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Catalytic adsorptive stripping determination of trace chromium based on the bismuth/MWCNTs modified electrode

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Abstract: A sensitive Bi/MWCNTs (multi-walled carbon nanotubes) composite film modified electrode was fabricated by two-step electrodeposition. First, the MWCNTs were electrodeposited instead of dropping coated on the glass carbon electrode(GCE), and the bismuth film was then deposited on the MWCNTs/GCE. A protocol used for the determination of total chromium and hexavalent chromium in water by square wave cathodic adsorptive voltammetry in the presence of cupferron (N-nitroso-N-phenylhydroxylamine ammonium salt) was proposed. In the presence of cupferron, Cr(Ⅲ) can form the complex with cupferron and be accumulated on the surface of the modified electrode by adsorption at a potential of −0.35 V, and then is reduced with the cathodic scan from −0.35 V to −1.10 V. An accumulation time of 2 min results in a detection limit of 0.05 μg/L Cr(Ⅵ) and a relative standard deviation of 5.2% (n=75) for 10 μg/L. Application to river water samples is demonstrated. The total chromium can be directly determined by standard addition of Cr(Ⅲ) or Cr(Ⅵ); the Cr(Ⅵ) can be separated with Cr(Ⅲ) by using an anion trapping column and then determined by standard addition of Cr(Ⅵ). The results are consistent with those detected by ICP-MS (inductive coupled plasma mass spectrometry). The attractive behavior of the new "mercury-free" chromium sensor holds great promise for on-site environmental and industrial monitoring of chromium.

Key words: Bi/MWCNTs (multi-walled carbon nanotubes) modified electrode; square wave cathodic adsorptive voltammetry; chromium; speciation analysis; cupferron

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铋膜/碳纳米管修饰电极催化吸附溶出伏安法测定痕量的铬

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摘要:通过两步电沉积方法制备了一种灵敏的铋/多壁碳纳米管复合膜修饰电极.首先用电解代替滴涂法将

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多壁碳纳米管沉积到玻碳电极表面，然后再把铋膜沉积到多壁碳纳米管上.提出了利用方波阴极吸附溶出伏安法分别测定水中总铬和六价铬的分析方法.在铜铁灵试剂的存在下，Cr(Ⅲ)和铜铁灵形成的络合物在－0.35 V时通过吸附富集在修饰电极的表面，然后在阴极扫描(－0.35～－1.10 V)过程中被还原.可以利用Cr(Ⅲ)或Cr(Ⅵ)的标准加入法直接测定水中总铬含量，也可以利用阴离子富集柱将Cr(Ⅵ)与Cr(Ⅲ)分离后单独测定水中Cr(Ⅵ)含量，分析结果与电感耦合等离子体质谱法(ICP-MS)相吻合.本法的检测下限在富集时间2 min时为0.05 μg/L，相对标准偏差为5.2%(n=75).

关键词：铋/多壁碳纳米管(Bi/MWCNTs)修饰电极；方波阴极吸附伏安法；铬；形态分析；铜铁灵

0 Introduction

Trivalent chromium is an important microelement for plant and animal nutrition and essential to the maintenance of glucose as well as for the lipid and protein metabolism. With regard to human health, trivalent chromium is a required nutrient, with 50 mg to 200 mg per day recommended for adults[1]. On the contrary, hexavalent chromium is toxic and carcinogenic[2], leading to lung cancer, skin allergy and probably also to asthma and renal diseases. A toxic effect for the biological systems is attributed to the ability of hexavalent chromium to migrate across the cell membrane, thus enhancing the intracellular chromium concentration. Major sources of chromium contamination are metallurgy, electroplating industry, pigment production, tannery, mining and refractory materials. The safe guideline value recommended by World Health Organization (WHO) for Cr(Ⅵ) in groundwater is 50 μg/L. Hence, the determination of chromium traces as well as its chemical speciation in environmental samples is very important because of the environmental impact, toxicity and bioavailability of chromium[3]. Due to a rather low chromium concentration and the complexity of the sample matrix, sensitive and accurate instrumental methods are required.

Many analytical procedures using different techniques have been reported in literature to quantify chromium species, including ultraviolet and visible spectrophotometry[4], high performance liquid chromatography[5], chemiluminescence[6], atomic absorption spectroscopy (AAS)[7] and inductive coupled plasma mass spectrometry (ICP-MS)[8]. Among them, AAS and ICP-MS are the most frequently employed. In general, previous treatment of samples involving pre-concentration and separation schemes is required, such as chromatography[9], co-precipitation[10], extraction[11], electrophoresis or ion-exchange resins[12]. However, these methods are not yet ready to be adapted to routine analysis, since they are somewhat complicated and time-consuming, and usually involve expensive instrumentation.

