Analytical Chemistry Research 5 (2015) 14–20

Contents lists available at ScienceDirect

Analytical Chemistry Research

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

Amperometric detection of carbohydrates based on the glassy carbon electrode modified with gold nano-flake layer

Huy Du Nguyen [a], T. Thuy Luyen Nguyen [a], Khac Manh Nguyen [a], Anh Mai Nguyen [a], Quoc Hien Nguyen [b,*]

[a] Central Laboratory for Analysis, University of Science, Vietnam National University in Ho Chi Minh City, 227 Nguyen Van Cu Street, Ho Chi Minh City, Viet Nam
[b] Research and Development Center for Radiation Technology, Vietnam Atomic Energy Institute, 202A, Street 11, Linh Xuan Ward, Thu Duc District, Ho Chi Minh City, Viet Nam

ARTICLE INFO

Article history:
Received 9 March 2015
Revised 8 June 2015
Accepted 9 June 2015
Available online 12 June 2015

Keywords:
Pulsed amperometric detection
Gold nano-flake
Electrochemical cell
Carbohydrate

ABSTRACT

An electro-deposition approach was established to incorporate the gold nano-flakes onto the glassy carbon electrode in electrochemical cells (nano-Au/GC/ECCs). Using pulsed amperometric detection (PAD) without any gold oxidation for cleaning (non-oxidative PAD), the nano-Au/GC/ECCs were able to maintain their activity for oxidizing of carbohydrates in a normal alkaline medium. The reproducibility of peak area was about 2 relative standard deviation (RSD,%) for 6 consecutive injections. A dynamic range of carbohydrates was obtained over a concentration range of 5–80 mg L^{-1} and the limits of detection (LOD) were of 2 mg L^{-1} for fructose and lactose and 1 mg L^{-1} for glucose and galactose. Moreover, the nano-Au/GC/ECC using the non-oxidative PAD was able to combine with the internal standard method for determination of lactose in fresh cow milk sample.

1. Introduction

The amperometric detection of carbohydrates following high performance liquid chromatographic (HPLC) separations has several advantages over other methods [1,2]. As a result, electrochemical cells (ECCs) with gold working electrode for carbohydrate analysis are commercially available. When operating in direct current (DC) mode, the loss of electrode activity arises. This can be ascribed to the fouling of the electrode by the reactant or product adsorption [3]. Thus, the pulsed amperometric detections (PADs) have been developed. In the PAD, anodic detection (*ca.* 50 mV) was alternated with oxidative and reductive cleaning steps by stepping the potential to a greater positive value (*ca.* 600 mV) and to a more negative value (*ca.* −600 mV), respectively. The electrochemical (EC) cleaning of adsorbed reactants or products reactivates the gold electrodes [2–5]. Gold electrode also forms stable oxide layer on the anodic polarization that can be fully reduced to the bare metal during the cathodic polarization [4]. Consequently, PAD approach normally leads to baseline drift [6]. Moreover, gold electrode is susceptible to corrosion in the presence of Cl^- anions [7], which were abundantly in many samples. This can deteriorate the performance of EC cells. Therefore, decreasing the gold oxidation in PAD without performance loss can offer the amperometric detection some further advantages in carbohydrate analysis.

By dropping an aliquot of gold(III) solution onto glassy carbon (GC) surface and cycling in a suitable potential range after drying the GC surface in oven, Casella et al. created a removable gold layer in EC cell for the amperometric detection of carbohydrates [8]. When using as HPLC detector, this gold layer was, however, only stable with mobile phase containing 1.0 μM of $AuCl_4^-$.

The aims of this study are to use an electro-deposition for preparation of gold nano-flake layer on the GC working electrode in EC cell (nano-Au/GC/ECC) that is able to detect carbohydrates precisely with a normal alkaline supporting electrolyte and based on the nano-Au/GC/ECC for decreasing the oxidation of gold in PAD.

2. Experimental

2.1. Chemical and reagents

$HAuCl_4{\cdot}3H_2O$, $ZnSO_4{\cdot}7H_2O$, $K_4[FeCN_6]{\cdot}3H_2O$, NaOH, HCl and H_2SO_4 were of PA-grade from Merck (Germany). All the agents (lactose monohydrate, galactose, glucose, and fructose) used in this work were of PA-grade from Sigma–Aldrich (Singapore). Deionized water (purified by Mili-Q, Millipore) was used throughout all experiments. Stock standard solutions of carbohydrates (*ca.* 1000 mg L^{-1}) were prepared in water and stored at 4 °C. Working standard solutions were prepared in water and used in each experiment. Carrez I solution was prepared by dissolving 3.60 g of $K_4[FeCN_6]{\cdot}3H_2O$ in 100 mL of water. Carrez II solution was prepared by dissolving 7.20 g of $ZnSO_4{\cdot}7H_2O$ in 100 mL of water.

