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Proceeding Paper

An in-situ AFM Study of Electrochemical Bismuth Film Deposition on a Glassy Carbon Substrate Electrode Using a Low Concentration of Bismuth Ions †

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Abstract: The bismuth film electrode (BiFE), which was first introduced in 2000 for electrochemical stripping analysis, is now widely used in electroanalytical laboratories worldwide. Numerous scientists have been inspired to conduct more research and broaden the understanding of the BiFE's favourable electroanalytical performance, which is comparable to, or in some cases even exceeds that of mercury counterparts, for the detection of heavy metal ions and selected organic compounds. Various types of bismuth-based paste electrodes as well as in-situ and ex-situ prepared BiFE have been presented in combination with potentiometric and voltammetric (stripping) protocols. Since the ex-situ prepared electrodes must be moved from the preparation/modification solution to the measuring cell device and often need to display improved stability for several measurements, the ex-situ prepared bismuth films require acceptable physical and chemical stability. In this study, we provided insight into the formation of bismuth film on a glassy carbon substrate electrode (GCE) when using a very low concentration of bismuth ions. We used our home-constructed AFM cell to fit in commercial working GCE, a platinum wire as the counter electrode, and an Ag/AgCl/NaCl (3 M) as the reference electrode.

Keywords: AFM; Electrochemical deposition; In-situ AFM; BiFE; nanodeposit

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1. Introduction

Bismuth (Bi) has a small carrier mass and a long electron free path at room temperature [1]. For potential uses of electronic quantum confinement effects in low-dimensional bismuth structures, these peculiar electronic characteristics are intriguing [2]. Owing to its physicochemical properties and the distinct environmentally friendly nature, Bi and its composites have been utilized in myriad applications (e.g., optoelectronic applications [3,4], electrocatalytic reduction [5], topological insulator [6], batteries [7–9], heavy metal ions detection and removal [10–12].

For electroanalytical applications, Bi electrodes have emerged as a viable, alluring, and popular substitute for conventional mercury-based electrodes since the introduction of bismuth film electrodes (BiFE) in 2000 [13]. Bi-based electrodes give characteristics that are most similar to those of mercury and have the advantage of being environmentally

friendly with a favourable insensitivity towards dissolved oxygen. The carbon substrate in its various forms (such as glassy carbon, carbon paste, pencil lead, carbon fibre, and screen-printed carbon ink) appears to be the most suitable support for the Bi film formation.

In situ AFM is a powerful technique especially when it is combined with electrochemical techniques [14–18], owing to its capability to monitor the change in solution with relatively high resolution. without the need for sophisticated equipment in comparison to the electron microscope when the sample under study is immersed in a solution.

In this work, we studied the in-situ formation of BiFE, i.e., the commencement of the bismuth film growth, on a glassy carbon substrate, using a very low concentration level of bismuth ions in acetate buffer solution. We used our home-constructed AFM cell to fit in the commercial working electrode GCE to facilitate electrochemical measurements.

2. Materials and Methods

2.1. Materials

Bismuth standard solution (1000 mg/L Bi(III) in nitric acid) was purchased from Merck. Acetic acid (analytical grade) and platinum wire of 99.99% purity were purchased from Sigma Aldrich. A glassy carbon rotating disk electrode (GCE) with an outer diameter of 12 mm and disk diameter of 5 mm was purchased from Pin research.

2.2. Method

First, the exterior of GCE was machined to have a screw thread, so it can be attached to the electrochemical cell. Then, an electrochemical cell similar to our previously designed cell [18] was manufactured in such a way that the working electrode's position was machined to have a screw thread that the working electrode (GCE) can fit in. The cell was cleaned by using an ultrasonic bath in acetone, isopropanol alcohol and then Milli-Q water for 15 minutes each. Before attaching GCE to the electrochemical cell, the electrode was polished using alumina powder and nylon polishing pads, afterwards it was rinsed with Milli-Q water. The platinum wire was used as the counter electrode forming a circle within the inner rim of the cell and the standard Ag/AgCl/NaCl (3M) (BASi) reference electrode was employed. The electrodes were positioned in the cell and connected to PalmSense 4 potentiostat.

