Sensors and Actuators B 220 (2015) 712–719

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Bismuth doped carbon xerogel nanocomposite incorporated in chitosan matrix for ultrasensitive voltammetric detection of Pb(II) and Cd(II)

Carmen I. Fort[a,*,1], Liviu C. Cotet[a,1], Adriana Vulpoi[b], Graziella L. Turdean[a], Virginia Danciu[a], Lucian Baia[b], Ionel C. Popescu[a]

[a] Department of Chemical Engineering, Laboratory of Electrochemical Research and Nonconventional Materials, Faculty of Chemistry and Chemical Engineering, "Babes-Bolyai" University, Arany Janos 11, RO-400028 Cluj-Napoca, Romania
[b] Faculty of Physics & Institute of Interdisciplinary Research in Bio-Nano-Sciences, "Babes-Bolyai" University, M. Kogalniceanu 1, RO-400084 Cluj-Napoca, Romania

ARTICLE INFO

Article history:
Received 21 January 2015
Received in revised form 31 March 2015
Accepted 31 May 2015
Available online 12 June 2015

Keywords:
Carbon xerogel
Bi nanoparticles
Nanocomposites
Pb(II) and Cd(II) trace detection

ABSTRACT

A new modified electrode based on a modified electrode incorporating Bi doped mesoporous carbon xerogel (Bi–CX), confined in a chitosan matrix (Chi) and deposited on a glassy carbon (GC), was elaborated and investigated for Pb(II) and Cd(II) voltammetric trace detection. Bi–CX was prepared by sol–gel method, coupled with drying under ambient conditions and followed by thermal pyrolysis. The morpho-structural characteristics of the new nano-material material such as specific surface area, pore size distribution, pore volume, phase composition and crystallite mean size were examined by using from N_2 adsorption/desorption isotherms, TEM, SEM and XRD measurements. The electrochemical behavior of the GC/Chi–(Bi–CX) modified electrode as well as its relevance for Pb(II) and Cd(II) trace detection were investigated by cyclic voltammetry and square wave anodic stripping voltammetry. The linear range, sensitivity, and detection limit of the new sensor were estimated as (0.2–2) ppb, 5.6 A/ppm and 0.07 ppb, for Pb(II), and (11.2–124) ppm, 22.7 nA/ppm and 5.06 ppm, for Cd(II), respectively. The excellent analytical parameters for Pb(II) detection were exploited for the determination of the Pb(II) concentration in drilled well water samples. The results were found in good agreement with those obtained by atomic absorption spectrophotometry.

1. Introduction

Recently, the detection of heavy metals was subject of many studies because of its importance in various domains, like biology [1], pharmacy [2], cosmetic industry [3], food production [4,5], agriculture [6], and environmental applications [7].

Aiming to perform rapid, accurate, and reliable heavy metals determination different techniques, such as atomic absorbance spectrometry [8], atomic fluorescence spectrometry [9,10], inductively coupled plasma–optical emission spectrometry [11], and inductively coupled plasma–mass spectrometry [12] were used. However, the above mentioned methods compared with the electrochemical methods [13,14] are considered more expensive and time-consuming. Besides this, the simplicity, intrinsic sensitivity and high selectivity recommend the electrochemical techniques among the most adequate options for heavy metals detection.

During the last decade, bismuth-based materials electrodes have been evidenced as a successful alternative to the traditional mercury electrodes for heavy metals trace detection. Being environmentally friendly and biocompatible Bi represents a very attractive material for sensors construction. In order to get fast electrode kinetics and low detection limit required for heavy metals detection, two important aspects were considered. One of this concerns the conductive material used as substrate for Bi deposition. Because it is well-known that the structure and the properties of the supporting material may exert major influences on the sensor behavior, various carbonaceous materials (glassy carbon [15], graphite [16], carbon fibers [17], carbon ink [18,19]), metals (Ag [14,20], Cu [21]), zeolite [22], polymers ((3-mercaptopropyl) trimethoxysilane [23], cyclic olefin copolymer [24], poly(p-aminobenzene sulfonic acid) [25], and polyaniline [26]) were used as substrate. However, the above mentioned substrates, especially the conventional ones, exhibit important