Electroanalytical techniques have frequently been used for the determination of chromium in various matrices. Voltammetric methods have been described in literature for the detection of Cr(Ⅵ) using metallic nanoparticle modified carbon screen-printed electrodes[13], pyridinium-based sol-gel film[14], AuNPs-ITO electrode[15], carbon paste electrode modified with surfactants[16], self-assembled gold nanoparticles[17], nano-sized gold particles[18], self-assembled monolayer modified electrode[19] and gold electrodes[20] etc.

The adsorptive voltammetry offers a highly sensitive detection of chromium in connection to low-cost portable instrumentation[21]. For this purpose, the voltammetric measurements of chromium by adsorptive collection of chromium complexes with different ligands were reported, such as pyrocatechol violet[22], hydroxyethyl-ethylenediaminetriacetic acid (HEDTA)[23], ammonium pyrrolidine dithiocarbamate[24], ethylenediaminetetraacetic acid (EDTA)[25], triethylenetetraaminehexaacetic acid (TTHA)[26],

diethylenetriammine pentaacetic acid (DTPA)[27] and cupferron[28]. Two basic electrode systems, the mercury-film electrode (MFE) and hanging mercury drop electrode (HMDE), are generally used for adsorptive voltammetric determination of chromium. Using DTPA as a complexing agent, Li et al.[29] developed an entire protocol for chromium speciation analysis at subnanomolar level, which was applied to natural samples. Dominguez et al.[26] used HMDE for the detection of chromium in wine using different complexing agents (TTHA, DTPA and cupferron). Korolczuk et al.[30] used cupferron for selective determination of Cr(Ⅵ) in water samples on HMDE. In 2008, they[25] made a better research on speciation analysis of chromium by adsorptive voltammetry in tap and river water samples. In other works, Wang et al.[28] obtained a lower detection limit of 1.0 ng · L^{-1} with a preconcentration time of 1 min. Brett et al.[31] detected Cr(Ⅵ) with the aid of batch injection analysis with a LOD (limit of detection) of 32 nmol/L.

Yet, because of the toxicity of mercury, new alternative electrode materials with a similar performance are highly desired, particularly for meeting the growing demands for on-site environmental monitoring of trace chromium. Bismuth is an environment-friendly element, with very low toxicity, and a widespread pharmaceutical use. The applicability of bismuth electrodes for adsorptive voltammetric studies has been reported to trace measurements of trace nickel[32] and cobalt[33] in the presence of dimethylglyoxime. The suitability of the bismuth film electrode (BFE) for adsorptive cathodic stripping voltammetry (AdCSV) measurements of trace Cr(Ⅵ) was demonstrated, using cupferron[34] and diethylenetriamine pentaacetic acid (DTPA)[35] as complexing agents. The results obtained by Jorge et al.[36] at a rotating disc bismuth film electrode demonstrated a better stripping performance for the BFE in comparison with the MFE.

Carbon nanotubes (CNTs), as a new form of carbon, becomes the focus of current research due to their special mechanical and electronic properties[37]. Multi-walled carbon nanotubes (MWCNTs) are an excellent electrode material for electrocatalysis because of their low electrical resistance and high specific surface area. There are many papers about the application of CNTs in electrochemical sensors. For example, Liu et al.[38] reported that CNTs nanoelectrode array coating with bismuth film offered an excellent electrochemical sensing platform for voltammetric analysis of trace cadmium and lead. Hwang et al.[39] detected trace lead, cadmium and zinc by anodic stripping voltammetry using a bismuth-modified screen-printing carbon nanotube electrode. Dropping coated is the common method for CNTs modified electrode, but is time-consuming and of poor reproducibility.

So far, there has been no report about Bi/MWCNTs modified electrode for detection of Cr(Ⅵ) with square wave cathodic adsorptive voltammetry (SWCAdV). Here, the MWCNTs were directly electrodeposited on the glass carbon electrode instead of the conventional method of dropping coated. A highly sensitive reduction adsorptive procedure for determining trace chromium at the Bi/MWCNTs film modified electrode was proposed. Cupferron was selected as complexing agent due to the increased sensitivity it exhibited in determination of chromium compared to other ligands such as DTPA[40].

