Sensors and Actuators B 215 (2015) 62–69

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Electrochemical deposition of bismuth on activated graphene-nafion composite for anodic stripping voltammetric determination of trace heavy metals

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ARTICLE INFO

Article history:
Received 13 July 2014
Received in revised form 7 March 2015
Accepted 11 March 2015
Available online 27 March 2015

Keywords:
Activated graphene
Bismuth
Heavy metals
Stripping voltammetry
Modified electrodes

ABSTRACT

In this study, we report the first example of a bismuth film electrode plated in situ using activated graphene (AG). The AG was prepared through of process of chemical activation of graphene oxide (GO) with KOH to create pores. The composite electrode was enhanced as an electrochemical sensing platform to determine trace Zn^{2+}, Cd^{2+}, and Pb^{2+} using differential pulse anodic stripping voltammetry. The surface morphology of the AG-NA/Bi composite film modified electrode was investigated by scanning electron microscopy and transmission electron microscopy. The electrochemical properties of the AG-NA/Bi composite electrode were evaluated to examine the effects of experimental variables, such as deposition potential, deposition time, bismuth concentration, and stirring speed during pre-concentration, on the determination of trace metals in 0.1 M acetate buffer solution (pH 4.5). Linear calibration curves ranged from 5 to 100 $\mu g\,L^{-1}$ for trace heavy metal ions. The detection limits were 0.57 $\mu g\,L^{-1}$ for Zn^{2+}, 0.07 $\mu g\,L^{-1}$ for Cd^{2+}, and 0.05 $\mu g\,L^{-1}$ for Pb^{2+} (S/N = 3). The limits of detection achieved are much lower than the guideline for drinking water quality provided by the World Health Organization (WHO). The AG-NA/Bi composite film electrodes were successfully applied to analysis trace metals in real samples.

1. Introduction

Among environmental pollutants, heavy metals, such as Pb^{2+}, Cd^{2+}, and Zn^{2+}, are considered to be the most important that cause major public-health concerns owing to their high stability and bioaccumulation [1]. Heavy metals affect several human organs in even very low concentrations. It is important to develop a simple and highly sensitive analytical method for assessing environmental pollutants in soil, water, and air to improve the quality of environment and human life. Analytical methods, such as electrothermal atomic absorption spectrometry (ET-AAS), inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS), and electrochemical (EC) techniques, have been developed for trace metal determination [2,3]. However, spectrometric methods are cumbersome, time consuming, expensive, and unsuitable in situ measurements owing to the required complex instrumentation. In contrast, electrochemical techniques are attractive because of their remarkable sensitivity, portability, and low cost. Among the electrochemical methods, anodic stripping voltammetric analysis is recognized as a powerful tool for the determination of trace metal ions [4–6]. In stripping voltammetry, mercury is commonly used as the working electrode because of the resultant of excellent reproducibility and high sensitivity. However, owing to the toxicity, various attempts have been made to design a mercury-free replacement. In recent years, bismuth film electrodes have attracted attention to the stripping technique because of remarkable low toxicity and environmentally friendly material. Moreover, it can be formed with alloy with many metals and has a wide potential window, which is an analytical advantage [7–11].

Graphene, which comprises two-dimensional nanostructures of sp^2-bonded carbon atoms in a hexagonal configuration, is an excellent nanomaterial for electrochemistry owing to its good electrical conductivity, low cost, mechanical properties, and high specific surface area [12–16]. In 2004, Geim and co-workers [17] reported graphene sheets prepared by mechanical exfoliation [18]. Since then, more studies were researched focusing on developing attractive applications in electroanalytical chemistry as a unique electrode material for manifolds [19,20]. Moreover, chemical modification of graphene oxide could be further improve in its electrochemical performance [21–26].

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http://dx.doi.org/10.1016/j.snb.2015.03.032
0925-4005/

Graphene formed through chemical activation of graphene oxide (GO) with KOH has a very high specific surface area and in-plane electrical conductivity resulting in its good electrochemical performance as an electrode material [27]. A chemically activated graphene has been proven to be excellent applications, including lithium-ion batteries and supercapacitors [27–29]. However, to the best our knowledge, activated graphene has never investigated in electrochemical analysis of heavy metal ions.

In this paper, we synthesized chemically activated reduced graphene (AG) with a Brunauer–Emmett–Teller (BET) surface area of up to 2335 $m^2 g^{-1}$. AG was used in combination with an in situ electrochemically deposited bismuth composite film to fabricate a sensitive and mercury-free electrochemical platform for the analysis of Zn^{2+}, Cd^{2+}, and Pb^{2+} ions. Nafion acts as an effective solubilizing agent for activated graphene (AG-NA) and anti-fouling coating to reduce the influence of surface-active macromolecules [10]. Both AG and nafion provide negative charge to bind positively charged Bi^{3+} to drive the formation of homogeneous, and stable nanocomposite materials [22]. In this work, we report the first example of the fabrication of an AG-NA/Bi composite film electrode for the detection of trace heavy metal ions using DPAVS; its performance was compared with that of synthesized reduced graphene oxide (RGO). Thus, the increased analytical performance of the AG-NA/Bi composite film electrode was verified: It showed the combined advantages of good electrical conductivity and large specific surface area together with the unique features of in situ-plated bismuth. Bismuth and the target metal ions nucleate on the surface of the electrode to directly form a "fused alloy," which facilitates the nucleation process during the deposition of heavy metals, and the target ions can be anodically stripped during the final analysis step, resulting in well-defined peaks for trace metals [4,32].

