Journal of Hazardous Materials 243 (2012) 232–241

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

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

Voltammetric analysis with the use of a novel electro-polymerised graphene-nafion film modified glassy carbon electrode: Simultaneous analysis of noxious nitroaniline isomers

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HIGHLIGHTS

- Construction of the poly-DHCBAQS/graphene–nafion/GCE.
- Simultaneous analysis of nitroaniline isomers.
- Satisfactory quantitative results were obtained by applying the PCR and PLS methods.
- To provide a new method of constructing electrodes for environmental analysis.

ARTICLE INFO

Article history:
Received 31 May 2012
Received in revised form 23 August 2012
Accepted 14 October 2012
Available online 22 October 2012

Keywords:
Electro-polymerised graphene–nafion film/GCE
Substituted benzene-azo-quinoline
Voltammetry
Nitroanilines
Water samples
Partial least squares

ABSTRACT

A new modified electrode was constructed by the electro-polymerization of 7-[(2,4-dihydroxy-5-carboxybenzene)azo]-8-hydroxyquinoline-5-sulfonic acid (DHCBAQS) at a graphene–nafion modified glassy carbon electrode (GCE). The construction process was performed stepwise and at each step the electrochemical characteristics were investigated particularly with respect to the oxidation of the three noxious analytes, 2-nitroaniline (2-NA), 3-nitroaniline (3-NA), 4-nitroaniline (4-NA); the electrode treated with the fluorescence reagent DHCBAQS performed best. At this electrode, the differential pulse voltammetry peak currents of the three isomers increased linearly with their concentrations in the range of 0.05–0.60 $\mu g\,mL^{-1}$, respectively, and their corresponding limits of detection (LODs) were all about 0.022 $\mu g\,mL^{-1}$. Furthermore, satisfactory results were obtained when this electrode was applied for the simultaneous quantitative analysis of the nitroaniline isomer mixtures by Principal component regression (PCR) and Partial least squares (PLS) as calibration methods (relative prediction error (PRE_T) – 9.04% and 9.23%) and average recoveries (101.0% and 101.7%), respectively. The above novel poly-DHCBAQS/graphene–nafion/GCE was successfully employed for the simultaneous analysis of the three noxious nitroaniline isomers in water and sewage samples.

1. Introduction

Polymer-modified electrodes have many advantages when used in electrochemical methods of analysis [1–3] and electropolymerization is a successful method for the immobilization of polymers [4,5], which allows the control of film thickness and permeation characteristics. Such electrodes have high selectivity, sensitivity, and homogeneity in electrochemical deposition, and strong polymer adherence, as well as chemical stability of the film [6–9]. Electro-deposition of nano-particles on electrode surface e.g. glassy carbon electrode (GCE), has been significantly improved [1,2,4,6] by electro-polymerization of suitable monomers such as 7-[(2,4-dihydroxy-5-carboxybenzene)azo]-8-hydroxyquinoline-5-sulfonic acid (DHCBAQS), a fluorescent reagent and a complex indicator, which has been used for analysis of metal ions [10,11]. It has three side groups (—OH, —COOH and $-SO_3H$) and good redox characteristics; it can be electropolymerized from aqueous solution, producing stable redox active layers. Also, its π–π conjugated bonds can facilitate electron transfer. In this investigation, a film of DHCBAQS was deposited on a previously deposited layer of graphene nano-particles on the GCE.

Graphene is a single, polymerized layer of carbon atoms closely packed into a two-dimensional honeycomb lattice and graphene-based nano-materials [12,13]; such graphene films in biosensors are known to be effective sensing platforms for small biomolecules.

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http://dx.doi.org/10.1016/j.jhazmat.2012.10.026

Compared with the comparatively costly carbon nanotubes (CNTs), graphene's performance with regard to, e.g. electrical conductivity and mechanical strength, is quite competitive [14]. Some different graphene based biosensors include: (1) a functionalized-graphene modified graphite electrode for the determination of dopamine [15]; (2) a graphene–chitosan composite film modified GCE for simultaneous determination for catechol, resorcinol and hydroquinone in water [16]; (3) a graphene/BMIMPF$_6$ (1-Butyl-3-methylimidazolium hexafluorophosphate) nano-composite modified electrode for simultaneous determination of hydroquinone and catechol [17].

To investigate the analytical performance of such an electropolymerized modified electrode for the simultaneous determination of small molecules, a series of noxious aniline derivatives such as 2-nitroaniline (2-NA), 3-nitroaniline (3-NA), 4-nitroaniline (4-NA) (Scheme 1), were selected. These compounds are important representatives of small molecules found commonly in many chemical products, e.g. antioxidants, pesticides, and pharmaceuticals. These water soluble substances are also widely spread in the environment e.g. industrial waste, or degradation products e.g. herbicides. However, they are known to be highly mutagenic and carcinogenic, and form adducts with proteins and DNA [18]; they are also included in the US Environmental Protection Agency (EPA) list of priority pollutants [19]. Thus, development of novel, inexpensive analytical methods, particularly for simultaneous determination of noxious analytes of this kind, is useful, especially for water samples [20].

