Sensors and Actuators B 256 (2018) 553–563

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Research Paper

Electrocatalytic performance enhanced of the electrooxidation of gamma-hydroxybutyric acid (GHB) and ethanol on platinum nanoparticles surface. A contribution to the analytical determination of GHB in the presence of ethanol

R. Jiménez-Pérez [b], J.M. Sevilla [b], T. Pineda [b], M. Blázquez [b], J. Gonzalez-Rodriguez [a,*]

[a] School of Chemistry, College of Science, University of Lincoln, Brayford Pool, Lincoln, LN67TS, UK
[b] Department of Physical Chemistry and Applied Thermodynamics, Institute of Fine Chemistry and Nanochemistry, University of Cordoba, Campus Rabanales, Ed. Marie Curie 2ª Planta, E-14014 Córdoba, Spain

ARTICLE INFO

Article history:
Received 11 August 2017
Received in revised form 9 October 2017
Accepted 25 October 2017

Keywords:
GHB
Cyclic voltammetry
Chronoamperometry
Platinum nanoparticles
Electrochemical sensor
Modified electrode
Platinum-catalysed
Electro-oxidation

ABSTRACT

The electrooxidation of GHB and ethanol on a glassy carbon/platinum nanoparticles/polyvinyl alcohol modified electrode (GC/PtNPs/PVA) in weakly acidic medium has been investigated by cyclic voltammetry and chronoamperometry. The study with the concentration, the scan rate and the analyses of j-t curves at several potentials for both compounds showed an enhanced electrocatalytic performance on the GC/PtNPs/PVA electrode.

Cyclic Voltammetry of ethanol-GHB mixtures was also performed observing that the presence of GHB in ethanol solutions significantly suppressed the oxidation peak currents of ethanol. This fact has been discussed in different experimental conditions and suggests that this behaviour is due to a competition of both alcohols for the active sites of the platinum surface according to a Langmuir-type expression. Depression of the current density of ethanol in the presence of GHB opens up new prospects for the development of strategies for the determination of GHB. The interval of detectable concentrations comprises between 1 and 75 mM (0.125 and 9.15 mg/mL) within the known toxic dose for GHB that is 0.5 mg/mL (4 mM). Detection limit of GHB, under these experimental conditions, was 0.872 mM (0.110 mg/mL). Analyses of test samples including typical recreational alcoholic beverages (vodka, lemonade + vodka, gin, rum, tequila and whisky) on the surface with the modified electrode have been successfully carried out. Precision (% RSD) values of alcoholic drinks and spiked GHB samples were tested in intra-assay and inter-assay.

1. Introduction

In recent years platinum nanoparticles have been of scientific and technological interest for their applications in different fields such as catalysis, energy storage and sensors [1,2]. The increasing interest in nanoparticles of this metal is due to their high catalytic efficiency and they are used in applications in medicine, electronics and recently as a catalyst for electrochemical reactions of fuel cells [3].

The distribution of size and morphology in platinum nanoparticles is very important from the point of view of their applications. Ultra-small particles exhibit a higher number of atoms giving rise to a larger surface with a remarkable effect in their activity. The reproducibility in the synthesis of ultra-small nanoparticles is therefore of great importance. Numerous synthetic methods are currently used, among them electrochemical deposition, colloid formation with polymers as well as various physical methods (solvothermal method, hydrothermal synthesis, sonochemistry, etc.) [4,5]. The most common synthesis is carried out by reducing a precursor salt using a reducing agent, typically sodium borohydride, in the presence of a stabilizing colloid, such as polyvinyl pyrrolidone (PVP), polyethylene glycol (PEG) or hexadecyltrimethyl-ammonium bromide (CTAB) [6]. The reduction with $NaBH_4$ is also considered the easiest and most effective method for the preparation of different nanostructured architectures [7]. In some cases, the synthesis has been described by a simple process, a kinetically controlled reduction with $NaBH_4$using no capping agent to obtain metal nanoparticles with a high surface area [8]. The advantage of the

---

* Corresponding author.
E-mail address: jgonzalezrodriguez@lincoln.ac.uk (J. Gonzalez-Rodriguez).

https://doi.org/10.1016/j.snb.2017.10.142
0925-4005/

synthesis process by reduction with $NaBH_4$ is evident: the possibility to quickly prepare structures at room temperature [9]. In addition, electrochemical methods also allow the formation of bimetallic/trimetallic nanostructures with adjustable compositions [10–12]. The use of surfactants plays an important role in controlling the size of nanoparticles of Pt, showing that the interaction of the surfactant on the surface of nanoparticles establishes the control in the particle size of Pt [13].

The best known reactions using catalyzed nanostructures containing platinum are those involving the oxidation of carbon monoxide, fuel cells hydrogen, fuel cell methanol, electrochemical oxidation of ethanol, electrochemical oxidation of formic acid, oxygen depletion and glucose detection among other [5]. Recently, studies on the oxidation of ethanol and other small molecules on surfaces of platinum nanoparticles synthesized by colloidal methods where higher electrocatalytic efficiency was found have been developed [14–16].

Other studies involving electrochemical applications with modified electrodes containing platinum nanoparticles synthesized using vinyl polymers as capping agent have also been reported. Their fundamental advantage consists on a one-step synthesis often producing nanoparticles with geometries which favor certain electrocatalytic routes. The most commonly polymers used in this synthetic approach are PVP (polyvinylpyrrolidone) [17], PVA (polyvinyl alcohol) [18] and PVAc (polyvinyl acetate) [19], among others.

