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Short communication

From a planar electrode to a random assembly of microelectrodes: A new approach based on the electrochemical reduction of 5-bromo-1,10-phenanthroline at gold electrodes

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ABSTRACT

A random assembly of microelectrodes (RAMs) was fabricated by electrochemical reduction of 5-bromo-1,10-phenathroline in N,N-dimethylformamide (DMF), generating the 1,10-phenanthroline radical, which was covalently grafted on gold electrodes. After several potential cycles, the gold surface was partially blocked with an insulating film of 1,10-phenanthroline and the resulting modified electrode exhibited the characteristics of a RAMs for the electrochemical reduction of the reversible probe 1,4-benzoquinone in DMF. Scanning electron microscopy and atomic force microscopy were used to examine the morphology of the electrodeposited film and to characterize the existence of micro-regions of gold not coated by the 1,10-phenanthroline film.

1. Introduction

Compared with conventionally sized electrodes, microelectrodes have many remarkable characteristics which make them a very powerful tool for electrochemical investigations, such as high mass-transport rate, immunity to ohmic drop and small capacitive-charging currents. However, currents are generally low, in the range of nA or pA, hence multimicroelectrode arrays have attracted attention because of their advantages in electroanalytical applications, including high signal to noise ratio compared to conventional electrodes with the same area [1–3]. To be used efficiently, i.e., to get a collective current response while maintaining the advantageous characteristics of a single microelectrode, individual microelectrodes in a microelectrode ensemble have to behave as isolated electrodes on the timescale of the experiment, hence their diffusion fields should not interact.

Multimicroelectrode arrays where individual microelectrodes are ordered at a fixed distance from their neighbours, usually named as "microelectrode arrays", have been fabricated by photolithography and screen-printing [4,5]. Microelectrodes assuming a random assembly of microelectrodes (RAMs) are usually constructed by dispersion of parallel conducting fibres in a nonconducting material [6] or by abrasive attachment induced acoustically [7]. A less explored approach for the construction of RAMs is the partial functionalisation of bare surfaces with organic groups.

Different methods for functionalisation of gold surfaces have been investigated. These include graft polymerization under UV irradiation [8–11], adsorption of organosulfur and selenium compounds on gold [9,11–15], reduction of $AuCl_4^-$ [16,17], plasma deposition of polymers [15], vapour deposition [15] and electrografting of organic molecules [15,18–23]. Most of the procedures employed for the gold surface modification involve the generation of highly reactive radicals, which is accompanied by formation of a gold–radical bond. Based on this principle, gold surfaces can be partially blocked by using similar procedures that involve the formation of radicals in solution [20,21,23–31], which can chemically react with gold. Accordingly, in this paper we show that the electrochemical reduction of 5-bromo-1,10-phenanthroline in aprotic medium leads to partial modification of gold surfaces and this constitutes a new strategy and an inexpensive proof of concept for the design of reproducible RAMs. This approach allows for control of the functionalisation level and is much cheaper and easier than other RAM designs such as photolithography [4,5].

2. Experimental

All solutions were prepared using N,N-dimethylformamide (DMF, Merck) as solvent, which was dried by vigorous stirring with CaH_2 at room temperature for 4 h and distilled under reduced pressure.

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5-Bromo-1,10-phenanthroline (BrPhen, G.F.S. Chemical Company), sublimed 1,4-benzoquinone (BQ) and tetrabutylammonium hexafluorophosphate (NBu_4PF_6, Fluka ≥ 98%) were used as received. Indium-doped tin oxide (ITO; Delta Technologies, sheet resistance < 20 Ω/cm, 0.7 cm × 3 cm in size) glass slides were cleaned by sonication in acetone, ethanol and deionized water for 5 min. The ITO substrates were coated with gold (thickness of the gold layer = 40 nm) using a sputter Cressington 208HR coater. A conventional three-electrode cell was used to carry out all electrochemical measurements on a PGSTAT128N Metrohm potentiostat. The working electrodes were a 3 mm diameter gold disc and a Au/ITO surface. The counter electrode was a platinum wire and an aqueous saturated calomel electrode (SCE), connected to the cell by a salt bridge containing 0.1 M n-Bu_4NPF_6 + DMF, was used as reference electrode. All electrochemical experiments were performed at 25 °C. Solutions were deoxygenated by bubbling dry argon and an argon atmosphere was maintained over the solutions during each experimental run.

Atomic force microscopy (AFM) images were obtained using a PicoSPM-LE Molecular Imaging System, slightly below their resonance frequency of approximately 294 kHz in air with cantilevers operating in the intermittent-contact mode (AAC mode) to measure the topographic surface and the roughness of the Au/ITO electrode and 1,10-phenanthroline/Au/ITO electrode.

Morphologic images of 1,10-phenanthroline/Au/ITO and Au/ITO electrodes were obtained from field emission scanning electron microscopy (FESEM, JSM-7401F from JEOL).

3. Results and discussion

3.1. Electrochemical behaviour of 5-bromo-1,10-phenanthroline

The electrochemical behaviour of 5-bromo-1,10-phenanthroline was examined in 0.1 M n-Bu_4PF_6 + DMF solution. Fig. 1A shows voltammograms obtained during a consecutive potential scan and the decrease of the reduction peak located at $E_p = -1.75$ V is clearly seen. This can be explained by taking into account the cleavage of carbon–halogen bonds in the electrochemical reduction of organic halides [24,25,32–34]. The first step corresponds to transfer of one electron from the electrode to 5-bromo-1,10-phenanthroline, generating 1,10-phenanthroline radical ($Phen^{\bullet}$) and bromide anion. The dissociation of the bond may follow stepwise or concerted pathways [25,32–34]. The $Phen^{\bullet}$ radical can interact with the gold surface, resulting in an increased passivation which decreases the available area and the current intensity. Scheme 1 presents the proposed steps for the electrode passivation.

