom range of 1.0-7.0x), GCEs were apparently not coated by a real Bi film but many Bi particles in a wide zone of diameter, which may be responsible for the poor stability and reproducibility of Bi/GCE towards Cr(VI) detection. Bi(III) ion tends to be randomly adsorbed onto GCE surface without SWNTs, and the electrodeposition of Bi is prone to grow on Bi particles, finally forming coarse and inhomogeneous Bi particles coated electrode surface, which likely affects the

electrochemical performance of the obtained electrode. In comparison, Bi was well deposited on the surface in the presence of carboxylic group-functionalized SWNTs (Fig. 2B). The size of Bi particle was so greatly decreased that SWNTs were more like being coated by well-deposited Bi film. As SWNTs were oxidized before use and thus negatively charged, Bi(III) ion was easily attracted to the surface of SWNTs and distributed in good order due to the electrostatic interaction. During the Bi deposition, a uniform and smooth Bi film not large coarse Bi particle was eventually produced on SWNTs surface, providing more active sites and space for electrochemical reactions and thus favorable for the highly sensitive stripping determination of Cr(VI), which also provides good explanation for the lowest impedance of Bi/SWNTs/GCE shown in Fig. 1.

3.3 Hydrophilicity study of improved Bi film wrapped SWNTs/GCE

The hydrophilicity of the electrode surface plays an important role in the efficient aqueous detection of Cr(VI). So it is necessary to characterize the hydrophilicity of Bi/SWNTs/GCE with contact angle. Fig. 3 displays the hydrophilicity of bare electrode and electrodes modified with Bi particles, SWNTs and Bi/SWNTs composite, respectively. Poor hydrophilicity was observed at bare electrode with a contact angle of 84.1° and a slight decrease in contact angle (63.7°) was obtained after being coated by Bi particles, indicating that Bi particles were more hydrophilic than glassy carbon. This is also in good accordance with the increased ability of electron transfer for bare GCE after being coated by Bi particles. The introduction of carboxylic group-functionalized SWNTs offered Bi/SWNTs/GCE a much lower contact angle of 11.5° than Bi/GCE (63.7°), suggesting the extraordinarily compatibility for aqueous detection.

3.4 Comparison of catalytic AdCSV behavior between Bi/GCE and Bi/SWNTs/GCE and possible reaction mechanism for catalytic adsorptive stripping voltammetric determination of Cr(VI)

According to the measurement procedure, the catalytic AdCSV behaviors of Bi/GCE and Bi/SWNTs/GCE towards aqueous detection of 5 nM Cr(VI) were thus compared in a buffer solution (pH 6.0) containing 0.25 M KNO_3 and 0.1 M NaAc/HAc (Fig. 4A). Prior to the detection, the solution was first deaerated with pure N_2 for 5 min to remove the dissolved oxygen, and then DTPA was added to reach a final concentration of 5 mM. Cr preconcentration was carried out by holding the voltage at -0.8 V for 140 s while stirring. SWV was subsequently carried out in an unstirred solution by negatively scanning from -0.8 to -1.4 V. Obviously, a remarkably increased stripping signal was observed for Bi film wrapped SWNTs composite modified GCE as expected. Compared with Bi/GCE, the accelerated electron transfer (Fig. 1), the well-improved morphology (Fig. 2B) and the fairly good hydrophilicity (Fig. 3) of Bi/SWNTs/GCE were believed to make major contributions to the increase in stripping signal.

Catalytic AdCSV is well known to have high sensitivity and low detection limits in the aqueous determination of ultratrace-level Cr(VI) due to the accumulation of Cr(VI) on BiFE by potential-controlled adsorption and subsequent electrochemical reduction of the preconcentrated Cr(VI). In this procedure, the detection pH of 6.0 and Cr concentrations at nanomolar level were used respectively, so Cr(VI) is mainly present as HCrO_4^- [3] that is

first electrochemically driven to electrode surface at -0.8 V and reduced to Cr(III) on the BiFE followed by the *in-situ* formation of an electroactive Cr(III)-DTPA (1:1) complex $[Cr^{III}(H_2O)HY]^-$ after the addition of DTPA(H_5Y)[21]. The complex is then adsorbed onto the BiFE surface and further electrochemically reduced to $[Cr^{II}H_2Y]^-$, originating a well-defined reduction peak at ~ -1.1 V. Whereas, nitrate as an oxidant is added in the supporting electrolyte solution to oxidize the Cr(II) species back to Cr(III) reforming $[Cr^{III}(H_2O)HY]^-$ complex. A catalytic reaction cycle with Cr(III) as catalyst thus arises here which significantly increases the sensitivity. The freshly produced Cr(III) is 30 times more reactive to form Cr(III)-DTPA complex than existing Cr(III) in the solution[21], so Cr(VI) is the main contributor to the voltammetric response, leading to a Cr(III) interference-free detection of Cr(VI). The possible reaction mechanism during the catalytic AdCSV detection of Cr(VI) was assumed as follows:

Although the combination of the adsorptive accumulation with a catalytic action leads to a significant increase in the analytical signal and the sensitivity of Cr (VI) detection with BiFE, both the repeatability and reproducibility of BiFE are not satisfactory for the detection, which play a crucial role in the practical applications of the method. This might be ascribed to the inhomogeneity and random distribution of large Bi particles on GCE surface (Fig. 2A), which can easily come off the electrode surface after running several measurements due to the weak adhesion of Bi to glassy carbon[4] and less active sites available for electrochemical reaction, finally affecting the catalytic AdCSV performances of Bi/GCE towards Cr(VI). Meanwhile, as mentioned above, in the presence of SWNTs the behavior of Bi/SWNTs/GCE was dramatically improved. The explanation could be given from three aspects. Firstly, the large surface area of Bi/SWNTs obviously increased the actual area of the working electrode as reflected in Fig. 2B, providing more space for Cr preconcentration and electrochemical reactions. Secondly, the well-improved morphology of Bi exposed more active sites to the transition from Cr(VI) to Cr(III) and from Cr(III) to Cr(II). Thirdly, the synergic effect of Bi/SWNTs composite endowed the designed electrode more advantages over Bi/GCE such as the greatly enhanced ability of electron transfer, better compatibility for aqueous detection and more homogeneous active sites as well. All these improvements made the Bi/SWNTs/GCE characteristic of higher sensitivity, better stability and repeatability towards trace Cr (VI) determination.

On the other hand, cupferron, another ligand used for Cr(VI) determination[30], was chosen to further investigate the voltammetric behavior of Bi/SWNTs/GCE for Cr (VI) analysis. As seen in Fig. 4B, a voltammetric peak at about -0.94 V was observed for 5 nM Cr(VI) determination with both Bi/GCE and Bi/SWNTs, while the peak current remarkably increased using the improved Bi film wrapped SWNTs composite based sensor. This phenomenon further approved the fact that the presence of SWNTs could enhance the analytical performance towards Cr (VI) determination by improving the quality of Bi deposition. Whereas, DTPA was utilized as an ideal complexing ligand to form complex with the freshly reduced Cr(III) from Cr(VI) in this work due to the higher peak current and the more well-defined peak as compared with Cr-cupferron complex based sensor.

3.5 Study of interference

For the Cr(VI) analysis in real samples, the elimination of interferences is pretty challenging. With the aim to evaluate the selective performance of Bi/SWNTs/GCE toward Cr(VI) determination, the effects of coexisting anions or cations such as In^{2+} , Cr^{3+} , Pb^{2+} , Mg^{2+} , Fe^{3+} , Cu^{2+} , Co^{2+} , Ce^{3+} , Ag^{+} , Sn^{2+} , Zn^{2+} , MnO_4^{-} and MoO_4^{2-} on the stripping signal of Cr(VI) detection were examined (Fig. 5). The voltammetric response of the designed electrode toward 20 nM Cr(VI) was first measured, and 500-fold excess of the coexisting ions were subsequently added into the Cr(VI)-containing solution. It was found that in the presence of much excess Cr(III) no obvious decrease in peak current was observed, further affirming that this fabricated sensor could run a Cr(III) interference-free detection of Cr(VI) [30]. Furthermore, the addition of other foreign ions did not interfere in Cr(VI) determination either. Although there was a slight decrease in peak current in the presence of MnO_4^{-} and MoO_4^{2-} , probably due to the physical adsorption and the large size of these two ions, the current difference was below 5% and considered acceptable. The desired high selectivity towards trace Cr(VI) detection was thus offered by the well-designed Bi/SWNTs/GCE with potential application for Cr (VI) analysis in real samples.