1 Experimental

1.1 Apparatus and reagents

Electrochemical measurements were carried out using LK2005 electrochemical work station (Tianjin LANLIKE Co., China) with a conventional three-electrode cell. The Bi/MWCNTs modified glass carbon electrode (3 mm in diameter) served as a working electrode, a platinum wire and a saturated calomel electrode (SCE) were used as the auxiliary electrode and

reference electrode, respectively. pH measurements were performed with a pH meter (Leici brand). Ultrasonic cleaning was carried out using an ultrasonic cleaner (40 kHz, Kunshan ultrasonic instrument company). The Schottky field emission scanning electron microscope (SEM), model SIRION 200, was used for characterization of the modified electrodes. The inductive coupled plasma mass spectrometry (ICP-MS), model Plasma Quad 3, was employed for control experiments. All glassware was soaked in 3 mol·L^{-1} nitric acid and rinsed several times with deionized water prior to use.

The carboxyl multi-walled carbon nanotubes (MWCNT-COOH) were purchased from Nanjing XFNano Material Tech Co., Ltd. All the other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. All solutions were prepared with deionized water obtained with a laboratory water purification system (GUO ZHI YUAN). Nitrogen (99.99%) was used to remove dissolved oxygen. Standard solutions of Cr(Ⅵ) and Cr(Ⅲ) were made by the dissolution of $K_2Cr_2O_7$ and $Cr(NO_3)_3 \cdot 9H_2O$ in water. A 0.1 mol·L^{-1} stock solution of cupferron was prepared daily by dissolving cupferron directly in water and stored in a refrigerator. The bismuth plating solution was 100 mg·L^{-1} Bi(Ⅲ) in 1.0 mol·L^{-1} acetate buffer (pH4.5). A 0.2 mol·L^{-1} acetate buffer solution was served as the supporting electrolyte, and its pH was adjusted to the desired value with ammonia.

1.2 Procedures

1.2.1 Preparation of the Bi/MWCNTs modified electrode

Prior to modification, the GCE (glass carbon electrode) was abraded with fine SiC paper, polished carefully with aqueous slurries of alumina powder of 1.0, 0.30 and 0.05 μm, successively, then sonicated for 3 min in nitric acid (1∶1), ethanol and water, respectively, and finally dried in N_2 blowing. Take appropriate amount of carboxyl MWCNTs in 0.2 mol·L^{-1} NaH_2PO_4-Na_2HPO_4 buffer solution (pH=8.0) to prepare the suspension solution with MWCNTs concentration of 0.15 g·L^{-1} by ultrasonication. The MWCNTs/GCE was prepared by cyclic potential scanning from 1.0 V to −1.2 V in the MWCNTs suspension solution at the scan rate of 50 mV·s^{-1} for 12 cycles. And then bismuth was further electrodeposited onto the MWCNTs/GCE at the potential of −1.0 V for 300 s with 100 mg·L^{-1} bismuth nitrate in 1 mol·L^{-1} acetate buffer solution under being stirred. After modification, the electrode was thoroughly rinsed with deionized water and kept at room temperature for further use.

1.2.2 SWCAdV measurements of chromium

For SWCAdV measurements of chromium, the supporting electrolyte, acetic acid solution, containing 0.3 mmol·L^{-1} cupferron, was purged with nitrogen for 8 min. The accumulation potential (usually −0.35 V) was applied to the modified electrode while the solution was stirred. When the accumulation was finished, the stir was stopped and after 15 s, the cathodic square wave scan voltammogram was recorded, with a frequency of 10 Hz, scan increment of 9 mV, and square wave amplitude of 30 mV. The scan was terminated at −1.2 V. Between successive measurements, a pre-cleaning step was applied at an applied potential of −1.20 V for 15 s to guarantee the efficient removal of the cupferron complex from the surface by desorption. Nitrogen was passed over the solution throughout the operation.

1.2.3 Respective detection of total chromium and Cr(Ⅵ) in water samples

Three real water samples (Hefei, China) were collected respectively from Glasses Lake in the campus of USTC, Daoxianglou Lake and Nanfeihe River, respectively, filtered through a 0.45 μm cellulose acetate syringe filter. For the determination of total Cr ($C_{Cr\,(total)}$), the samples were mixed with equal volumes of acetate buffer, and then quantified by means of the increment of the peak current with addition of Cr(Ⅵ) or Cr(Ⅲ)

standard solution. For Cr(Ⅵ), the water samples were flowing through an anion trapping column to separate Cr(Ⅵ) with Cr(Ⅲ), Cr(Ⅵ) was then eluted and diluted to an appropriate concentration with acetate buffer, after which Cr(Ⅵ) was detected by standard addition method.