Various analytical methods for the determination of the three NA isomers in water include solid-phase extraction (SPE) and high-performance liquid chromatography (HPLC) with ultraviolet detection (UVD) [20], liquid-phase microextraction (LPE) and HPLC [18,21], ultraviolet spectroscopy (UV) [22–24], gas chromatography (GC) [25,26], and capillary electrophoresis (CE) [27]. Some applications include: (1) an SPE-HPLC-UVD method for the simultaneous determination of five nitroaniline and dinitroaniline isomers in wastewaters (limits of quantification (LOQ) for spiked sewage sample – 2.0×10^{-9} M for 2-NA, 3-NA and 2,6-dinitroaniline, and 4.5×10^{-9} M for 4-NA and 2,4-dinitroaniline [20]); (2) a spectrophotometric simultaneous determination for nitroaniline isomers in water samples (linear calibrations within 1.0–17.0 $\mu g\,mL^{-1}$; limits of detection (LODs) – 0.05–0.08 $\mu g\,mL^{-1}$ range [22]); (3) CE method for the simultaneous determination of nitroaniline isomers in wastewater (linear calibrations within 4.53×10^{-8} to 3.91×10^{-3} mol L^{-1}; LODs – 9.09×10^{-9}–3.92×10^{-8} mol L^{-1} range [27]). Although the determination of the three analytes by the mentioned methods is promising, some of the instruments involved are quite costly to maintain and run, and the methods are rather time-consuming.

Voltammetric methods using various electrodes, have been reported for the determination of the above mentioned analytes [28,29]. However, these methods have been applied only for the determination of individual compounds rather than for their simultaneous analysis. The principal difficulty for such analysis is the overlapping voltammograms of the individual compounds, and chemometrics modeling is required to resolve such complex profiles. Principal component regression (PCR) and partial least squares (PLS) are two well-known multivariate calibration methods [30] and have been described in detail elsewhere [31,32]. These methods transform measured data into orthogonal components such that the significant information is compressed into the first few. Each object has a score value on each component and likewise, each variable is described by a loadings value. Calibration models may be constructed with the use of concentrations of the analyte objects and related scores from significant components; such models were applied in this work [32].

The aims of this investigation were: (1) to produce a novel graphene–nafion modified glassy carbon electrode, which, for the first time, has been electro-polymerized with the use of the DHCBAQS fluorescence reagent, (2) to investigate the efficacy of this modified electrode for the simultaneous analysis of the closely related nitroaniline isomers, with the use of electroanalytical techniques such as cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

2. Experimental

2.1. Instrumentation

Electrochemical experiments were performed with the use of a CHI660A electrochemical workstation (Chenhua Apparatus Co., Shanghai) in conjunction with a three-electrode system: the working electrode – poly-DHCBAQS/graphene–nafion/GCE (3 mm diameter), the counter electrode – a platinum wire electrode, and the reference electrode – a saturated calomel electrode (SCE). Electrode potentials were reported with respect to the SCE. A cell stand (Model BAS C1A) was used for voltammetric scanning and to stir the testing solution during the pre-concentration step.

HPLC measurements were carried out on an Agilent 1100 Series HPLC-DAD system equipped with a G1379A vacuum degasser, a G1311A quaternary pump, a G1313A autosampler, an injector with a 100 μL loop, and a G1315B diode array detector. For chromatographic measurements, an Agilent ZORBAX Eclipse XDB-C18 column (250 mm × 4.6 mm, 5 μm) was used together with an Agilent Zorbax high pressure reliance cartridge guard-column (C18, 12.5 mm × 4.6 mm, 5 μm).

Scanning electron microscopy (SEM) was performed on an FEI Quanta200F instrument. The samples were usually deposited or dropped onto the detachable GCE. The same magnification was used for all samples (10,000×) and the power level was 20 kV.

2.2. Reagents

2-NA, 3-NA and 4-NA were purchased from Aladdin Chemistry Co., Ltd. Nafion (5 wt.% dissolved in lower aliphatic alcohols and water) was obtained from Sigma–Aldrich Co., Shanghai. Graphene Oxide was purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. DHCBAQS was supplied by Prof. Wu, Department of Chemistry, Nanchang University. All other chemicals (Analytical Grade reagents) were obtained from Beijing Chemical Reagent Company (Beijing, China) and used without further purification. A Britton–Robinson (B–R) buffer (pH 2.00) was prepared by adding 5 mL 0.2 mol L^{-1} sodium hydroxide to 100 mL of mixed acids; this acid mixture contained 0.392 g 85% ortho-phosphoric (0.034 mol L^{-1}), 0.240 g acetic (0.040 mol L^{-1}) and 0.247 g boric (0.040 mol L^{-1}) acids. Twice-distilled water was used throughout the experiments.

2.3. Preparation of Poly-DHCBAQS/graphene–nafion/GCE

Before modification, the GCE (3 mm diameter) was polished with emery paper and alumina slurry; then, it was rinsed successively with dilute nitric acid, ethanol and distilled water in an ultrasonic bath, and finally, it was electrochemically treated by potential cycling between −1.0 and 1.0 V in 0.25 mol L^{-1} H_2SO_4 until a steady state was reached.

1.0 mg graphene was added to 1.0 mL 0.5% Nafion solution (N,N-dimethylformamide as the solvent), followed by ultra-sonication for 2 h to form a homogenous mixture of graphene–Nafion, and 15 μL of this mixture suspension was then dropped onto the freshly polished GCE surface. The solvent was evaporated in air for 5 h, and