



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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ARTICLE INFO

Article history:

Received 5 August 2013

Received in revised form 29 October 2013

Accepted 30 October 2013

Available online 8 November 2013

Keywords:

Microelectrodes

Electrochemical sensors

Microelectrode ensembles

Scanning electron microscopy

Atomic force microscopy

Random assembly of microelectrodes

ABSTRACT

A random assembly of microelectrodes (RAMs) was fabricated by electrochemical reduction of 5-bromo-1,10-phenanthroline 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.

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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 AuCl₄⁻ [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 CaH₂ 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 $\geq 98\%$) were used as received. Indium-doped tin oxide (ITO; Delta Technologies, sheet resistance $< 20 \Omega/\text{cm}$, $0.7 \text{ cm} \times 3 \text{ cm}$ 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 $n\text{-Bu}_4\text{NPF}_6$ + 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 $n\text{-Bu}_4\text{NPF}_6$ + DMF solution. Fig. 1A shows voltammograms obtained during a consecutive potential scan and the decrease of the reduction peak located at $E_p = -1.75 \text{ V}$ 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 ($E^\circ = -0.29 \text{ V/SCE}$), 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)

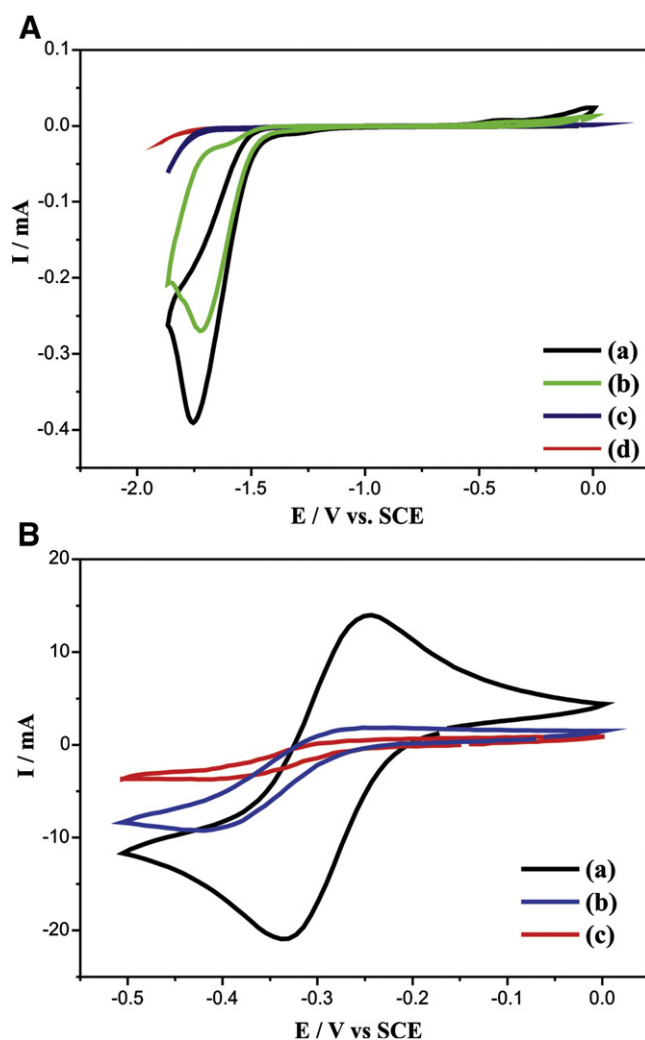
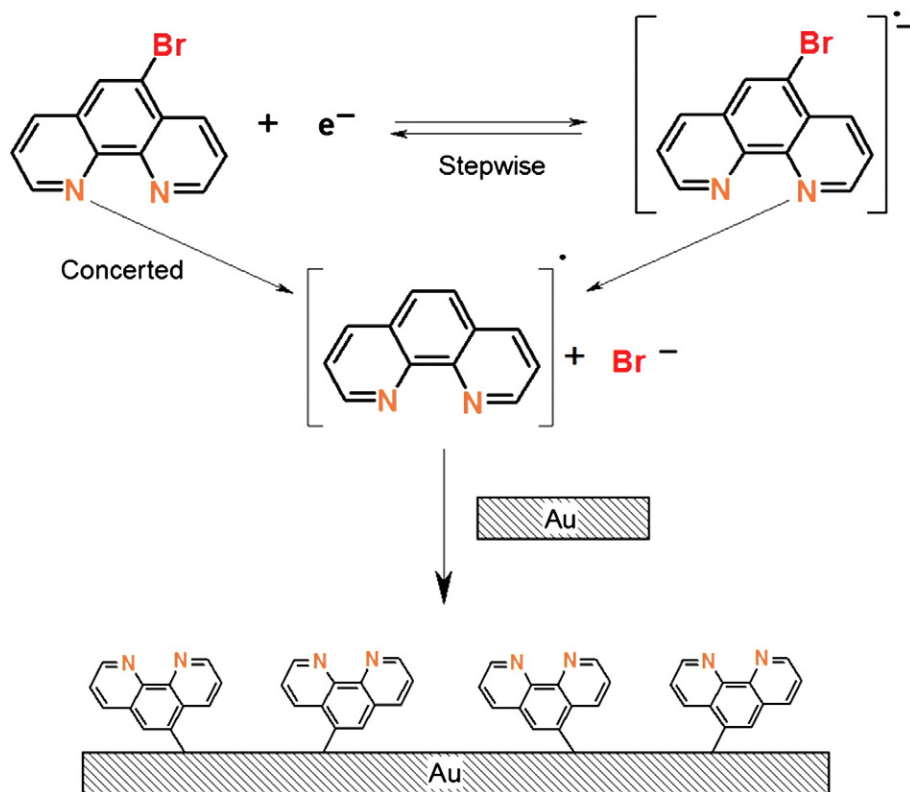


