Sensors and Actuators B 191 (2014) 320–325

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Antimony nanoparticle-multiwalled carbon nanotubes composite immobilized at carbon paste electrode for determination of trace heavy metals

Amir M. Ashrafi [a], Sandra Cerovac [b], Sanja Mudrić [b], Valéria Guzsvány [b], Lenka Husáková [a], Iva Urbanová [a], Karel Vytřas [a,*]

[a] Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 53210 Pardubice, Czech Republic
[b] Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 3, 21000 Novi Sad, Serbia

ARTICLE INFO

Article history:
Received 14 June 2013
Received in revised form 23 August 2013
Accepted 26 August 2013
Available online 23 September 2013

Keywords:
Anodic stripping voltammetry
Sb nanoparticles multiwalled carbon nanotube composite
Lead and cadmium ions
Wheat flour

ABSTRACT

A nanocomposite based on multiwalled carbon nanotubes (MWCNT) modified with antimony nanoparticles (SbNPs) was synthesized chemically and has been applied to construct an electrode using carbon paste as substrate (SbNP-MWCNT). The developed electrode was applied for the determination of trace heavy metals Pb^{2+} and Cd^{2+} by square-wave adsorptive stripping voltammetry. The results were compared with those obtained by related electrode configurations such as Sb-film carbon paste electrode (SbF) and Sb-microsphere-multiwalled carbon nanotube composite carbon paste electrode ($Sb_{microsphere}$-MWCNT) in model solutions. The analytical signals for Pb^{2+} and Cd^{2+} decreased in the order $I_{Sb\text{-}nanoparticle} > I_{Sb\text{-}film} > I_{Sb\text{-}microsphere}$, indicating that the size of the Sb particles on the coating layer influenced the oxidation current signals of Pb and Cd. The detection limits of the analytes were 0.77 $\mu g\,L^{-1}$ and 0.65 $\mu g\,L^{-1}$ for Cd^{2+} and Pb^{2+}, respectively. The designed electrode was tested for the determination of target ions in wheat flour certified reference material, and the results compared well with those obtained by inductively coupled plasma time-of-flight mass spectrometry, showing satisfactory performance of the composite electrode.

1. Introduction

Because of the high toxicity of trace heavy metals to humans, their analysis has attracted attention of many researchers. Among the methods that have been used for this purpose stripping voltammetric techniques occupy a special place because of their excellent sensitivity and selectivity, simple sample pretreatment, and also because of the possibility of using portable and relatively inexpensive instrumentation. During the recent period, numerous papers appeared dealing with applications of different new electrode configurations, frequently used in stripping voltammetry.

A remarkable stripping performance for measuring trace metal ions in acidic media has offered the use of Sb-FE [1]. Several types of Sb-based electrodes such as Sb–based film electrodes [1], Sb-film carbon paste electrodes (SbF), Sb–Bi codeposited film, sputtered Sb-film electrode, Sb nanoparticles modified boron-doped diamond electrode and Sb porous electrode have been constructed and applied successfully for the determination of heavy metals, imposing the need for its further systematic investigation [2–14].

In the recent years, special attention has been paid to the development of electrodes based on various nanomaterials, such as nanotubes, nanoballs, nanodots and in particular, nanoparticles [15–19].

Metallic nanoparticles (NPs) constitute a class of smart materials that exhibit unique properties including enhanced diffusion based on convergent rather than linear diffusion at the smaller NPs, high active surface area, improved sensitivity and selectivity, catalytic activity, higher signal-to-noise ratio. These features make them ideally suited for electroanalytical applications [19].

Anyway it should be mentioned that long time ago many other scientists worked with them but at their time the particles were called “colloids”. Such metal NPs studied presently are usually represented by colloids of gold [20], silver [21] and platinum [22]. However, electroanalytical applications of such nanomaterials have been found quite extensive, suggesting the potential for the study of a wide variety of other metal NPs. For example SbNPs were synthesized by both physical and chemical methods; the former category includes a vapor deposition [23] or a spark discharge generation [24], based on the thermal evaporation of solid Sb and its

* Corresponding author. Tel.: +420 466 037 512; fax: +420 466 037 068.
E-mail address: karel.vytras@upce.cz (K. Vytřas).

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http://dx.doi.org/10.1016/j.snb.2013.08.087

vapor condensation. The latter comprises the reduction of $SbCl_3$ by $NaBH_4$ in N,N-dimethylformamide (DMF) [25], a microwave assisted reduction of antimony sodium tartrate by Zn powder [26], a photochemical polythiol processes [27], and a thermal decomposition of Sb precursor Sb(acetylacetonate)$_3$ [28].

Similarly carbon nanotubes (CNTs) are used in electrochemical sensors due to their unique properties, e.g. high chemical stability, good electrical conductivity, high surface/volume ratio, and high adsorption capacity resulting in an increased sensitivity of the sensor [29].

Recently, substantial efforts have been made to design and prepare CNTs-metal composites, not only because the CNTs can improve the electrical and mechanical properties of the composites, but also because the composites possess the properties of individual components with a synergistic effect [30–32]. Such nanocomposites formed from the combination of CNTs and metal-NPs or metal oxide-NPs showed an excellent catalytic properties of nanoparticles without losing any of the electronic properties of CNTs [33–36].

The aim of this study was to synthesize SbNPs by a chemical procedure, using Nafion as a stabilizer and MWCNT as a substrate and then apply the prepared nanocomposite (SbNP-MWCNT) to modify a carbon paste electrode for the determination of Pb^{2+} and Cd^{2+} as model heavy metals. To investigate the effect of Sb particle size on the current signals obtained by square-wave adsorption stripping voltammetry (SWASV) using this, SbNP-MWCNT, electrode comparative measurements were performed using Sb-film carbon paste electrode (SbF) and $Sb_{microsphere}$-MWCNT composite carbon paste electrode. According to our best knowledge, there is only one report in which such kind of electrode configuration was used to determine bisphenol [37].