2 Results and discussion

2.1 Characterization of the modified electrode

Fig. 1 shows the SEM micrographs of the electrodeposited carboxyl MWCNTs (a), bismuth film (b) and Bi/MWCNTs (c) composite on the glass carbon electrode. From Fig. 1(a), it can be seen that the MWCNTs were successfully deposited on the GCE by direct electrochemical deposition, which was never reported in literature. This method is simple, fast and reproducible compared with the dropping coated method. The bismuth film consisted of two forms of deposition, the granular and leaves-like (Fig. 1(b)). But, when bismuth was deposited on MWCNTs, the deposits were the leaf-shaped (Fig. 1(c)), whose shape not only increased the efficient active surface area of the modified electrode, but also enhanced the surface conductivity due to the co-existence of MWCNTs.

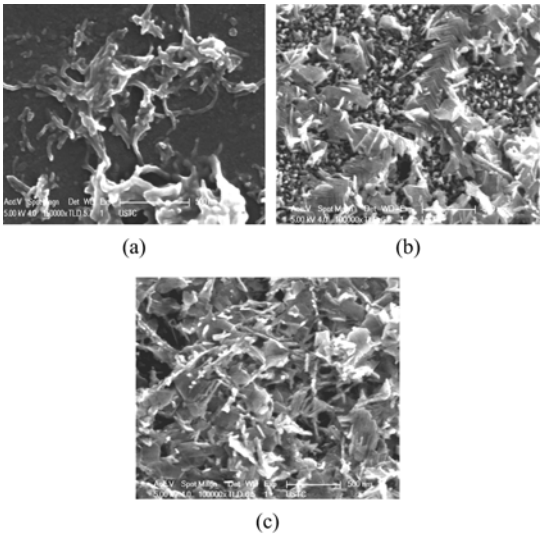
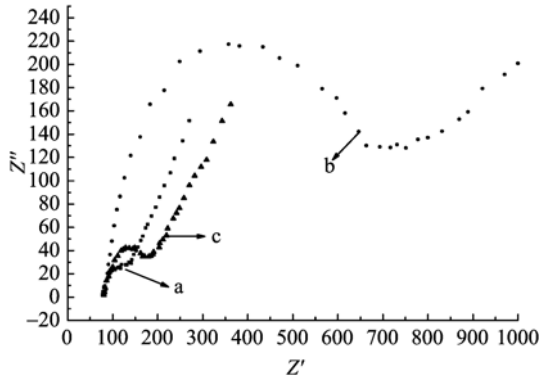


Fig. 1 Typical SEM images of the electrochemical deposited MWCNTs film (a), Bi film (b), and Bi/MWCNTs composite film (c)

Electrochemical impedance spectroscopy (EIS) is an effective method for probing the interfacial properties of the surface modified electrodes. The corresponding Nyquist diagrams for different modified electrodes are shown in Fig. 2. In EIS, the diameter of the semicircle is equivalent to the charge transfer (CT) resistance (R_{ct}), which controls the electron transfer kinetics of the probe at the electrode surface. In Fig. 2, curve a shows the EIS of the MWCNTs/GCE. The semicircle is very small because of the good conductivity of MWCNTs. As can be seen from curve b, the Bi film/GCE displays a large CT resistance indicating that the bismuth particles layer impeded the charge transfer of the electrochemical probe. From curve c, the resistance of the Bi/MWCNTs/GCE is a little larger than MWNTs/GCE but much smaller than the Bi film/GCE indicating the lower CT resistance of the composite film due to the introduction of MWCNT.



curve a: MWCNTs/GCE, curve b: Bi film/GCE, and curve c: Bi/MWCNTs/GCE

Fig. 2 Nyquist plots of the different modified electrodes in 5.0 mmol · L^{-1} $K_3Fe(CN)_6$ + 5.0 mmol · L^{-1} $K_4Fe(CN)_6$ solution containing 0.1 mol · L^{-1} KCl

2.2 Adsorptive behavior of chromium-cupferron complex at the Bi/MWCNTs/GCE

The reductive complexation adsorption of Cr(Ⅵ) with cupferron at the Bi/MWCNTs/GCE might be spontaneous. It is shown in Fig. 3, in the presence of only cupferron, no reduction peak appeared in the cathodic scan from −0.35 to