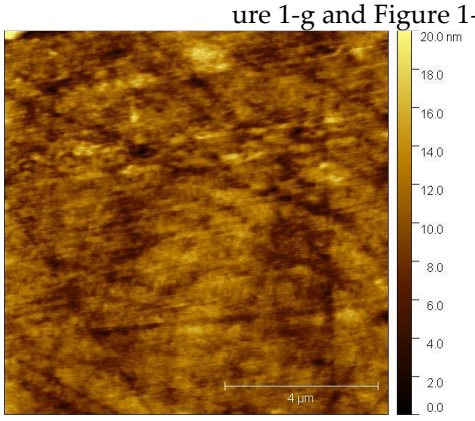
2.3. AFM-Electrochemical Measurements

The GCE, Pt-wire and reference electrodes were inserted in the electrochemical cell, and then the analyte (1mg L^{-1} of Bi(III) in 0.5 M acetate buffer solution) was injected into the cell and scanned using Agilent 5500 AFM by operating it in AFM tapping mode. The electrode was scanned using a MikroMasch tip with a force constant of 5 N/m, 125 μm length and coated with gold. The samples were scanned at a scanning rate of 1 HZ with a scanning area of 10 × 10 μm^2.

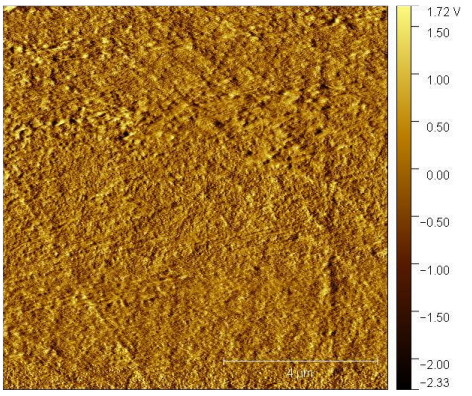
3. Results and Discussion

First, after injecting the solution into the electrochemical cell, the tip was brought close enough to the electrode's surface to scan it. Figure 1 shows selected AFM images of the GCE with the features formed on it. The left column encompasses the topography images, while the right column comprises the deflection images to additionally clarify the features at the surface of GCE. As can be seen in Figure 1-a, there are no deposits on the glassy carbon substrate surface except the scratches from the polishing process which is confirmed in the corresponding deflection image (Figure 1-b). A cathodic potential of -1.0 V/Ag/AgCl/NaCl (3M) was applied to GCE for a duration of 600 s. Then, the surface was scanned again at open circuit potential (OCP) at the same scanning area. The topography image in Figure 1-c demonstrates the change in the surface and the formation of new nano features that look to be nanotubes which is clearer in the deflection image (Figure 1-d)

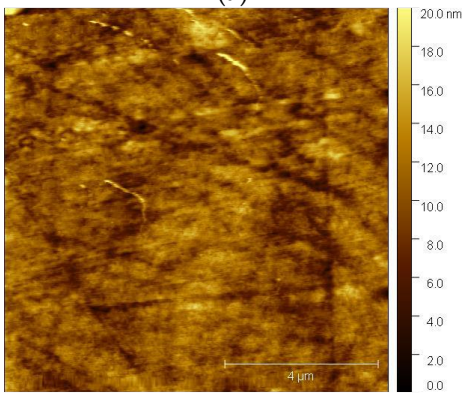
when compared with Figure 1-b. Next, to study the electrochemical manipulation of the formed nanofeatures, an anodic potential of 0.3 V/Ag/AgCl/NaCl (3M) was applied to GCE for 20 s, followed by AFM scanning of the same surface area, resulting in topography and deflection images, i.e., Figure 1-e and Figure 1-f, respectively. Upon the application of anodic potential, the bismuth nanodeposits were dissolved from the glassy carbon substrate. The application of the same cathodic potential accompanied by the same duration resulted in the formation of new nanostructured features (nanotubes) as depicted in Figure 1-g and Figure 1-h.



