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In situ bismuth-modified gallium nitride electrode for sensitive determination of cadmium (II) with high repeatability

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ABSTRACT

Bismuth-modified gallium nitride (Bi/GaN) electrode was fabricated using an in situ plating technique and simultaneously investigated for the detection of Cd^{2+} by square wave anodic stripping voltammetry (SWASV). Under the optimized conditions, the Bi/GaN electrode showed good linear amperometric responses for Cd^{2+} in the concentration range from 1 to 150 μg/L. The sensitivity was 0.54418 μA L μg^{-1} (i.e., 59.8598 A M^{-1}) and the limit of detection (LOD) was 0.3 μg/L (i.e., 2.72 nM). Furthermore, the as-prepared Bi/GaN sensor has high repeatability, and retains 95% of its initial stripping peak current after 50 cycles. More importantly, the applicability of the sensor in real samples such as tap water, milk, and fetal bovine serum was researched. The recovery ranges from 92.3 to 106.7%, indicating that the as-fabricated Bi/GaN sensor has potential to monitor Cd^{2+} in practical environments.

1. Introduction

Heavy metal ions as common pollutants are harmful to environment, human health and ecological systems due to their toxicity and non-biodegradability [1–4]. Especially, Cd^{2+} is widely distributed in the food and cigarette, which could induce a variety of diseases such as itai-itai, skeletal damage, and cardiovascular disease [5,6]. Therefore, the detection of Cd^{2+} is becoming increasingly important. Recently, various analytical techniques have been developed to determine Cd^{2+} such as atomic absorption spectroscopy [7], inductively coupled plasma-mass spectrometry [8], colorimetry [9], chemiluminescence [10], and electrochemical techniques [11], etc. Among them, electrochemical techniques have been recognized as effective techniques due to their merits of low cost, high sensitivity, and fast response [12–15]. Up to now, the application and performance of the electrochemical Cd^{2+} sensors is determined by the structure and property of the electrode materials.

Bismuth (Bi) electrodes have replaced the mercury electrodes for the detection of heavy metal ions owing to their wider negative potential window, well-defined stripping response, and low toxicity [16]. At present, Bi was often loaded onto conductive materials such as Au [17], boron-doped diamond (BDD) [18,19], and carbon nanotubes (CNTs) [20]. The Au electrodes have higher catalytic activity for hydrogen evolution. As a result, higher background currents occurred at negative potentials, which limit the application of the Au electrodes [21]. The large-scale production for BDD electrode is still expensive and difficult owning to the complex and toxic preparation process. The CNTs electrodes have some shortcomings in the practical application. On one hand, they require relatively complicated operational procedures and suffer from high background current; on the other hand, the reactive functional groups of CNTs are easily lost when they interact with heavy metal. The latter could result in a low repeatability of the modified electrode. Hence, the development of the electrode material with low background current and high repeatability is essential for the determination of Cd^{2+}.

Gallium nitride (GaN), as a typical wide bandgap semiconductor, has a promising application in the field of highly accurate electrochemical sensors due to its excellent biocompatibility, large potential window, and low background current [22,23]. In comparison with Si and TiO_2, GaN is chemical and thermal inertness, and generates less noise and thus can spot smaller signals tighter with its high electron mobility [24]. In recent years, many studies show that GaN surfaces have the appropriate biocompatible properties, which make GaN-based material an excellent candidate for high sensitivity biofunctional-sensing applications [25,26]. For instance, Luo et al. assembled the GaN-based ethanol sensor with good selectivity [27]. Abdullah et al. fabricated the GaN-based gas sensor with good repeatability and high sensitivity [28]. More importantly, the GaN can be produced on a large-

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scale with mature preparation process.

In this work, the novel Bi-modified GaN (Bi/GaN) electrode was fabricated with a simple in situ plating approach and simultaneously investigated for the detection of Cd^{2+} via square wave anodic stripping voltammetric (SWASV). The as-fabricated Bi/GaN electrode exhibited good reproducibility and high sensitivity.

2. Experimental

2.1. Reagents

Single crystalline GaN films were grown on *c*-plane (1.0° Offcut) sapphire substrates by hydride vapor phase epitaxy (HVPE) [29]. The GaN layers were 5 μm thick, Si-doped, and with a carrier concentration of 4.8×10^{18} cm^{-3}. The size of GaN chips was 0.3 cm × 1.5 cm. Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), nitric acid (HNO_3), cadmium chloride ($CdCl_2$), acetic acid (CH_3COOH), and anhydrous sodium acetate (CH_3COONa) were of analytical grade, and purchased from Sinopharm Chemical Reagent Co., Ltd. The milk sample was purchased from a supermarket in Suzhou (China). The fetal bovine serum (FBS) sample was purchased from Nanjing Sunshine Biotechnology Ltd. The acetate buffer solution (ABS, 0.1 M, pH 4.5) was prepared by mixing stock solutions of CH_3COOH and CH_3COONa. All solutions were prepared by using Milli-Q water (18.2 MΩ).

2.2. Apparatus

CHI 660D potentiostat/galvanostat (Shanghai ChenHua Co., Ltd.) was used in all electrochemical measurements at room temperature. The morphology and structure of the as-prepared Bi/GaN electrode were examined by Hitachi-S4800 scanning electron microscope (SEM) at 5 kV. The surface chemical state of the GaN electrode was characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XI, Thermo Fisher Scientific) with an Al K Alpha X-ray source.