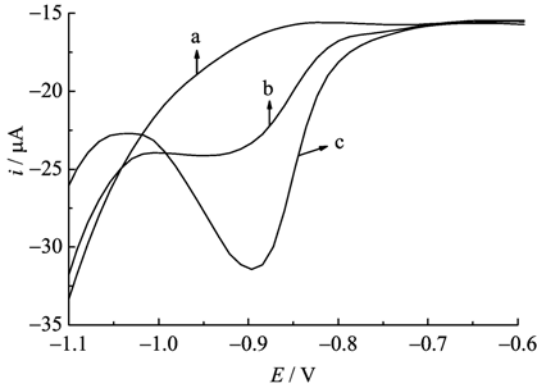
−1.10 V (Fig. 3, curve a). But with addition of Cr(Ⅵ), there was a reduction peak observed at ca. −0.90 V in direct scan (Fig. 3, curve b). The peak current was substantially enhanced under a short accumulation time of 60 s (Fig. 3, curve c). This reduction peak could be attributed to the reduction of the central metal (Cr(Ⅲ)) in the complex rather than the ligand[28]. The ECEC' mechanism of the reduction of Cr(Ⅵ) at the Bi/MWCNTs/GCE can be suggested as follows.

$$Cr(Ⅵ) + 3e^- \rightarrow Cr(Ⅲ) \quad (1)$$

$$Cr(Ⅲ) + (cupferron)_{ad} \rightarrow [Cr(Ⅲ)\text{-}cupferron]_{ad} \quad (2)$$

$$[Cr(Ⅲ)\text{-}cupferron]_{ad} + e^- \rightarrow [Cr(Ⅱ)\text{-}cupferron]_{ad} \quad (3)$$

$$[Cr(Ⅱ)\text{-}cupferron]_{ad} + cupferron \rightarrow [Cr(Ⅲ)\text{-}cupferron]_{ad} + [cupferron]_{red} \quad (4)$$



curve a: without chromium, curve b: in presence of 15 μg/L Cr(Ⅵ) without accumulation, and curve c: in presence of 15 μg/L Cr(Ⅵ) with an accumulation time of 60 s. The supporting electrolyte: 0.1 mol·L^{-1} acetate buffer (pH6.0) + 0.3 mmol·L^{-1} cupferron. Accumulation potential: −0.35 V, equilibrium time: 15 s; square wave amplitude: 30 mV; scan increment: 9 mV; square wave frequency: 10 Hz.

Fig. 3 Typical square wave cathodic adsorptive voltammograms of chromium

Apparently, cupferron serves not only as the complexing agent but also as an oxidizing agent in a manner analogous to its role in the adsorptive-catalytic procedure for molybdenum reported by Kui et al.[41]. Obviously, according to the ECEC' mechanism, Cr(Ⅵ) was first reduced to Cr(Ⅲ) at the accumulation potential, and then formed a complex with the adsorbed cupferron. For Cr(Ⅲ), the Cr(Ⅲ) in the bulk solution complexed with cupferron adsorbed on the electrode surface, and then were catalytically reduced, so that Cr(Ⅲ) was accumulated at the electrode surface and produced the same response as Cr(Ⅵ)[28]. Subsequent work employed Cr(Ⅵ) standard solution.

The composition of the supporting electrolyte and solution acidity seriously influenced the adsorption of Cr(Ⅲ)-cupferron complex. There was no peak appearing in the phosphate buffer solution or citrate buffer solution due to the complexation ability of the acid groups. And a small cathodic peak was obtained using ammonia buffer instead of acetate buffer as the supporting electrolyte in the same acidity. As a result, acetate buffer solution was employed in this study. The effect of the solution pH on the peak height and peak shape was also evaluated in the range of pH3.0 to pH8.0. Experiments show that no peak appeared while pH was lower than 2.0 due to the intense acid effect of cupferron as well as the bismuth film damage in strong acid solution. When pH was higher than 9.0, no peak appeared due to the extra-low hydrogen ion concentration required in the reduction of Cr(Ⅵ). Along with the solution pH changing from 3.0 to 8.0, the peak potential linearly and negatively shifted with a slope of 0.059 7 V/pH, and a regression equation was obtained as $E_p = -0.0597\text{pH} - 0.544$ with a correlation coefficient of 0.998 8. And it was shown that the peak height and peak shape were the best at pH=6.0.