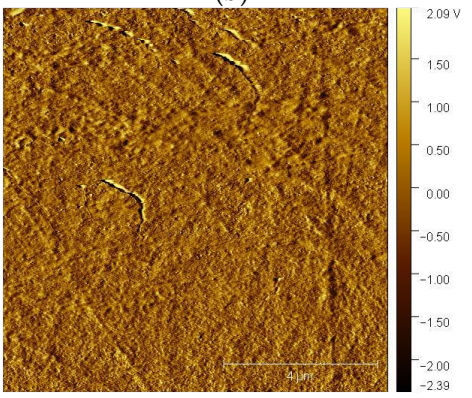
(**a**)



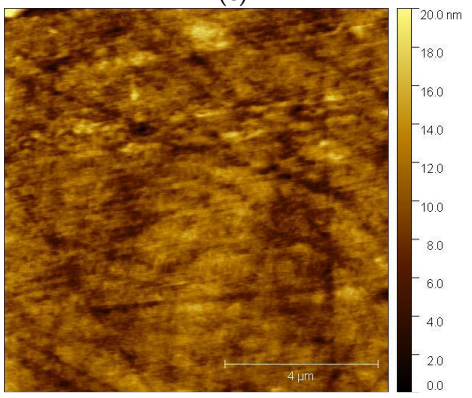
(**b**)



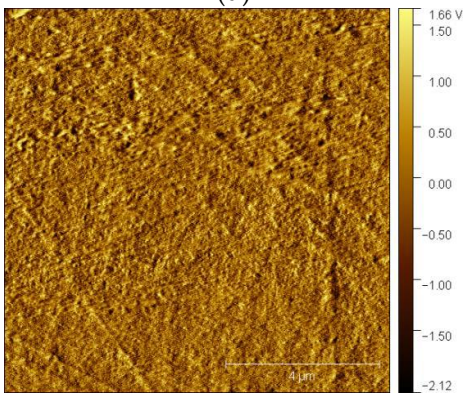
(**c**)



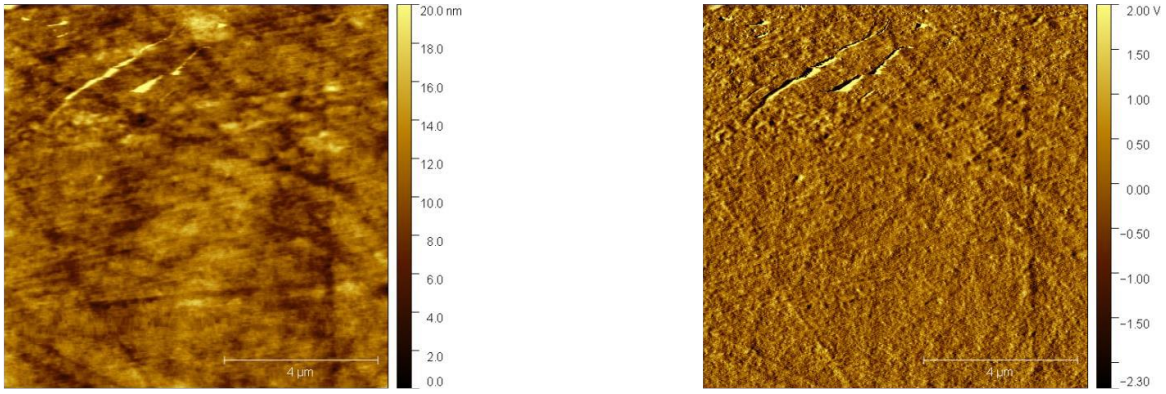
(**d**)



(**e**)



(**f**)



(**g**) (**h**)

Figure 1. In situ AFM images of GCE electrode surface in 0.5 M acetate buffer solution. The left column shows the topography, and the right column shows the deflection images: (a, b) fresh surface of GCE before electrochemical deposition; (c, d) after applying a cathodic potential of -1.0 V for 600 s; (e, f) after applying an anodic potential of +0.3 V for 20 s; (e, f) after applying a cathodic potential of -1.0 V for 600 s.

4. Conclusions

The combination of AFM with electrochemistry is a powerful approach for obtaining insight into the electrochemical processes at the conductive substrate surface. The formation/nucleation and dissolution of bismuth film with a low concentration of bismuth could be monitored directly in the solution by using in-situ AFM measurements. The beginning of the formation of bismuth film was in a form of nanostructures resembling nanotubular features when using a cathodic potential of value -1.0 V for 600 s. The electrochemically synthesized nanostructures were completely dissolved upon the application of an anodic potential of +0.3 V for 20 s and redeposited again using the same cathodic potential.

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