Fig. 1. Cyclic voltammetry on a gold electrode ($\phi = 3 \text{ mm}$) in a 0.1 M $n\text{-Bu}_4\text{NPF}_6$ + DMF solution. A) Successive voltammograms of the reduction of 51 mM 5-bromo-1,10-phenanthroline at 0.1 V s^{-1} (cycles 1 (a), 2 (b), 20 (c) and 40 (d)). B) Cyclic voltammograms recorded in 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 $n\text{-Bu}_4\text{NPF}_6$ + 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



Scheme 1. Mechanism of the electrochemical reduction of 5-bromo-1,10-phenanthroline on a gold surface.

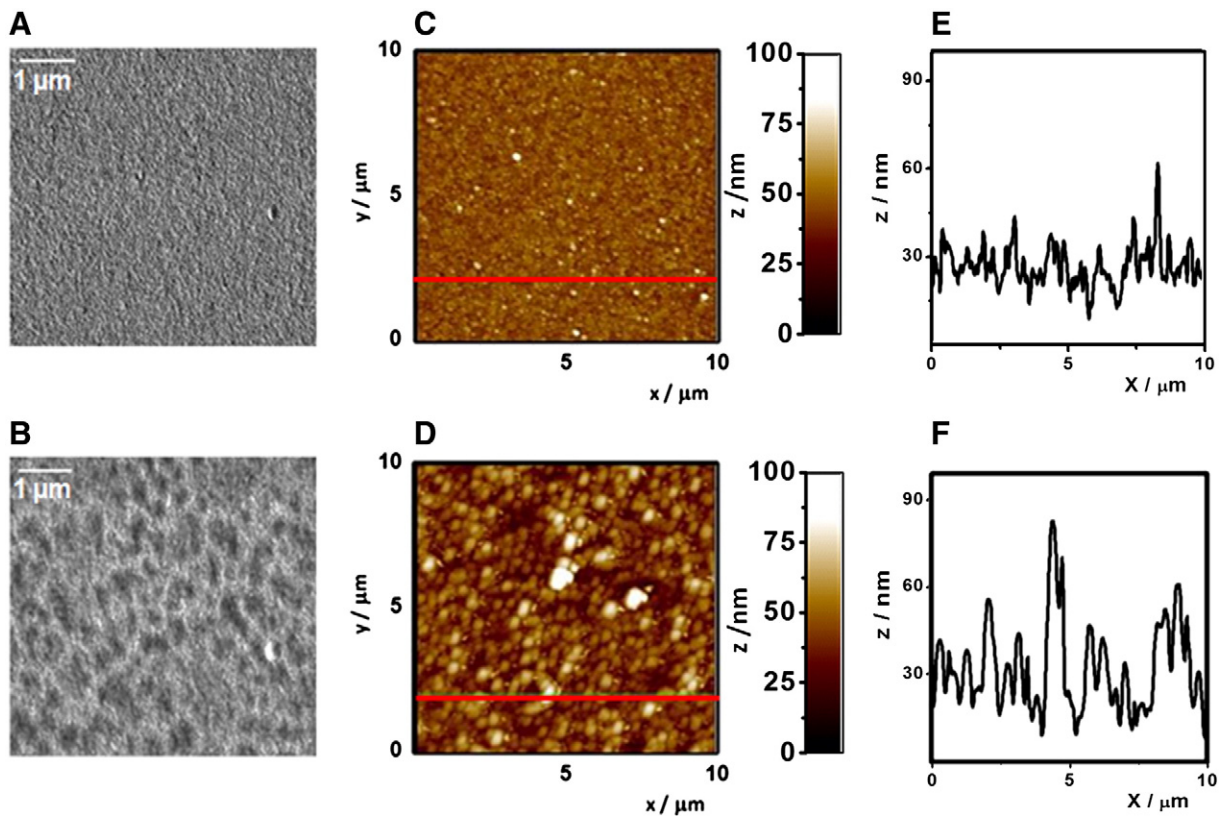


Fig. 2. FESEM and AFM topographic images of a bare gold surface before and after modification with a 1,10-phenanthroline film (40 potential cycles). A) FESEM image of bare gold surface. B) FESEM image of the modified gold surface. C) AFM image of gold surface. D) AFM image of the modified gold surface. E) Cross-section representing the height profile of the red line shown in the AFM image of C. F) Cross-section representing the height profile of the red line shown in the AFM image of D.

values changed at around 7% in the 0.05 to 1 V s⁻¹ range. This is in agreement with theoretical predictions on the mass transport to electrodes of microscopic dimensions and the influence of scan rate on the voltammetric response of RAMs [35,36].

3.3. FESEM and AFM studies of Au surfaces modified with a film of 1,10-phenanthroline

In order to get further information on the electrochemical reduction of BQ at the fabricated RAMs, AFM and FESEM images of a gold surface were obtained before and after the electroreduction of 5-bromo-1,10-phenanthroline. The partial passivation of the gold surface was obtained by using the procedure described in the previous section, i.e., 40 potential cycles in a solution containing 5-bromo-1,10-phenanthroline. Then, the modified electrode was rinsed with alcohol and water prior to the acquisition of AFM and FESEM images. Fig. 2A presents a FESEM image of a typical granular structure obtained when gold is sputtered in a flat surface. This same granular structure is still visible in some areas after the modification of the electrode surface with the phenanthroline film, as shown in Fig. 2B. However, Fig. 2B also reveals the existence of patterns of phenanthroline, characterized by the dark domains in the image. Since these patterns are not continuous, the space between them still presents regions where bare gold is still available for electrochemistry. As shown in the image, these regions present submicrometer dimensions and can act as spots for the electron transfer in the RAMs.