2. Experimental

2.1. Reagents and sample

Analytical grade purity of N,N-dimethylformaldehyde (DMF), Nafion (wt. 5%), $NaBH_4$, and paraffin oil, Sb powder (particle size $\leq$ 150 μm), $SbCl_3$ were purchased from Merck. The multi-walled carbon nanotubes (MWCNT) type 1030 (diameter, 10–30 nm, length; 1–2 μm, purity > 95%) were obtained from Shenzhen Nanotech Port Co. Ltd., China. Graphite carbon CR-5, was purchased from Maziva Týn nad Vltavou, Czech Republic. Stock solution (1000 mg L^{-1}) of Pb^{2+} and Cd^{2+} were from Sigma Aldrich. High purity H_2O_2 (30%, m/v) of Selectipur quality (Fluka, Buchs, Switzerland) and sub-boiling distilled nitric acid (65%, m/v, Lach-Ner, Neratovice, Czech Republic) prepared using a BSB system 939IR (Berghof, Germany) were used for the digestion of the sample. The GBW certified reference material 08503 Wheat flour (National Research Centre for Certified Reference Materials, NRCRM, China) was analyzed as a real sample.

2.2. Apparatus

Voltammetric experiments were performed with the Autolab electrochemical analyzer operated *via* GPES 4.9 software (Metrohm Autolab, Utrecht, The Netherlands). The conventional three-electrode configuration with different kinds of surface modified carbon paste electrodes as working ones was employed throughout the work. The Ag/AgCl 3 mol L^{-1} KCl electrode and a Pt wire served as the reference and auxiliary ones. For comparison, the wheat flour was analyzed using inductively coupled plasma time-of-flight mass spectrometer Optimass 8000 ICP-TOF-MS (GBC Scientific Pty. Ltd., Australia) [38]. Scanning electron microscopic measurements were performed on JEOL JSM-5500LV/EDX microanalyser – IXRF Systems (detector GRESHAM Sirius 10).

2.3. Real sample preparation

A sample of the wheat flour (certified sample GBW 08503) was digested using a microwave oven (Berghof Speedwave™ MWS-3$^+$) in a closed vessel following the same procedure and the temperature programme as described in Ref. [38]. Briefly, the sample was digested in closed-vessels with a microwave oven decomposition system. For this decomposition purpose the samples (500 mg) were weighed into a 100-mL pressure resistant PTFE vessel, to which (65%, m/v) HNO_3 (5 mL) and (30%, m/v) H_2O_2 (2 mL) were added. Samples were digested according to following 5 steps programme: (i) 5 min at 160 °C and 80% power (ramp 3 min), (ii) 10 min at 220 °C and 90% power (ramp 5 min), (3rd–5th) 5 min at 100 °C and 10% power (ramp 1 min). The resulting colourless solution was adjusted to pH ~ 2 by adding NaOH solution and then diluted to 50 mL with 0.01 mol L^{-1} HCl for voltammetric and ICP-TOF-MS investigations.

2.4. Carbon paste electrode preparation

Carbon paste was prepared by thorough hand-mixing of graphite powder (0.5 g; CR-5, Maziva Týn nad Vltavou, Czech Rep.) with highly viscous paraffin oil (0.3 mL). Both components were homogenized to obtain a mixture that was subsequently packed into a piston-driven carbon paste holder [39]. Whenever needed, the surface of carbon paste (with diameter of 2 mm) was mechanically renewed by extruding *ca.* 0.5 mm carbon paste out of the electrode holder and smoothing with a wet filter paper.

2.5. Pretreatment of multiwalled carbon nanotube

Before use, the MWCNT was treated to remove graphitic nanoparticles, amorphous carbon, and catalyst impurities. According to the literature [40] the performed pretreatment can be explained briefly; MWCNT (0.05 g) dispersed in 2.2 M HNO_3 (60 mL) for 20 h at room temperature with the aid of ultrasonic agitation (for 30 min), then washed with distilled water to neutrality and dried in an oven at 37 °C.

2.6. Working electrode materials preparation

In the experiments, four types of surface-modified electrodes were compared for the determination of Pb^{2+} and Cd^{2+}. Three types of materials; SbNP-MWCNT nanocomposite, MWCNT and $Sb_{microsphere}$-MWCNT were prepared *ex situ* for modification of CPE by drop coating and the SbF by common *in situ* modification procedure [1]. For the *ex situ* drop coating of CPE substarte electrodes, three different suspensions were prepared from the above mentioned materials. From each of them, 2 mg were dispersed in the mixture of ethanol (0.9 mL) and Nafion 0.5% (0.1 mL), and agitated in an ultrasonic bath for 20 min. From the resulting suspension, 5.0 μL were dropped on the CPE surface and dried at room temperature.

The modifying materials are described below:

SbNP-MWCNT nanocomposite (1): $SbCl_3$ (20 mg), MWCT (16.4 mg) and 5% Nafion solution (100 μL) were dispersed in DMF (10 mL) using an ultrasonic bath for 30 min. Aqueous solution of 1.8 mol L^{-1} $NaBH_4$ (0.25 mL) was added to the dispersion and stirred for 10 min, then the solid part was precipitated using a centrifuge (600 rpm for 15 min) and decanted. The participate was transferred to the oven and dried at 220 °C for 20 min, then washed with ethanol (2×) and acetone (1×). The scanning electron microscope was used to realize the range of synthesized NPs size.