3.6 Analytical performance for the determination of Cr(VI)

The performance of Bi/SWNTs/GCE toward the detection of Cr(VI) at different levels was tested by catalytic AdCSV in detail to evaluate the reliability of the proposed method. Fig. 6 shows the current response of the designed electrode toward Cr(VI) in the concentration range from 0 to 25 nM. A well-defined voltammetric peak at -1.06 V appeared and the peak current proportionally increased with the increasing Cr(VI) concentration, noting that a slight positive shift (~ 40 mV) of the peak potential was observed by comparison with previous report for Cr (VI) detection using Bi/GCE[21]. This was not surprising since this shift was more likely caused by the modification of Bi/SWNTs composite which might affect the overpotential for the reduction of $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})\text{HY}]^{-}$ to $[\text{Cr}^{\text{II}}\text{H}_2\text{Y}]^{-}$. The calibration plot showed a good linear relationship with the regression equation of $i = 1.30c + 2.96$, where the peak current ($i, \mu\text{A}$) was used as a function of the Cr(VI) concentration (c , nM) (Fig. 6 inset). The correlation coefficient was 0.998 and the detection limit (LOD) was calculated to be 0.036 nM according to a ratio of signal to noise of 3, which was lower than those of previously reported Cr(VI) detection using electrochemical techniques[22,23,27], demonstrating the high sensitivity of the proposed method. This is perhaps because more active sites over the Bi/SWNTs surface were available for the electrochemical reduction

from $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})\text{HY}]^-$ to $[\text{Cr}^{\text{II}}\text{H}_2\text{Y}]^-$, resulting in a wide detection range of Cr(VI) as well as a fairly low LOD.

3.7 Reproducibility, repeatability and the life time of the proposed sensor

The preparation of the improved Bi film wrapped SWNTs composite modified GCE is controllable and simple, thus it can be produced in batch. Five independently prepared sensors for catalytic AdCSV determination of Cr(VI) based on Bi/SWNTs/GCE showed a RSD of 3.2% for measurements of 5 nM Cr(VI), indicating a good fabrication reproducibility. At the same time, the regeneration of sensors showed a good repeatability with a RSD of 2.5% ($n=5$) for inter-group detection of Cr(VI). In comparison, the RSDs for outer and inter-group measurements of 5 nM Cr(VI) were as high as 11.5 and 9.7 % with Bi/GCE, implying the designed sensor was more reproducible and reliable for trace Cr(VI) detection. Such good reproducibility and repeatability could be ascribed to both the improved morphology of Bi film and the synergistic effect of Bi wrapped SWNTs composite. The designed sensor, once made, could be used for the continuously repeated measurements without obvious decrease in stripping signal (Fig. 7A), but for the Bi film modified electrode, the stripping signal clearly decreased after each run (Fig. 7B), causing poor repeatability. The long-term stability is also a significant parameter for evaluating the performance of the sensor. A response current of 20 nM Cr(VI) was determined every other two days (Fig.8). The results showed that the response signal was 90% of its initial value after being stored at 4 °C for 3 weeks, indicative of the good stability of the sensor.

3.8 Sample analysis

Considering the aforementioned good properties of the Bi/SWNTs composite based sensor, the river samples collected from the Huangpu River, in Shanghai, China, were selected to test its reliability and practicality for Cr(VI) determination. Recovery experiments were carried out with standard addition of 3 and 8 nM Cr(VI) in the 10 times diluted river samples. The typical catalytic AdCSV signals for Cr(VI) determination in the diluted river samples were observed with Bi/SWNTs/GCE in Fig.9. The original concentration of Cr(VI) in the river samples were measured to be 62.4 ± 2.1 nM. A RSD of 3.4% and good recoveries of 98.5% and 102% for the additions of 3 and 8 nM Cr(VI), respectively, were obtained without interference, revealing that the new method was highly selective, sensitive, reliable and practical. It can be potentially used for direct analysis of other Cr(VI) contaminated real samples.

4 Conclusion

The high-quality Bi film was successfully achieved by introducing carboxylic-group functionalized SWNTs as suitable substrate for Bi deposition in this work. The electrostatic interaction between negatively charged SWNTs and Bi(III) cation makes major contributions to the improvements in Bi film such as the enhanced electron transfer, the larger surface area and the better morphology as well as the well-improved hydrophilicity. The effect of electrostatic interaction on the improvement of metal film deposition has been further approved as well in our currently ongoing research. Just by reducing Bi(III) randomly adsorbed on GCE surface, rather coarse and inhomogeneous Bi particles not a real

Bi film were produced indeed, which was considered to have negative effect on the electrochemical behaviors of Bi/GCE. In comparison, several advantages like wide linear range, very low detection limit and good reproducibility and repeatability were achieved using the well-deposited Bi film wrapped SWNTs composite modified GCE which was successfully applied to detect Cr(VI) in the collected river samples. Therefore, the proposed methodology appears to be very promising as the basis of a highly sensitive, selective and reliable voltammetric procedure for Cr(VI) detection at trace level, and can find potential application in the electroanalysis of other environmentally toxic metal ions.