* Corresponding author. Tel.: +40 264 591998; fax: +40 264590818.
E-mail address: iladiu@chem.ubbcluj.ro (C.I. Fort).
[1] First authors.

http://dx.doi.org/10.1016/j.snb.2015.05.124
0925-4005/

drawbacks such as low active surface, easy inactivation or expensiveness. The second aspect, affecting strongly the size and the activity of the sensor working surface, is related to the method used for the Bi deposition on the substrate: (i) "*ex-situ*" plating or preplated material [24,27,28], (ii) "*in-situ*" plating [5,17,25,27,29,30], (iii) "bulk" method [16,18,27].

Nowadays, due to their large specific surface area and excellent conductivity, the carbonaceous nanomaterials such us, graphene [28,31,32], carbon nanotube [10,33], and carbon tape [28] opened interesting opportunities for introducing of the nanomaterials as Bi support in the construction of electrochemical sensors. In this context, taking into account the easy preparation, the good chemical and structural characteristics, combined with some peculiar properties such as huge specific surface area, very low density, high porosity and electrical conductivity [13], a homemade carbon xerogel (CX) was investigated as supporting matrix for the preparation of Bi-modified electrodes. Recently, CXs were used, with excellent results, as electrode materials for supercapacitors and rechargeable batteries, as efficient catalyst support, as well as adsorbent material and molecular sieve [34]. Supplementary, should be mentioned that the morpho-structural properties of CXs can be easily controlled by changing one or more of the processing parameters [13,34].

Additionally, the N-deacetylated derivative of chitin, better known as chitosan (Chi), is one of the biopolymers considered as the best suited to be used for the immobilization of electroactive materials on the electrode surface. This is the result of an unusual combination of properties among should be included: the excellent membrane-forming ability, the high water permeability, a good adhesion, a remarkable biocompatibility, and a high mechanical strength [35].

Continuing our previous research work in the field of "green nanomaterials" that can be applied in the development of electrochemical sensors [13,36], in this work the interest was focused on the obtaining of a new modified glassy carbon (GC) electrode, based on Bi nanoparticles incorporated in carbon xerogel. Thus, a sample of homemade carbon xerogel was impregnated with Bi nanoparticles and the obtained new material (Bi–CX) was immobilized in a film of Chi deposited on the surface of a GC electrode. The GC/Chi–(Bi–CX) modified electrode behaves as an ultrasensitive voltammetric sensor for Pb(II) and Cd(II) determination. To the best of our knowledge, here is the first report on the use of CX as supporting material for Bi nanoparticles immobilized onto GC electrode, for the construction of an electrochemical sensor for trace determination of Pb(II) and Cd(II). Moreover, the sensitivity toward Pb(II) estimated for the new amperometric sensor is among the highest ever reported for Bi modified electrodes.

The morphological and structural parameters (surface area, pore size distribution, pore volume, phase composition and mean crystallite mean size) of the new nanocomposite (Bi–CX) were estimated from N_2 adsorption/desorption isotherms, TEM, SEM and XRD measurements. The electrochemical behavior and the applicability of the new GC/Chi–(Bi–CX) modified electrode for voltammetric trace detection of Pb(II) and Cd(II) were investigated by cyclic and square wave anodic stripping voltammetry measurements, respectively.

2. Experimental

2.1. Reagents

Resorcinol (99% purity), formaldehyde solution (37 wt% in H_2O, containing 10–15% methanol as stabilizer), bismuth(III) nitrate pentahydrate [$Bi(NO_3)_3{\cdot}5H_2O$], acetic acid (99.7%), sodium carbonate (Na_2CO_3, 99.95%) were purchased from Sigma–Aldrich.