* Corresponding author.
E-mail address: hien7240238@yahoo.com (Q.H. Nguyen).

http://dx.doi.org/10.1016/j.ancr.2015.06.001
2214-1812/

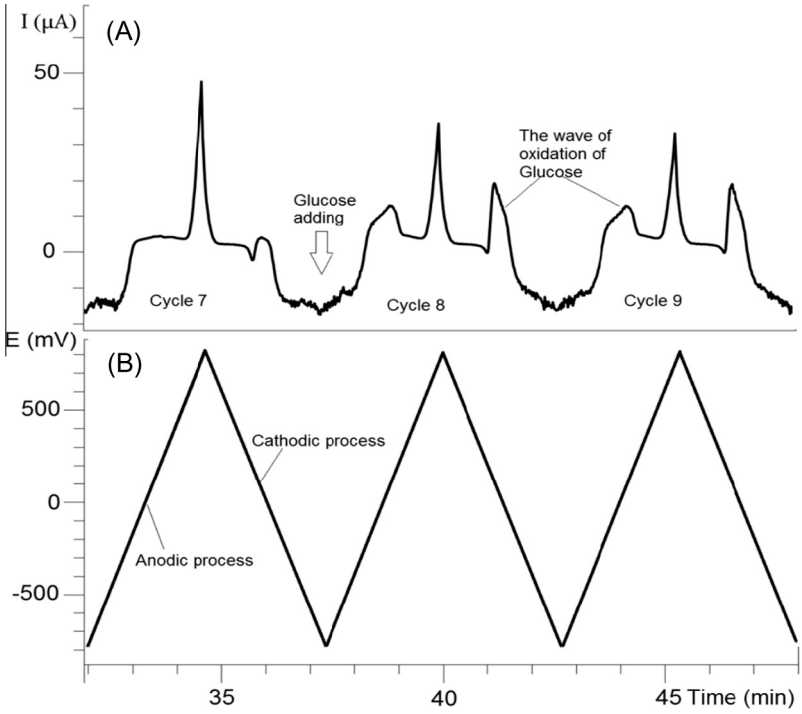

Fig. 1. Current (A) and voltage (B) versus time of the Au-RD electrode in 100 mM NaOH solution. A 0.5 μg of glucose was added into CV cell at 8th cycle.

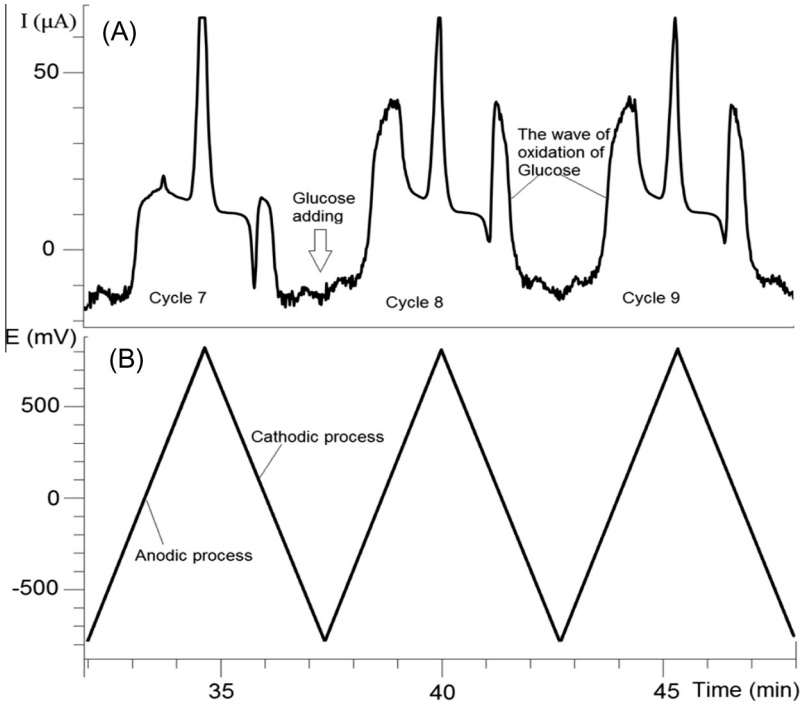

Fig. 2. Current (A) and voltage (B) versus time of the nano-Au/Au-RD electrode in 100 mM NaOH solution. A 0.5 μg of glucose was added into CV cell in 8th cycle.

Gold(III) solution was prepared from $HAuCl_4 \cdot 3H_2O$ in the mixture solution of 0.5 M H_2SO_4 and 0.05 M HCl.

2.2. Apparatus

The Waters HPLC systems (Waters, USA) consisted of a binary pump (Waters 1525, USA), a 20 μL loop, a column oven, and an EC detector consisting of an EC flow cell. The EC detector or potentiostat (Waters 2465, USA) can operate in DC, pulse and scan mode. The EC flow cell is in wall-jet structure consisting of a 2 mm diameter GC working electrode, an in-situ silver/silver chloride reference electrode (diameter of 2 mm) and the platinum body counter electrode. A typical three-electrode cell consisted of a 2 mm diameter gold rotating disk working electrode, an Ag/AgCl,