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References

- [1]. Gómez V, Callao MP. TRAC-Trend. Anal. Chem. 2006; 25:1006–1015.
- [2]. Svancara I, Foret P, Vytras K. Talanta. 2004; 64:844–852. [PubMed: 18969679]
- [3]. Kachosangi RT, Compton RG. Sensor. Actuat. B-Chem. 2013; 178:555–562.
- [4]. Jorge EO, Rocha MM, Fonseca ITE, Neto MMM. Talanta. 2010; 81:556–564. [PubMed: 20188962]
- [5]. Fraústo da Silva, JJR.; Williams, RJP. The Biological Chemistry of the Elements-The Inorganic Chemistry of Life. first ed. Clarendon Press; Oxford: 1994. p. 541
- [6]. Sereshti H, Khojeh V, Samadi S. Talanta. 2011; 83:885–890. [PubMed: 21147333]
- [7]. Cespon-Romero RM, Yebra-Biurrun MC, Bermejo-Barrera MP. Anal. Chim. Acta. 1996; 327:37–45.
- [8]. Recommendations. second ed. Vol. 1. WHO; Geneva: 1993. Guidance for Drinking Water Quality; p. 45-46.
- [9]. Jena BK, Raj CR. Talanta. 2008; 76:161–165. [PubMed: 18585258]
- [10]. Zazoua A, Kherrat R, Samar MH, Errachid A, Jafferzic-Renault N, Bessueille E, Léonard D. Mater. Sci. Eng. C. 2008; 28:1014–1019.
- [11]. Dobrowolski R, Pawlowske-Kapusta I, Dobrzynska J. Food Chem. 2012; 132:597–602.
- [12]. López-García I, Briceo M, Vicente-Martínez Y, Hernández-Córdoba M. Talanta. 2013; 115:166–171. [PubMed: 24054574]
- [13]. Wang L, Wang J, Zheng Z, Xiao P, Hazard J. Mater. 2010; 177:114–118.
- [14]. Peräniemi S, Ahlgrén M. Anal. Chim. Acta. 1995; 315:365–370.
- [15]. Cieslak W, Pap K, Bunch DR, Reineks E, Jackson R, Steinle R, Wang S. Clin. Biochem. 2013; 46:266–270. [PubMed: 23127384]
- [16]. Weldy E, Wolff C, Miao ZX, Chen H. Sci. Justice. 2013 available online.
- [17]. Singh AK, Gupta VK, Gupta B. Anal. Chim. Acta. 2007; 585:171–178. [PubMed: 17386662]
- [18]. Turyan I, Mandler D. Anal. Chem. 1997; 69:894–897. [PubMed: 21639227]
- [19]. Hanrahan G, Patil DG, Wang J. J. Environ. Monit. 2004; 6:657–664. [PubMed: 15292947]
- [20]. Miao YQ, Wang H, Shao YY, Tang ZW, Wang J, Lin YH. Sensor. Actuat. B. 2009; 138:182–188.
- [21]. Sander S, Navrtil T, Novotny L. Electroanalysis. 2003; 15:1513–1521.
- [22]. Lin L, Lawrence NS, Thongngamdee S, Wang J, Lin Y. Talanta. 2005; 65:144–148. [PubMed: 18969776]
- [23]. Yong L, Armstrong KC, Dansby-Sparks RN, Carrington NA, Chambers JQ, Xue ZL. Anal. Chem. 2006; 78:7582–7587. [PubMed: 17073430]