The next influencing factor is the concentration of cupferron used. As expected, the peak current was dependent strongly on the cupferron concentration. It can be seen from Fig. 4(a) that the peak height was increased continuously with the ligand concentration increasing from 0.05 mmol·L^{-1} to 0.5 mmol·L^{-1}, but the peak was of a bad defined shape when the concentration of cupferron was bigger than 0.3 mmol·L^{-1}, so the concentration of cupferron was

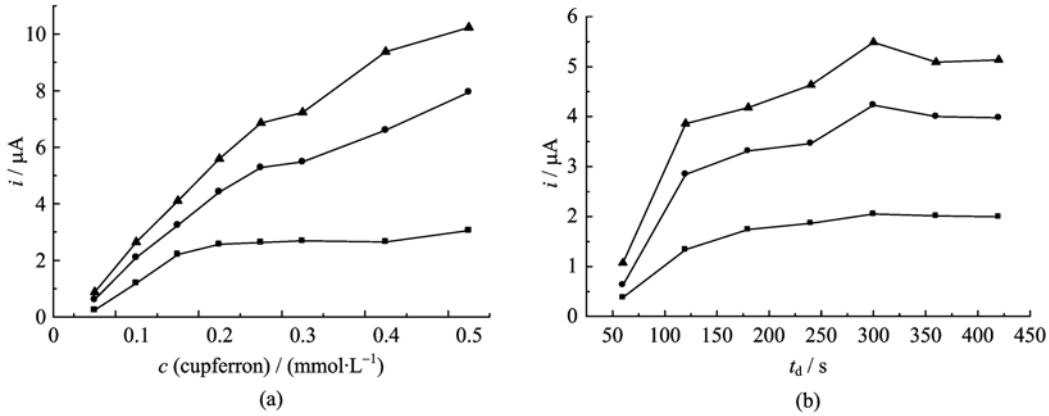
chosen as 0.3 mmol • L^{-1} for chromium detection.

Another influencing factor is the preparation of the bismuth film. The thickness of the bismuth film was relative to both the concentration of bismuth ion contained in plating solution (100 mg/L here) and the deposition time. The influence of the film deposition time (t_d) on the adsorptive cathodic peak current is shown in Fig. 4 (b) for different concentrations of chromium. The peak height increased fast with the deposition time increasing up to 300 s, and then increased slightly. Here 300 s was chosen as best deposition time for the preparation of bismuth film.

2.3 Optimization of experimental parameters

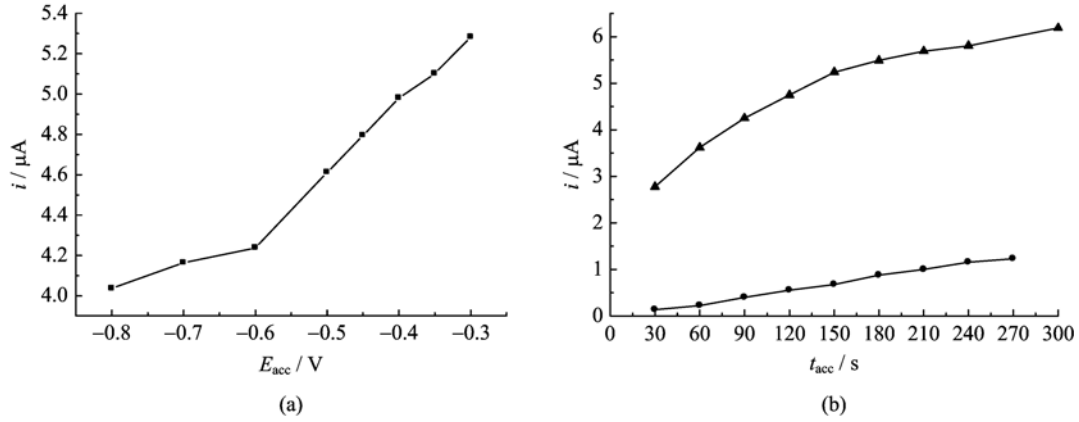
Fig. 5 gives the influences of accumulation potential and accumulation time on the response peak current of chromium. The accumulation potential (E_{acc}) ranged from −0.3 V to −0.8 V, and the peak currents decreased rapidly (Fig. 5 (a)). As expected, in progressing to more negative accumulation potential, the hexa-valence chromium was predominantly reduced to Cr(Ⅱ), and the amount of Cr(Ⅲ)-cupferron complex was less and less formed at the electrode surface. The results revealed that −0.35 V was good enough for the reduction of Cr(Ⅵ) and the formation of adsorbed Cr(Ⅲ)-cupferron complex, since the bismuth film would be oxidized and dissolved in the enrichment process if $E_{acc} > -0.30$ V.