Fig. 2C and D shows AFM images obtained for the bare and the modified gold electrode, respectively, and it is also possible to notice the change of the gold surface after the electrodeposition of the 1,10-phenanthroline film. The modification is accompanied by a change in the RMS roughness factor, which varies from 47 Å for the Au/ITO surface to 111 Å for the 1,10-phenanthroline/Au/ITO surface. The change of the roughness is noticed by the red lines presented in Fig. 2C and D, which correspond to a representative height profile (z axis) of the unmodified and modified gold surfaces, as exhibited in Fig. 2E and F, respectively. FESEM cross-section images were used to determine the height of the patterns of the 1,10-phenanthroline film and the thickness value was found to be at around 125 nm (data not shown). This is consistent with the small thickness required for the electrons to be able to tunnel between gold and monomer during the growth of the low conductive film.

4. Conclusions

The 1,10-phenanthroline radical is produced directly on the electrode by electrochemical reduction of 5-bromo-1,10-phenanthroline with cleavage of these species over the surface. The partial surface passivation with 1,10-phenanthroline film enables the formation of a RAMs as observed by analysing steady-state voltammograms recorded in DMF solutions containing BQ and by morphologic studies with FESEM and AFM. This simple, fast and inexpensive method of fabrication of RAMs, combined with advantageous features such as film stability and signal

reproducibility, makes the proposed approach a new versatile strategy for electrochemical sensor design. For instance, the attractive features of the proposed RAMs raise potential possibilities for its use to plate heavy metals into the nanopores for further determination by stripping voltammetry.

Acknowledgements

Authors are thankful to FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for the financial support.

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