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Facile one-step direct electrodeposition of bismuth nanowires on glassy carbon electrode for selective determination of folic acid

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ABSTRACT

In the present work, we have developed a facile one step route to electrodeposition of stabilizer-free bismuth nanowires (BiNWs) on glassy carbon (GC) substrates by using a simple potentiostatic method. Formation of BiNWs on GC substrate was confirmed by field emission scanning electron microscopy (FE-SEM). The growth of BiNWs on the GC substrate was monitored by cyclic voltammetry and found that continuous in-situ generation of hydrogen bubbles during electrodeposition provides a stagnant template for the formation of BiNWs on the GC substrate. Phase-purity of the deposited BiNWs on GC substrate studied by XRD indicates no other oxide formation. The electrodeposited BiNWs on GC substrate was used for electro-reduction of folic acid (FA) and its quantitative determination in Britton-Robinson buffer of pH 4.5 solutions. The observed cyclic voltammetric reduction current of FA on BiNWs/GC is almost 15 times higher with 0.015 V less negative overpotential compared to bare GC substrate alone. This result clearly reveals the electrocatalytic activity of the deposited BiNWs. In addition, square wave voltammetry (SWV) showed a perfectly linear response in the concentration range of 1×10^{-8}–15×10^{-8} mol L^{-1} with a correlation coefficient of 0.9956. The limit of detection (LOD) and limit of quantitation (LOQ) are determined to be 9.53×10^{-9} and 31.68×10^{-9} mol L^{-1} respectively. The response of the BiNWs/GC sensor matrix is not affected by any usual interference from excess concentrations of metal ions and biomolecules such as ascorbic acid, dopamine, and glucose. Further, we have also performed real sample analysis using pharmaceutical tablets containing folic acid using our BiNWs/GC in the form of recovery studies and the obtained results are found to be in good agreement with the results from high performance liquid chromatography analysis (HPLC). Based on the experimental results, it may be stated that the electrodeposited BiNWs/GC could be an ideal sensor platform for FA determination and may open up applications in biosensor design.

1. Introduction

Fabrication of size- and shape-controlled bismuth nanostructured layers on conducting substrates is an important research theme especially in electroanalytical based biosensor device applications [1]. The size- and shape-control continues to pose a challenge. So, electrochemical methods appear to attract attention of even non-electrochemists because of their advantages over the chemical methods- they are simple, of low-cost and easy to control the size and shape of nanostructured materials without the need for additional surfactants or stabilizers [2,3]. It is well known in literature that template-assisted (especially hard-templates like porous alumina membranes) electrochemical deposition method is ideal for obtaining control over size and shape of NWs [4]. For example, Jin et al. [5] have reported the synthesis of BiNWs using potentiostatic electrochemical deposition into the channels of an anodic alumina membrane (AAM). However, making and removing hard templates from the conducting substrates are tricky and often time-consuming. In this context, Shin and Liu [6] proposed a new dynamic template comprising hydrogen gas bubbles which could be prepared by simple tuning of the cathodic overpotential as well as choice of suitable electrolyte for the potentiostatic deposition. The advantage of using hydrogen bubble template is the ease of preparation as well as removal from the substrate, without involving any other hazardous chemicals or corrosive reagents. However, exercising control over the formation of hydrogen-bubble template, nucleation and growth of bismuth deposition is an important step that demands optimization of deposition

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conditions. In the present work, we demonstrate controlled conditions for the formation of the dynamic template and its use in producing BiNWs directly on the conducting surfaces.

In recent times, bismuth film electrodes have become very attractive as they provide viable solutions to problems in electroanalysis, where they replace toxic mercury. Wang et al. [7] introduced bismuth coated electrodes for anodic stripping voltammetric determination of trace heavy metals more than a decade ago. Since then, numerous studies highlighted the benefits of using bismuth-modified electrodes for the trace metal analysis because, it exhibits relatively large cathodic hydrogen overvoltage, good mechanical stability, low background (i.e., high signal-to-noise ratio), negligible interference from oxygen and also it is environmentally friendly [8,9]. In most cases, bismuth film electrodes have been employed only for trace metal analysis and attempts to use them for other electroanalytical purposes are sparse, barring its role in the quantification of (a) cysteine [10], (b) aminosalicylate [11], (c) sulfadiazine [12], (d) paraquat [13], (e) vitamin B_{12} [14], (f) progesterone [15] and (g) electrocatalyzing CO_2 reduction [16]. Unlike in the case of metals, the electrochemical determination of biomolecules requires more sensitive materials as electrode-modifiers. To the best of our knowledge, no attempt has so far been made towards electroreduction-based estimation of FA using BiNWs modified electrodes.