Gamma-hydroxybutyric acid (GHB) is a molecule that has become a notoriously famous substance because it is frequently used as a drug of abuse in places of leisure and can cause disorders that can lead to death in doses above 500 mg/L [20]. It also has a short life in the body that makes its determination difficult. Currently there are no portable and fast methods for quantitative detection, hence the importance of manufacturing sensors to detect this drug.

This work presents the synthesis of platinum nanoparticles with PVA, the surface modification of graphite vitrified electrodes with the nanoparticle colloid obtained and their application related to the electrooxidation of ethanol and GHB, where the electrocatalytic efficiency of the manufactured electrode is highlighted. Electrooxidation of GHB has been previously studied by electrochemical and spectroelectrochemical methods on polycrystalline surfaces showing a reaction mechanism similar to those observed for other aliphatic alcohols and where the carboxylic group of the molecule together with the electrolyte and water coadsorption plays an important role [21–28]. In this context, the surface modified with platinum nanoparticles exhibits optimal characteristics as a sensor, in particular, for the determination of GHB.

2. Experimental

2.1. Reactant and synthesis of PtNPs-PVA

Gamma-hydroxy butyric lactone (GBL) was obtained from Aldrich (reagent, minimum 99% purity). Sulphuric acid (98% purity), phosphoric acid (85% purity), and sodium hexachloroplatinate salt (99%+ purity) were purchased from Merck. Semiconductor grade purity sodium hydroxide, polyvinyl alcohol (Mw 15000) and Sodium borohydride was purchased from Sigma-Aldrich. Glassy carbon (GC) was obtained from Goodfellow. Nafion ® 117 (NF) was purchased from Fluka. All solutions were prepared with deionized water produced by a Millipore system.

GHB, sodium salt, was prepared and identified as described in reference 21.

Nitrogen was bubbled in the electrochemical cell for 20 min before analysis. All the measurements realized in this work were carried out with a freshly prepared solution.

Samples of beverages were firstly taken and diluted, lead to quantities of ethanol in the range studied. The vodka drink used is 40% (density 0.940 g/mL), so that 250 mL of a vodka solution in 0.1 M phosphoric acid, pH 4 was prepared. For this, 3.06 mL of the original drink were taken to prepare a concentration of 100 mM ethanol. For the lemonade-vodka combination was assumed a volume ratio of 3:1, and 250 mL of the mixture was prepared in 0.1 M phosphoric acid pH 4. Other distilled alcoholic beverages used in this study under the same experimental conditions were: gin, rum, tequila and Scotch whisky, all to 40% (respective densities: 0.9375, 0.9490, 0.9496 and 0.9480 g/mL) [29].

Platinum nanoparticles were prepared using chemical reduction in $NaBH_4$ and were capped in a polyvinyl alcohol (PVA) colloidal suspension similar to described in reference 17. The preparation takes place by a soft solution technique starting from a solution of K_2PtCl_6 in deionized water and an aqueous solution of $NaBH_4$ and PVA. $NaBH_4$ was used as a reducing agent and PVA as a capping agent. In a typical synthesis, PVA (20 mg) was dissolved in hot deionized water (2 mL), and 1 mL of this second solution was then mixed with 5 mL of K_2PtCl_6 solution (0.01 M) under vigorous stirring. 5% $NaBH_4$ solution was added dropwise to the mixture. The colour of the reaction solution gradually changed from light yellow to dark brown. This solution is filtered through a 0.45 μm filter (Filter-Lab from filter ANOIA).

2.2. Working electrodes

Two different working electrodes were used for the different experiments. A 1.6 mm diameter polycrystalline platinum electrode was obtained from Bioanalytical Systems (Kenilworth, UK). This working electrode was polished with 0.05 μm Al_2O_3 slurry, rinsed and sonicated in 18 M Milli-Q water (Millipore, Maryland, US) and dried before use. The PtNPs-PVA modified glassy carbon electrode was rinsed with 18 M Milli-Q water and dried under a nitrogen stream before use.

The electroactive surface areas of the working electrodes were determined using the hydrogen adsorption/desorption voltammetric peaks of platinum electrode with a known charge density of 210 $\mu C/cm^2$ in 1.0 M H_2SO_4. A value of $0.036 \pm 0.001\ cm^2$ was found and used for normalize the current intensity in the cyclic voltammograms presented in this work for polycrystalline platinum electrode. Values ranging from 5 to 1 cm^2 were obtained for GC/PtNPs/PVA electrode over the effective life of the electrode.

Prior to the electrode surface modification, a bare glassy carbon sheet (GC) with a width of 1 cm was polished mechanically with 0.05 μm alumina slurry on a polishing pad, washed with deionized water in an ultrasonic bath for 5 min and dried with a N_2 gas flow. For the modification of electrode, a 70 μL of the uniform PtNPs-PVA solution was dropped directly onto a clean GC surface to obtain the proposed modified electrode (GC/PtNPs) and then 30 μL of Nafion ® 117 (0.05%) were added, this last in order to stabilize the nanoparticles on the carbon surface. The GC/PtNPs-PVA electrode was dried at room temperature for 12 h. The system was stable for more than 10 weeks during which the electrode was subjected to daily experiences.

2.3. Electrochemical instrumentation

Cyclic voltammetry (CV) and chronoamperometry analyses were performed with a Autolab (Ecochemie model Pgstat3) instrument attached to a PC with proper software (NOVA) for the total control of the experiments and data acquisition. A three elec-