The dependence of the peak current on the



Cr(Ⅵ) concentration: 5 μg/L (■), 10 μg/L (●), and 15 μg/L (▲). Other conditions are the same as in Fig. 2

Fig. 4 Effects of cupferron concentration (a), and deposition time of bismuth (b) on the adsorptive peak current



Chromium concentration: 5 μg/L in (a), 1 μg/L (●) and 8 μg/L (▲) in (b). Accumulation time: 2 min in (a); accumulation potential: −0.35 V in (b). Other conditions are the same as in Fig. 2

Fig. 5 Effects of accumulation potential (a), and accumulation time (b) on the response to Cr(Ⅵ)

accumulation time is shown in Fig. 5(b) for two levels of chromium, 1 μg/L (●) and 8 μg/L (▲). The longer the accumulation time (t_{acc}), the more the chromium complex was adsorbed and the larger the peak current was. The peak current increased rapidly with accumulation time increasing up to 120 s, but then flattened out for 8 μg/L Cr(Ⅵ). To save time, 120 s was selected in the experiment.

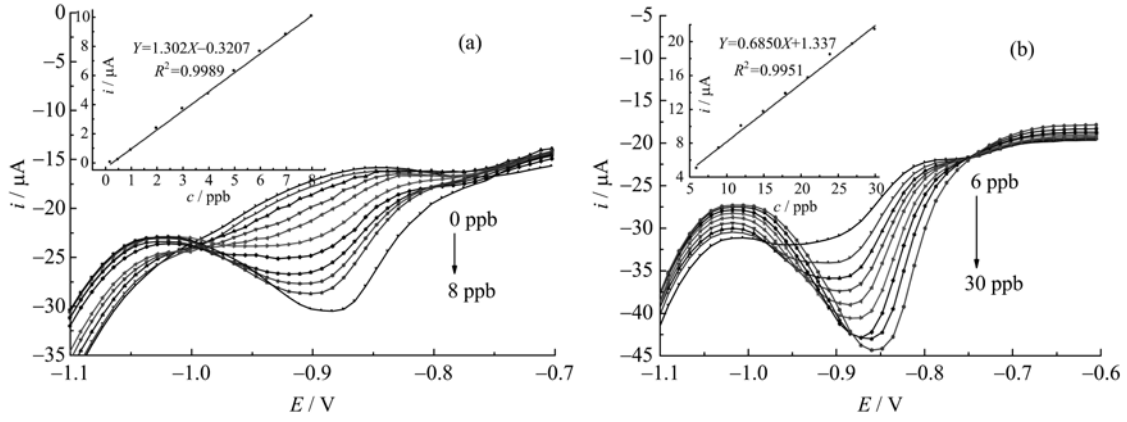
The square wave parameters, square wave amplitude, frequency and scan increment were also optimized. The optimal square wave parameters were evaluated experimentally as square wave amplitude 30 mV, frequency 10 Hz and scan increment 9 mV, respectively.

2.4 Calibration plot and detection limit

The cathodic adsorptive square wave voltammograms of chromium obtained under the optimized conditions are demonstrated in Fig. 6. The calibration graphs are linear in the range from 0.2 to 8 μg/L and from 6 to 30 μg/L with accumulation time 300 s (Fig. 6(a)) and 120 s (Fig. 6(b)), respectively. The linear equations were calibrated as $i_p = 1.302c - 0.3207$ ($R^2 = 0.9989$) and $i_p = 0.6850c + 1.337$ ($R^2 = 0.9951$). The limit of detection (LOD), calculated at a signal-to-noise ratio of 3 with accumulation time of 300 s, was 0.048 μg/L and the limit of quantification (LOQ) was 0.145 μg/L. The sensitivity was 957.82 A · M^{-1} · cm^{-2}. The results demonstrate that the proposed Bi/MWCNTs/GCE is sensitive for detection of Cr(Ⅵ) at trace level, which is promising for use in analysizing real samples.