- [24]. Domínguez-Renedo O, Ruiz-Espelt L, García-Astorgano N, Arcos-Martínez MJ. *Talanta*. 2008; 76:854–858. [PubMed: 18656669]
- [25]. Ouyang RZ, Bragg SA, Chambers JQ, Xue ZL. *Anal. Chim. Acta*. 2012; 722:1–7. [PubMed: 22444528]
- [26]. Kreft GL, de Braga OC, Spinelli A. *Electrochim. Acta*. 2012; 83:125–132.
- [27]. Zhang Q, Zhong SW, Su JL, Li XJ, Zou H. *J. Electrochem. Soc.* 2013; 160:H237–H242.
- [28]. Tsai MC, Chen PY. *Talanta*. 2008; 76:533–539. [PubMed: 18585318]
- [29]. Wang J, Lu J, Hocevar SB, Farias PAM, Ogorevc B. *Anal. Chem.* 2000; 72:3218–3222. [PubMed: 10939390]
- [30]. Chatzitheodorou E, Economou A, Voulgaropoulos A. *Electroanalysis*. 2004; 16:1745–1754.
- [31]. Grabarczyk M. *Electroanalysis*. 2008; 20:2217–2222.
- [32]. Li Y, Xue H. *Anal. Chim. Acta*. 2001; 448:121–134.
- [33]. Boussemart M, van den Berg CMG, Ghaddaf M. *Anal. Chim. Acta*. 1992; 262:103–115.
- [34]. Domínguez O, Alonso MA, Arcos MJ. *Electroanalysis*. 2002; 14:1083–1089.
- [35]. Bobrowski A, Bas B, Dominik J, Niewiara E, Szalinska E, Vignati D, Zarebski J. *Talanta*. 2004; 63:1003–1012. [PubMed: 18969527]
- [36]. Grabarczyk M, Kaczmarek L, Korolczuk M. *Electroanalysis*. 2007; 19:1183–1188.
- [37]. Wang J, Wang J, Lu J, Tian B, MacDonald T, Olsen K. *Analyst*. 1999; 124:349–352.
- [38]. Brett CMA, Filipe OMS, Neves CS. *Anal. Lett.* 2003; 36:955–969.
- [39]. Rehacek V, Hotovy I, Vojs M, Kups T, Spiess L. *Electrochim. Acta*. 2012; 63:192–196.
- [40]. Romann T, Lust E. *Electrochim. Acta*. 2010; 55:5746–5752.
- [41]. Zhang Q, Li XJ, Shi H, Hong Z, Yuan ZB. *Electrochim. Acta*. 2010; 55:4717–4721.
- [42]. Nunes LMS, Faria RC. *Electroanalysis*. 2008; 20:2259–2263.
- [43]. Barrera-Díaz CE, Lugo-Lugo V, Bilyeu B. *J. Hazard. Mater.* 2012; 223-224:1–12. [PubMed: 22608208]

Fig. 1.

(A) EIS measurements of 0.01 M $\text{Fe}(\text{CN})_6^{3-/4-}$ and 0.1 M KCl at bare GCE, Bi/GCE, SWNTs/GCE, Bi/SWNTs/GCE and (B) EIS comparison between Bi/GCE and Bi/SWNTs/GCE in the real impedance range of 100-500 Hz by doing curve regression.

Inset: Zoomed-in curves of Bi/GCE and Bi/SWNTs/GCE in the real impedance range of 100-200 Hz.

Fig. 2.

SEM images of (A) Bi/GCE; (B) Bi/SWNTs/GCE, and images for surface morphologies of (C) and (D) Bi/GCE taken using a regular optical microscopy (zoom range of 1.0-7.0x). Note: Bi deposition in photos (C) and (D) was carried out under the exact same conditions.

Fig. 3.

Contact angles of bare electrode, and electrodes modified with Bi particles, SWNTs and Bi/SWNTs composite, respectively.

Fig. 4.

Comparison of catalytic AdCSV behaviors of Bi/GCE and Bi/SWNTs/GCE towards 5 nM Cr (VI) detection using (A) DTPA and (B) cupferron as complex ligands.

Fig. 5.

Voltammetric responses of Bi/SWNTs/GCE toward 20 nM Cr(VI) with and without 500-fold excess of coexisting ions. a: HCrO_4^- , b: Pb^{2+} , c: Sn^{2+} , d: Mg^{2+} , e: In^{2+} , f: Co^{2+} , g: Ce^{3+} , h: Cr^{3+} , i: Fe^{3+} , j: Cu^{2+} , k: MnO_4^- , l: Ag^+ , m: MoO_4^{2-} , n: Zn^{2+} , o: Cd^{2+}

Fig. 6.

Catalytic AdCSV performance and the corresponding calibration plot (*inset*) of Bi/SWNTs/GCE toward Cr(VI) determination in the concentration range from 0 to 25 nM. Error bar: $n=3$.

Fig. 7.

Variation of peak current of (A) Bi/SWNTs/GCE and (B) Bi/GCE towards 5 nM Cr(VI) during five continuously repeated measurements (R1-R5, R: repeat).

Fig. 8.

Changes of stripping signal at Bi/SWNTs/GCE with the store day toward 20 nM Cr(VI) determination.

Fig. 9.

Catalytic AdCSV performance of Bi/SWNTs/GCE toward Cr(VI) determination in the diluted river sample. Addition of Cr (VI) in the river sample a: 0; b: 3 nM; c: 8 nM.

Illustration of the fabrication of Bi film wrapped SWNTs composite modified GCE and the mechanism of the preconcentration and determination of Cr(VI) by the electrode.