2. Materials and methods

2.1. Reagents

All the chemicals used were of analytical reagent grade, and the water was double-distilled. Bismuth (III), lead (II), zinc (II), and cadmium (II) were prepared from 1000 mg L^{-1} atomic absorption standard solutions via dilution. Nafion (NA, 5 wt % solution in a mixture of water and lower aliphatic alcohols) was purchased from Sigma–Aldrich (USA), and sodium acetate and acetic acid were purchased from Aldrich (USA). The working supporting electrolyte comprised 0.1 M acetate buffer (pH 4.5), which was prepared by mixing appropriate amounts of acetic acid and sodium acetate.

2.2. Apparatus

The electrochemical experiments were performed using an Autolab potentiostat (Metrohm, USA) with conventional three-electrode system. A modified glassy carbon electrode (3 mm in diameter, Bioanalytical Systems, Inc.) served as the working electrode, while a Ag/AgCl electrode (Bioanalytical Systems, Inc.) and platinum wire were used as the reference and counter electrodes, respectively. The BET specific surface area was determined via

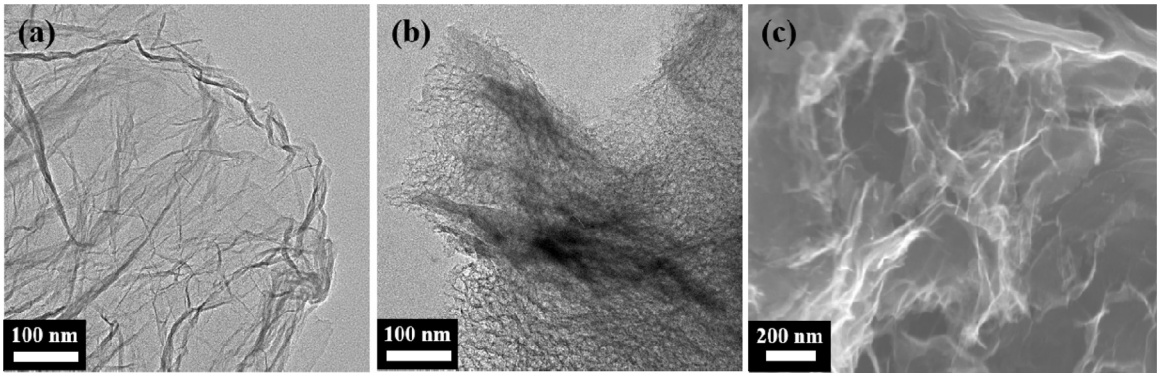

Fig. 1. TEM and SEM images of reduced graphene oxide (a), chemically activated graphene oxide (b), (c).

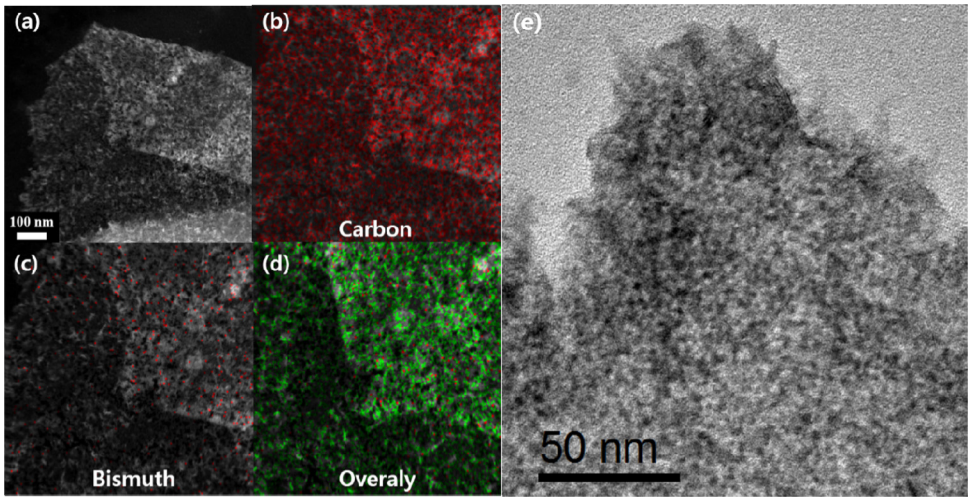

Fig. 2. TEM images of activated graphene/Bi composite film (a), (e) and the corresponding elemental mapping of carbon (b), bismuth (c) and overlay (d) for AG-NA/Bi composite film.