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Reactivity at the film/solution interface of ex situ prepared bismuth film electrodes: A scanning electrochemical microscopy (SECM) and atomic force microscopy (AFM) investigation

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Abstract

Bismuth film electrodes (BiFEs) prepared ex situ with and without complexing bromide ions in the modification solution were investigated using scanning electrochemical microscopy (SECM) and atomic force microscopy (AFM). A feedback mode of the SECM was employed to examine the conductivity and reactivity of a series of thin bismuth films deposited onto disk glassy carbon substrate electrodes (GCEs) of 3 mm in diameter. A platinum micro-electrode ($\phi = 25\ \mu\text{m}$) was used as the SECM tip, and current against tip/substrate distance was recorded in solutions containing either $Ru(NH_3)_6^{3+}$ or $Fe(CN)_6^{4-}$ species as redox mediators. With both redox mediators positive feedback approach curves were recorded, which indicated that the bismuth film deposition protocol associated with the addition of bromide ions in the modification solution did not compromise the conductivity of the bismuth film in comparison with that prepared without bromide. However, at the former Bi film a slight kinetic hindering was observed in recycling $Ru(NH_3)_6^{3+}$, suggesting a different surface potential. On the other hand, the approach curves recorded by using $Fe(CN)_6^{4-}$ showed that both types of the aforementioned bismuth films exhibited local reactivity with the oxidised form of the redox mediator, and that bismuth film obtained with bromide ions exhibited slightly lower reactivity. The use of SECM in the scanning operation mode allowed us to ascertain that the bismuth deposits were uniformly distributed across the whole surface of the glassy carbon substrate electrode. Comparative AFM measurements corroborated the above findings and additionally revealed a denser growth of smaller bismuth crystals over the surface of the substrate electrode in the presence of bromide ions, while the crystals were bigger but sparser in the absence of bromide ions in the modification solution.

Keywords: Bismuth film electrode; Reactivity; Ex situ; SECM; AFM; NaBr

1. Introduction

Since its introduction in stripping analysis [1], the bismuth film electrode (BiFE) has been accepted in many electroanalytical laboratories worldwide [2]. The electroanalytical performance of the BiFE, which approaches, or in some cases even surpasses that of mercury analogues, has encouraged many scientists to further investigate and expand its scope and applicability for measurement of numerous heavy metals and some selected organic compounds [3–5]. Different kinds of bismuth electrodes have been proposed, including in situ and ex situ prepared BiFE [1,6], bismuth bulk electrode (BiBE) [7], and several modifications of bismuth-based paste electrodes [8,9]. Among various types of bismuth film electrode, the ex situ prepared bismuth films require adequate physical and chemical stability, as they have to be transferred from the preparation/modification solution to the measuring cell device, and usually need to exhibit enhanced stability for multiple measurements. Recently, it was observed that the addition of complexing bromide ions into the modification solution is beneficial for the ex situ preparation of a bismuth film in connection with its electrochemical stripping operation [10–12]. This deposition route, reported for the first time by Krolicka et al. [10], has provided BiFEs of higher (physical) stability and enhanced reproducibility of measurements associated with the electrochemical stripping analysis. However, whether or not the latter improvements could also be

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ascribed to an enhanced chemical stability of the ex situ prepared bismuth deposits in contact with the electrolyte solution has not been investigated yet.

Scanning electrochemical microscopy (SECM) [13] is a technique that has been exploited to obtain valuable information concerning spatial localization of chemical reactions of a variety of substrate surfaces and thin solid films [14–16]. This can be done by using SECM operating in the feedback mode [17], where a micro-electrode tip-current is perturbed from its value in the bulk solution by the presence of substrate in a close proximity. In particular, when the micro-electrode tip approaches an insulator, the current decreases with the tip/substrate distance due to blockage of diffusion of the electroactive species toward the tip (negative feedback). When the tip approaches a conductor, the current increases with decreasing the distance due to regeneration of the redox mediator at the substrate/solution interface (positive feedback). This regeneration may be due to lateral charge-transfer process or it may proceed by reaction between the substrate and the tip-generated species at the substrate/solution interface [18]. Therefore, the plots of the current against the tip/substrate distance (approaching curves) along with their analysis may provide useful information about the nature and reactivity of the investigated substrate [13].

