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Simultaneous determination of Cd(II) and Pb(II) using square wave anodic stripping voltammetry at a gold nanoparticle-graphene-cysteine composite modified bismuth film electrode

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ABSTRACT

A sensitive platform for the simultaneous electrochemical determination of Cd(II) and Pb(II) in aqueous solution has been developed based on the gold nanoparticle-graphene-cysteine composite (Au-GN-Cys) modified bismuth film glassy carbon electrode (GCE) using square wave anodic stripping voltammetry (SWASV). The synergistic effect of cysteine as well as the enlarged, activated surface and good electrical conductivity of gold nanoparticles and graphene contributed to the deposition of Cd(II) and Pb(II) on the electrode surface. Under the optimum conditions, a linear relationship existed between the currents and the concentrations of Cd(II) and Pb(II) in the range between 0.50 $\mu g\,L^{-1}$ to 40 $\mu g\,L^{-1}$ with the detection limits of 0.10 $\mu g\,L^{-1}$ for Cd(II) and 0.05 $\mu g\,L^{-1}$ for Pb(II), respectively, based on a signal-to-noise ratio equal to 3 (S/N = 3). The interference experiments show that some metal cations had little influence on the SWASV signals of Cd(II) and Pb(II). In addition, the developed electrode displayed a good repeatability and reproducibility. These studies imply that the Au-GN-Cys composites might be an alternative candidate for practical applications in electrochemical detection of metal ions.

1. Introduction

Toxic heavy metals pose a great threat to living organisms due to their non-biodegradability and persistence [1]. Over the past few decades, there has been an increasing interest in the development of highly sensitive analytical methods for the detection of trace amounts of toxic heavy metals. Various techniques including colorimetric analysis [2], UV-vis spectrometry [3], surface enhanced Raman spectrometry (SERS) [4], atomic absorption spectrometry (AAS) [5], atomic fluorescence spectrometry [6], ion chromatography [7], inductively coupled plasma mass spectrometry (ICP-MS) [8] and inductively coupled plasma optical emission spectrometry (ICP-OES) [9] have been used for heavy metals analysis. However, these methods have some drawbacks such as time-consuming, high cost, demand for complex instrumentation and unsuitability for on-field analysis.

Electrochemical detection of heavy metals offers several advantages such as simplicity, accurateness, low-cost, remarkable sensitivity, high stability and suitability for determination of multiple analytes. Anodic stripping voltammetry (ASV) has been widely recognized as a powerful technique for the determination of trace metal ions due to an effective preconcentration step followed by electrochemical stripping measurements of the accumulated analytes [10]. Stripping analysis using chemically modified electrode has been proved to show significant selectivity toward some metal ions. The choice of the working electrode is crucial for the success of the stripping operation [11]. Mercury-based electrode has been mostly used for ASV due to their wide potential window toward negative potential values. However, the defects of mercury, for example, toxicity and difficulties associated with storage and disposal, restrict its use [12]. Two approaches have been generally utilized to displace mercury in the construction of chemical modified electrode for trace level determination of heavy metals. One is the use of other conductive materials, like bismuth, gold, silver, antimony film, carbon, and boron-doped diamond [13–17], etc. Nowadays, bismuth film electrode has attracted considerable interests because it possesses behavior similar to mercury-based electrode and presents remarkable low toxicity [18]. The other involves the use of some receptors including phenanthroline [19], ethylenediaminetetraacetic acid (EDTA) [20], dimethylglyoxime [21], diazoles [22] cysteine [23] and aspartic acid [24], which have either electrostatic interaction or complexation with metal ions and promote the preconcentration of the latters on the electrode surface.

Carbon-based nanomaterials such as carbon nanotubes and graphene have been shown to be ideal for sensor applications since

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they possess unique physical and chemical properties including high surface area, strong mechanical strength, excellent thermal conductivity and electric conductivity. One can find some reports on the determination of heavy metals using carbon nanotube-modified electrode [25,26] and graphene-modified electrode [27]. In addition, some carbon-based nanocomposites containing metal receptors such as cysteine, which can react with metal ions and produce stable complexes, have been successfully prepared and employed in the heavy metal analysis [28].

Graphene (GN) is a novel class of 2D carbon-based nanomaterial in which sp^2 bonded carbon atoms are arranged into a honeycomb structure. It can exhibit a lower charge-transfer resistance than graphite and glassy carbon electrodes and a comparable wide electrochemical potential window [29]. Gold nanoparticles (Au NPs) have received increased attention in electrochemical detection since they enhance the electrode conductivity and facilitate the electron transfer due to quantum size effects [30–32]. In our opinions, the decoration of Au NPs and cysteine to carbon-based nanomaterials should create new nano-hybrid materials with the integrated properties of the three components, which offers new opportunities for the development of sensors with improved analytical performance. In the present work, a new nanocomposite containing Au NPs, graphene and cysteine was prepared and characterized by UV-vis, infrared spectrophotometry and SEM. An electrochemical sensor for the determination of trace Cd(II) and Pb(II) ions using the new nanocomposite-modified bismuth film electrode based on square wave anodic stripping voltammetry (SWASV) was developed. The optimized conditions in electrochemical analysis were investigated. The interference study, repeatability and reproducibility measurement of the developed sensor were also performed.