2.3. Measurement procedures

The GaN chips were cleaned successively in aqua regia, acetone and ethanol for 15 min, rinsed in DI water, and dried by nitrogen stream prior to use. Planar GaN, platinum plate and Ag/AgCl (saturated KCl) were used as the working, counter and reference electrodes, respectively. Electrolytes consist of different concentrations of Cd^{2+} and 600 μg/L Bi^{3+} in 0.1 M acetate buffer solution (pH 4.5, ABS). All the potentials were reported with respect to Ag/AgCl electrode. Square wave anodic stripping voltammetric (SWASV) measurements were performed with an in situ deposition of the Bi and Cd, and the detailed measurements were executed as follows. (a) The preconcentration step was carried out at the applied potential of − 1.1 V for 300 s under magnetic stirring (300 rpm). (b) The system was equilibrated for 15 s. (c) The stripping voltammogram was recorded by applying a positive-going square-wave voltammetric potential scan from − 1.1 to 0.3 V with the following parameters: amplitude of 25 mV, frequency of 20 Hz and step potential of 4 mV. (d) The clean step was executed at the potential of + 0.3 V for 60 s under stirring condition (300 rpm), prior to the next cycle measurement.

3. Results and discussion

3.1. Cd^{2+} detection using unmodified and Bi-modified GaN electrode

Fig. 1 shows the typical SWASVs of the GaN electrode in three different electrolytes. A sharp and well-defined stripping peak of Cd (curve a) was observed at − 0.81 V at the Bi-modified GaN (Bi/GaN) electrode. However, the small stripping peak current (5 μA) of Cd was obtained in curve b, and such voltammetric response was not found in blank ABS (curve c) at the GaN electrode. The improvement of the peak currents of Cd at the Bi/GaN electrode can be ascribed to two aspects. First, GaN electrode has a high electron mobility, which contributes to the rapid balance of the system. Second, the formation of the fusible alloys of Bi with Cd promotes the nucleation process during the deposition of Cd^{2+} [30].

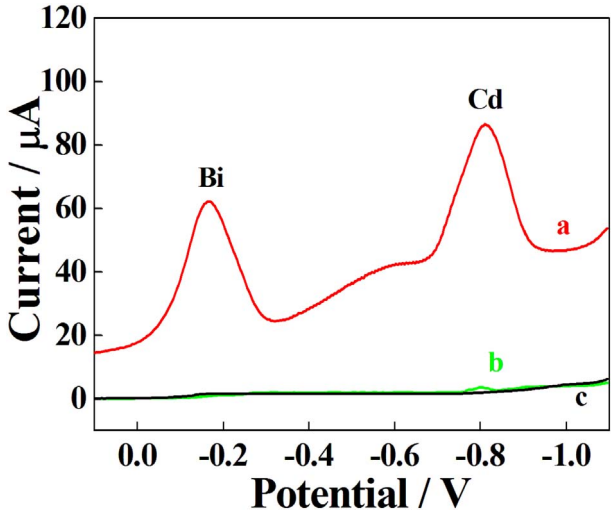

Fig. 1. Square wave anodic stripping voltammograms (SWASVs) of the GaN electrode in electrolytes (a) 600 μg/L Bi^{3+} and 50 μg/L Cd^{2+} in ABS, (b) 50 μg/L Cd^{2+} in ABS and (c) blank ABS. Preconcentration time 350 s at − 1.1 V.

3.2. Preconcentration potential and time optimization

Fig. 2a shows SWASVs of the Bi/GaN electrode in the preconcentration potential from − 0.8 to − 1.4 V. The line graph of Fig. 2b is further establish the relationship of the peak current of Cd and potential, the rapid increase of the Cd^{2+} peak currents were observed with the potential from − 0.8 to − 1.1 V. When the potential was below − 1.1 V, the current rose gently to reach a stable value. In order to avoid the occurrence of background hydrogen evolution, − 1.1 V was selected as the optimal potential. Fig. 2c shows the SWASVs of the Bi/GaN electrode under different preconcentration times. The peak currents of Cd^{2+} were increased with the time from 50 to 300 s. The peak currents would reach saturation at ca. 300 s (Fig. 2d). This indicates that the accumulation of Cd^{2+} has almost been completed at ca. 300 s [31,32]. Therefore, 300 s was selected as the optimal time for the following experiments.

3.3. Electrochemical detection of Cd^{2+}

Fig. 3a shows a series of SWASVs responses of the Bi/GaN electrode toward different concentrations of Cd^{2+}. The stripping peak currents of the Cd^{2+} are significantly increased with the Cd^{2+} concentration. It is obvious that the background currents increase with the Cd^{2+} concentrations. This is possibly because the deposited Cd is electrochemically active and can enhance the conductivity of GaN electrode, which simultaneously results in the increase of background current. Moreover, the amount of Cd deposits increases with the Cd^{2+} concentrations, leading to the ever-increasing interfacial contact area between GaN and Cd@Bi alloy [16,30]. Fig. 3b shows the SWASVs responses of the GaN electrode toward Cd^{2+}, and no obvious stripping peak was found toward 20 μg/L Cd^{2+}. A small stripping response (4.5 μA) was observed on the GaN electrode for 150 μg/L Cd^{2+}, whereas the stripping response at Bi/GaN electrode was up to 80 μA. It can be attributed that no fusible alloys are formed when the absence of Bi^{3+}. Fig. 3c shows the linear relationship between stripping peak currents of the Bi/GaN electrode and different concentrations of Cd^{2+}. The peak current was obtained by calculating arithmetic average of ten