FA is water-soluble and also part of vitamin B complex, found in leafy vegetables, egg yolk, legumes, liver and citrus fruits and it is considered as one of the important biomolecules essential during the period of cell growth and division [17–19]. The deficiency of FA causes a range of diseases such as congenital anomalies of brain and spine, colorectal cancer, megaloblastic anemia, mental devolution, neural tube defects and heart attack [20,21]. In addition, it also possesses antioxidant properties which help protecting the DNA against free radical attack [22]. Therefore, the determination of FA is a significant research interest and hence several analytical methods have been reported for quantifying FA that include fluorimetry [23], spectrophotometry [24], high performance liquid chromatography [25] and flow injection chemiluminescence [26]. However, these techniques are complex, tedious, time consuming, require sophisticated and expensive instruments [27]. As mentioned earlier, electrochemical techniques are most preferred ones considering their simplicity, rapid response, excellent reproducibility, good stability, low cost and lower achievable detection limits [28]. In literature, Han et al. [29] and Alvarez and co-workers [30] studied the electrochemical reduction and adsorption of FA at mercury electrodes using adsorptive stripping voltammetry. Gall and Van den Berg [31] also reported the FA determination at hanging mercury drop electrode using cathodic stripping voltammetry achieving very low limits of detection: 10^{-11}–10^{-12} mol L^{-1}. However, the toxicity as well as poor reproducibility in the direct determination of FA limits their application. In order to solve this problem, other chemically modified electrodes have been used for the quantification of FA which include carbon nanotubes [1,32,33], carbon paste [34,35], ordered mesoporous carbon [36,37], calixarene [38], lead film electrode [39], nanostructured α-Fe_2O_3 [40], phosphomolybdic-polypyrrole film [41] and 2-mercaptobenzothiazole self-assembled gold electrode [42]. All these modified electrodes are used for the determination of FA based on its oxidation reaction. However,

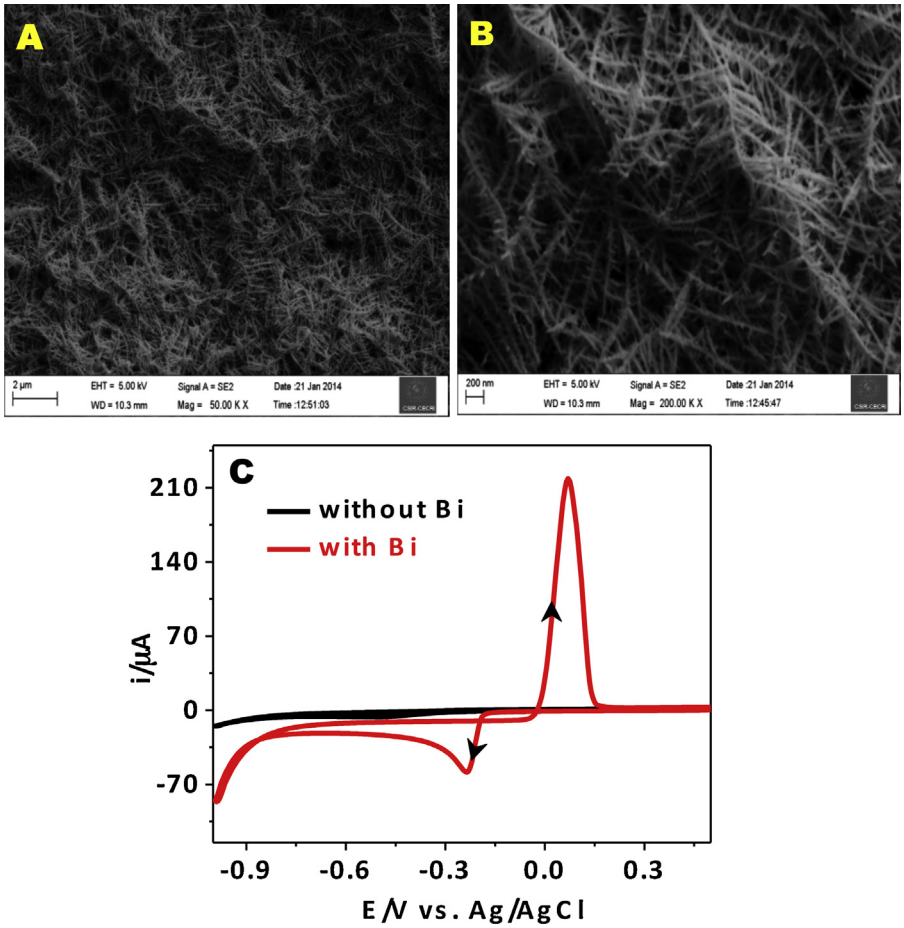

Fig. 1. FE-SEM images of electrodeposited BiNWs/GC at (A) low, (B) higher magnification and (C) Cyclic voltammograms of GC electrode in electrolyte solution containing with and without 1×10^{-3} mol L^{-1} $Bi(NO_3)_3$ in acetate buffer of pH 4.5 at the scan rate of 0.05 V s^{-1}.