2.5 Interferences, selectivity and stability

The possible interfering ions which are commonly presented in real water samples were added in test solution to evaluate the selectivity of the Bi/MWCNTs/GCE for detection of Cr(Ⅵ). First, the tri-valent chromium generated identical adsorptive peaks in the presence of cupferron, indicating that the method is applicable to the measurement of the total chromium content. The adsorptive peak of Cr(Ⅲ)-cupferron complex was reproducible. Most of the other metals tested did not interfere. For the determination of 5 μg/L chromium, it was not affected by the addition of 200 μg/L of Pb(Ⅱ), Cd(Ⅱ), Cu(Ⅱ), Mn(Ⅱ), Fe(Ⅲ), Co(Ⅱ) and Ni(Ⅱ). But, the excess of 100 μg/L Zn(Ⅱ) would cause interference with an overlapping peak. The interferences of surface active substances was also studied using sodium dodecyl sulfate (SDS) and cetyltrimethyl ammonium bromide (CTAB) as model substances. It was found that the addition of SDS and CTAB did not affect the peak current with concentration of 50 μg/L. However, at a higher concentration, both SDS and CTAB would cause decrease or



(a) 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 μg/L, and (b) 6.0, 9.0, 12, 15, 18, 21, 24, 27 and 30 μg/L from top to bottom as the arrows indicated, respectively. The insets depict the corresponding calibration plots

Fig. 6 The adsorptive voltammograms of different concentrations of Cr(Ⅵ) at Bi/MWCNTs/GCE

disappearance of the chromium peak due to their strong adsorption competitiveness on the electrode's surface. So, samples with high a concentration of surface active substances should be pretreated before analysis.

A relative standard deviation (RSD) of 5.2% was obtained from 75 continuous measurements of 10 μg/L Cr(Ⅵ) solution, indicating that the prepared modified electrode was of high stability.

2.6 Real water sample analysis

The environmental water samples were assayed to evaluate the practical utility of the proposed modified electrode. The determination of chromium in real water samples was carried out with the standard addition method. The water samples were pretreated as mentioned above (see section 1.2.3). For total chromium detection, the water samples were spiked with Cr(Ⅲ) or Cr(Ⅵ) at different concentration levels, and then analyzed with the proposed method. For the hexa-valent chromium detection, the Cr(Ⅵ) was first concentrated 100-fold and separated with Cr(Ⅲ) by using an anion trapping column, diluted 10 times with buffer solution and then determined by standard addition of Cr(Ⅵ). That is to say, the detection value of Cr(Ⅵ) was 10 times higher than the real Cr(Ⅵ) content in water samples. As a result, the detected original concentrations of total chromium and enriched concentrations of Cr(Ⅵ) in the three water samples were in good agreement with those obtained from ICP-MS (Tab.1). Besides, good recoveries were also obtained from 95% to 105%, indicating that the proposed method was highly precise and reproducible and can be used for direct analysis of surface water samples.

3 Conclusion

In this study, a composite film of bismuth and MWCNTs modified electrode was fabricated by two steps of electrodeposition on the glassy carbon electrode. The as-prepared modified electrode was successfully employed to detect total chromium and hexa-valence chromium in surface water with square wave cathodic adsorptive voltammetry. The combination of Bi with MWCNTs was stable and effective, so that the active surface of the bismuth-based modified electrode was remarkably increased. As a result, the sensitivity and stability of the modified electrode towards chromium detection were greatly improved. On the other hand, the interferences from the most common metals in environmental waters were preferably avoided by use of cupferron, and more favorably, the different chemical speciation of chromium in surface water could be detected respectively. Three different real water samples, from the river, lake and pond respectively, were actually analyzed in agreement with the control test by ICP-MS, indicating that the proposed method is of practical utility.

Tab. 1 Analytical results for detection of chromium in real water samples

sample	ICP-MS total Cr /(μg·L^{-1})	SWCAdV total Cr[a] /(μg·L^{-1})	ICP-MS Cr(Ⅵ) /(μg·L^{-1})	SWCAdV Cr(Ⅵ)[a] /(μg·L^{-1})	added Cr(Ⅵ) /(μg·L^{-1})	found by SWCAdV[a] /(μg·L^{-1})	recovery /%
Nanfeihe river	2.07	2.14±0.13	1.75	1.79±0.09	2.00	3.75±0.04	98.0±4.2
					4.00	5.91±0.03	103±2.4
					6.00	7.57±0.10	96.3±4.8
Daoxianglou lake	4.08	4.24±0.18	4.03	3.97±0.11	2.00	5.84±0.10	93.5±8.7
					4.00	7.83±0.05	96.5±4.9
					6.00	9.57±0.06	93.3±10.7
Glasses lake in campus	3.70	3.97±0.22	1.72	1.84±0.04	2.00	3.78±0.07	96.5±7.8
					4.00	5.61±0.03	94.0±3.1
					6.00	7.37±0.08	92.0±6.7

【Note】 [a] The average of three measurements at a confidence level of 0.95.

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