2. Experimental

2.1. Materials and apparatus

Graphene (GN) was purchased from Nanjing CJNANO Tech Co., Ltd., (China). DL-Cysteine hydrochloride and $HAuCl_4$ was obtained from Sinopharm Chemical Reagent Co., Ltd. (China). The buffer for the assay was 0.1 M acetate buffered saline (ABS), prepared by mixing stock standard solution of HAc and NaAc. Other chemicals were of analytical reagent grade and all aqueous solutions were prepared in Milli-Q ultrapure water ($\geq$18 MΩ cm).

Electrochemical measurement experiments were performed with a CHI660 C electrochemical workstation (CH Instruments, China) by using a three-electrode electrolytic cell. Glassy carbon electrode (GCE, 3 mm in diameter) acted as the working electrode. A KCl saturated calomel electrode served as the reference electrode. A platinum plate served as the counter electrode. The absorption spectra were recorded on a UV-2450 UV-VIS spectrophotometer (Shimadzu, Japan). A Nicolet Nexus 670 FTIR spectrometer (Nicolet, USA) was employed for the infrared spectral measurements. The images of the modified electrode surface were obtained with a Quanta^{TM} 250 FEG scanning electron microscope (SEM, FEI, USA).

2.2. Preparation of gold nanoparticle-graphene-cysteine composite (Au-GN-Cys) suspension

1.4 mg graphene was suspended in 2 mL ultrapure water by sonication for 30 min to make graphene dispersed equally. 200 μL 1% $HAuCl_4$ solution was added and the mixture solution was heated to boiling. Then 400 μL 0.1 mol L^{-1} trisodium citrate was added to this solution drop by drop under vigorous stirring for 20 min. After the heating was stopped, the mixed solution was stirred continuously until it was cooled to room temperature. The prepared Au-GN composites were separated by centrifugation (10000 rpm) and washed with ultrapure water for three times. Next, the precipitate was re-suspended with 2 mL ultrapure water and mixed with 2 mL DL-cysteine hydrochloride. After stirring for at least 12 h at room temperature under nitrogen atmosphere, the nanocomposites were centrifugated at 10000 rpm for 20 min and washed with ultrapure water for three times. Finally the such-made Au-GN-Cys composites were re-dispersed in 1 mL ultrapure water and the suspension was stored in a brown glass bottle at 4 °C for further use.

2.3. Preparation of the modified electrode and measurement procedures

Prior to modification, GCE was polished with 0.05 μm α-Al_2O_3 power slurries until a mirror shiny surface appeared, and was sonicated sequentially in acetone, HNO_3 (1:1, v/v), NaOH (1 mol L^{-1}) and double distilled water for 3 min. The treated electrode was scanned between -1.0 and 1.0 V versus SCE in 0.5 mol L^{-1} H_2SO_4 aqueous solution for sufficient cycles to obtain reproducible cyclic voltammograms. After the electrode was thoroughly rinsed with doubly distilled water and dried with a stream of nitrogen gas, 3 μL of the prepared Au-GN-Cys suspension was dropped on the GCE surface and allowed to dry at room temperature. The prepared electrode was marked as Au-GN-Cys/GCE and preserved in a refrigerator at 4 °C before use.

The square wave anodic stripping voltammetry (SWASV) measurements were performed in a 10 mL electrochemical cell, containing 10 mL 0.1 mol L^{-1} pH 4.5 ABS, 300 μg L^{-1} Bi(III) and appropriate amounts of Cd(II) and Pb(II). The preconcentration was carried out at -1.2 V for 800 s under stirring where Bi(III) and the target metals were simultaneously deposited on the surface of the electrode. After the accumulation time, the stirring was stopped. The voltammogram was recorded between -1.0 V to -0.4 V by applying SWASV with a frequency of 15 Hz, step increment of 4 mV and amplitude of 25 mV. The electrode was cleaned at 0.3 V for 120 s to remove the residual metals and bismuth film under stirring condition. All experiments were conducted at room temperature (25 ± 2 °C) in air atmosphere.

3. Results and Discussion

3.1. Characterization of Au-GN-Cys composites

Figure 1A shows the UV-vis spectra of the GN, Au NPs, cysteine and Au-GN-Cys composite in aqueous solution from 200 to 700 nm, respectively. A sharp absorption peak could be found at 217 nm in the spectrum of GN, which might be related to the ring-shaped conjugated structure of carbon atoms in graphene. Au NPs had a prominent peak at about 520 nm that is regarded as a characteristic absorbance peak [33]. One can find an obvious absorption peak at 270 nm in the spectrum of cysteine. The spectrum of Au-GN-Cys composite appeared to be an overlapping of three spectra for GN, Au NPs and cysteine but the absorption peak in the visible region was weakened and presented a plateau (as indicated by arrows). It suggests that Au-GN-Cys composite comprised the three components. FTIR spectra of GN, Au NPs, cysteine and Au-GN-Cys composite in the range of 4000-400 cm^{-1} are shown in Figure 1B. For GN, the absorption band at ~1580 cm^{-1} was attributed to the stretching vibration of C = C in π-conjugation structure. The absorption bands at ~1720 and ~1254 cm^{-1} were derived from the C = O and C–O stretching vibration of carboxylic group (COOH), respectively. It suggests that some COOH groups were present at the graphene surface. The characteristic peaks of Au NPs at ~1632 and ~1405 cm^{-1} were ascribed to the asymmetric and symmetric stretching