3.2. Electrochemistry of 1,4-benzoquinone at the modified electrode

Despite the apparent complete passivation of the gold electrode, shown in Fig. 1A (curve d), it seemed that not the entire surface was covered by the insulating 1,10-phenanthroline film. This can be evinced by looking at the voltammogram obtained with the modified gold electrode in a DMF solution containing a reversible probe, 1,4-benzoquinone, BQ. Fig. 1B shows the electrochemical reduction of BQ carried out with a gold electrode before (Fig. 1B, curve a) and after electrodeposition of different amounts of the 1,10-phenanthroline film (Fig. 1B, curves b and c). The voltammogram obtained with the bare gold electrode (prior to the electrodeposition of the passivating layer) shows the quasireversible behaviour of BQ in DMF ($E° = -0.29$ V/SCE), as revealed from the correlation between cathodic peak current and anodic peak current ($i_{pc}/i_{pa} \approx 1$) and anodic to cathodic peak potential separation (0.078 V at 0.05 V s^{-1}). On the other hand, a very different electrochemical behaviour was noticed when the experiment was repeated with the modified electrode containing a self-assembled multilayer of 1,10-phenanthroline. As Fig. 1B (curves b and c)

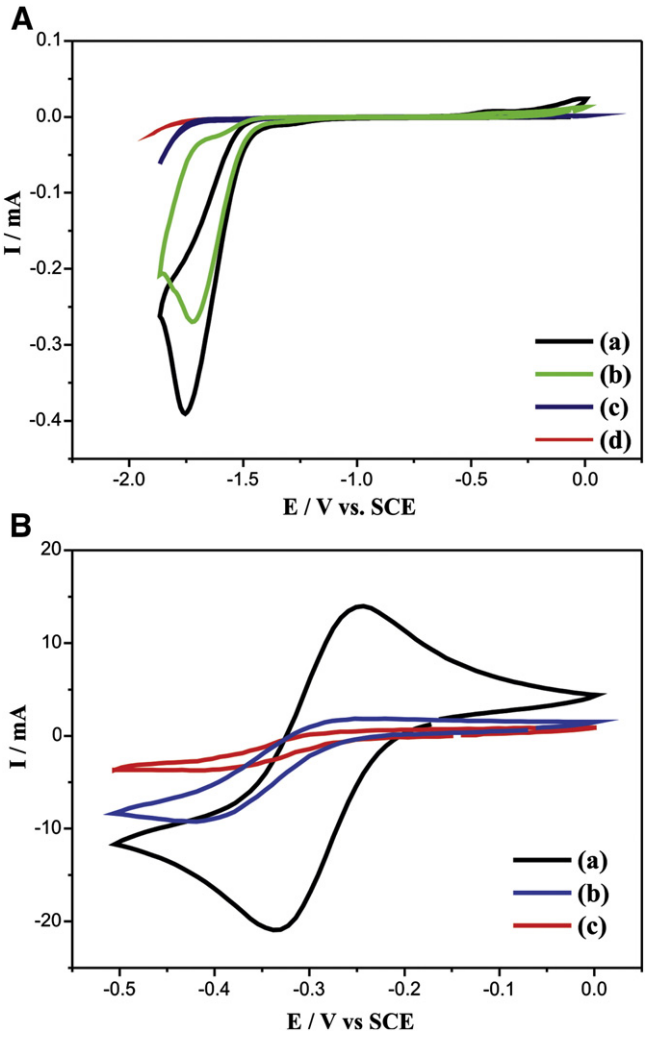

Fig. 1. Cyclic voltammetry on a gold electrode (ϕ = 3 mm) in a 0.1 M n-Bu_4NPF_6 + DMF solution. A) Successive voltammograms of the reduction of 51 mM 5-bromo-1,10-phenanthroline at 0.1 V s^{-1} (cycles 1 (a), 2 (b), 20 (c) and 40 (d)). B) Cyclic voltammograms recorded in a 1 mM 1,4-benzoquinone solution at 0.05 V s^{-1} with the gold electrode before (a) and after coating with the 1,10-phenanthroline film by 20 (b) and 40 (c) potential cycles.

shows, the voltammogram changed from the one corresponding to a macroelectrode to a typical sigmoid curve obtained when microelectrodes are used. This sigmoidal behaviour is typical of those obtained when mass-transport is fast, hence there is no indication of a time-dependent event and steady-state situation is rapidly achieved. The small hysteresis noticed in the voltammograms may be a consequence of a possible partial overlapping of diffusion layers.

The variability of measurements examined as the inter-assay reproducibility was found to be 8.9% from steady state current values measured in a DMF solution containing BQ with 5 RAMs fabricated using the same procedure (40 potential cycles in a 5-bromo-1,10-phenanthroline + 0.1 M n-Bu_4NPF_6 + DMF solution). This demonstrates that the fabrication process is reproducible once the electrodeposition parameters remain the same. The repeatability of the voltammetry measurements was evaluated by recording 10 consecutive cyclic voltammograms in a BQ solution and the difference between the first signal and the last one was less than 4.3%, hence one can assume that the film is stable and retains its features.

In order to investigate the influence of the timescale on the voltammetric profile, experiments with the fabricated RAMs were carried out in a BQ solution at different scan rates. Results showed that the sigmoidal curve is not drastically affected as limiting current