In this paper we utilized SECM operating in both feedback and scanning mode to probe the local properties of bismuth films, which were deposited ex situ on a glassy carbon substrate electrode (GCE) either in the presence or absence of complexing bromide ions in the modification solution. The GCE has been chosen, as it is typically employed as a substrate for deposition of bismuth films [3]. The SECM investigation is performed with the substrate being unbiased, thus allowing the measurements to be carried out on the bismuth films as grown in pristine conditions, without any direct electrochemical perturbation. Two different redox mediators hexaaminoruthenium(III) trichloride and potassium hexacyanoferrate(II) having different formal potentials were employed, thus allowing us to investigate the effect of redox couple upon the SECM feedback characteristics of the ex situ prepared bismuth films. In addition, AFM was used to illustrate the influence of the modification solution conditions upon the bismuth film growth and its morphology.

2. Experimental

2.1. Apparatus

Unless otherwise stated, voltammetric measurements were performed in a three-electrode electrochemical cell. A glassy carbon electrode (GCE) of 3 mm in diameter was employed as the working/substrate electrode for deposition of bismuth film, an Ag/AgCl (sat. KCl) served as the reference electrode and a platinum spiral wire was used as the counter electrode. The surface of the glassy carbon electrode was polished to a mirror-like appearance with alumina powder (0.3 and 0.05 μm) on a polishing pad. For SECM measurements a platinum micro-disk of 25 μm in diameter was employed as the tip-electrode. The platinum micro-disk was prepared by sealing a platinum wire of 25 μm in diameter into a glass capillary, which was afterward tapered to a conical shape, such that the overall tip to electrode radius ratio (RG) was equal to 10. The micro-disk was polished with graded alumina powder of different sizes (1, 0.3 and 0.05 μm) on a polishing pad.

The SECM micro-positioning device consisted of a set of three stepper motor stages with a 0.1 μm resolution (MICOS) with optical encoder (ZEISS), and the motion was controlled by a closed loop motion controller board PCI-7324 (National Instruments). The data acquisition was performed by a PCI-6035E Multifunction I/O board controlled with Lab View (National Instruments). A CH700B workstation (CH Instruments) was employed for SECM measurements and for other electrochemical experiments. All measurements were carried out in a three-electrode electrochemical cell placed in a Faraday cage.

AFM measurements were performed in a Veeco electrochemical cell with MultiMode V in combination with NanoScope V controller and Veeco Univecpot Bipotentiostat. A glassy carbon pellet ($\phi = 1$ cm) was used as the substrate electrode for electrochemical deposition of bismuth films, an Ag/AgCl wire was employed as the quasi-reference electrode, and a platinum wire as the counter electrode.

2.2. Reagents and solutions

All chemicals employed were of analytical-reagent grade. $K_4Fe(CN)_6$, KCl, CH_3COOH, CH_3COONa and NaBr were obtained from Aldrich. Hexaamminoruthenium(III) trichloride was purchased from J. Mattey and used as received. All solutions were prepared by using water, which was purified via a Milli-Q system (Gradient, Millipore, Bedford, USA). Acetate buffer solution (0.1 M, pH 4.5) was prepared by mixing together appropriate amounts of CH_3COOH and CH_3COONa. All SECM measurements were performed in aerated aqueous solutions containing 0.1 M KCl as a supporting electrolyte. All measurements requiring no oxygen were carried out in solutions that had been purged with pure nitrogen (99.99%) provided by Siad, Italy.

2.3. Ex situ preparation of BiFEs

The ex situ BiFE was prepared by electrodeposition of metallic bismuth onto a glassy carbon substrate electrode from a 0.1 M acetate buffer solution (pH 4.5) containing 100 mg/L bismuth(III) by applying a potential of −1.0 V for 5 min while the solution was stirred. BiFE in the presence of bromide ions was prepared similarly from a 0.1 M acetate buffer solution (pH 4.5) containing 50 mg/L bismuth(III) and 50 mg/L NaBr by applying a potential of −0.3 V for 60 s. The above plating conditions were adopted from previous investigations, since they provided long-term electrochemical and mechanical stability of the bismuth film as well as its good electroanalytical stripping performance [12]. Other details regarding the ex situ BiFE preparation can be found also in Ref. [12]. Following its preparation, BiFE was transferred directly into the cell of SECM device. In the case of AFM measurements, the bismuth film was grown directly in an AFM electrochemical cell onto the surface of a glassy carbon substrate electrode as described above.