A 0.1 M acetate buffer solution was prepared from acetic acid and sodium acetate (Merck, Darmstadt, Germany). The pH of the buffer solution was adjusted to the desired value by adding acetic acid or KOH solutions (Merck, Darmstadt, Germany). $Cd(NO_3){\cdot}4H_2O$ and $Pb(NO_3)$ (Reactivul, Bucuresti, Romania) were dissolved in the acetate buffer in order to obtain the analyte solutions. Bidistilled water was used for the preparation of all solutions. All reagents were of analytical grade and were used without any further purification.

2.2. Preparation of Bi doped carbon xerogel

Synthesis of the Bi doped carbon xerogel started with the preparation of a resorcinol–formaldehyde wet gel using a mixture of resorcinol (R), formaldehyde (F) and Na_2CO_3 (C), and bidistilled water (W). 0.29 mol of resorcinol were dissolved in the appropriate volume of bidistilled water (R/W = 0.65 g/cm^3). The formaldehyde was added to the resorcinol solution (R/F molar ratio = 0.5) under vigorous stirring. Afterwards, 0.1 M Na_2CO_3 aqueous solution was added to the previous solution (R/C molar ratio = 100), and the resulted mixture was placed in tightly closed glass molds (tubular shape with 1.5 cm diameter) and cured for 3 days at 80 °C. Then, the obtained wet gel was carefully washed with bidistilled water and subsequently was dried for 5 days, under ambient conditions. Finally, the resulted xerogel was thermally treated for 2 h at 550 °C (in Ar atmosphere). In order to obtain the Bi doped carbon xerogel, the thermal treated carbon xerogel was immersed, for 1 day, into a Bi(III) solution [1.02 g of $Bi(NO_3)_3{\cdot}5H_2O$ dissolved into 10 ml of acetic acid glacial]. After 5 days of drying under ambient conditions, the Bi-impregnated sample was pyrolyzed for 2 h at 800 °C (in Ar atmosphere), when Bi doped carbon xerogel (Bi–CX) was obtained. The blank samples of carbon xerogel (CX) were prepared by the pyrolysis of the thermal treated carbon xerogel for 2 h at 800 °C (in Ar atmosphere).

2.3. Morpho-structural measurements on Bi–CX

The morpho-structural characterization of Bi–CX was performed by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and nitrogen adsorption–desorption analysis. A FEI Quanta 3D FEG dual beam – in high vacuum mode using EDT (Everhart Thornley Detector) electron microscope (equipped with an ApolloX SDD Energy Dispersive X-ray (EDX) detector) and a FEI Tecnai F20 field emission, high resolution Transmission Electron Microscope (TEM) operating at an accelerating voltage of 200 kV and equipped with Eagle 4k CCD camera were used for performing the electron microscopy measurements. The milled samples were supported on carbon taped aluminum SEM holders in a thick layer, or was added drop wise after dispersed in water on a carbon film covered cooper grid for TEM analyses. With both microscopic techniques several zones were analyzed. In order to assess the Bi nanoparticle diameter distribution in the sample, particle size histograms were made out of particle counts from TEM and SEM images by using the imageJ software (Figs. S1 and S2). EDX spectroscopy was used to evaluate the elemental composition (wt%) of various zones investigated by SEM (Figs. S3–S5).

X-ray diffraction (XRD) measurements were performed by using a Shimadzu 6000 diffractometer using Cu-Kα radiation (λ = 1.5406 Å), equipped with a graphite monochromator.

Nitrogen adsorption–desorption analysis was performed with degassed samples (100 mg of the investigated material were degassed under <1 mPa vacuum, for 20 h at 106 °C) using a Sorptomatic ADP (Thermo Electron Corp.) equipment. The specific surface areas were obtained by using the BET (Brunauer–Emmet–Teller) method, while the pore size distribution and pore specific