



Original Dual Microelectrode: Writing and Reading a local click reaction with Scanning Electrochemical Microscopy



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ABSTRACT

A dual gold-copper microelectrode (diameter 25 μm) was fabricated to be employed in a scanning electrochemical microscopy (SECM) configuration, and was used in feedback mode to both modify (write) and analyze (read) a substrate. This write-and-read procedure was performed on a glassy carbon electrode on which azide groups were introduced by electrochemical reduction of a diazonium salt. The copper part of the microelectrode was used to electrogenerate Cu(I) that catalyzed a “click” reaction between azide moieties on the surface and dissolved ethynylferrocene. This created a pattern of ferrocene moieties on the surface that was analyzed with the gold part of the microelectrode.

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1. Introduction

“Simultaneously writing and reading electrochemical information using the same microelectrode is an interesting concept in Scanning ElectroChemical Microscopy (SECM). Even if standard lithography method allow to obtain patterns with a high spatial resolution their complexity and high cost led to the proposition of alternative procedures, for example nanofabrication by molding or by printing [1,2]. SECM is a promising technique in this context. In SECM, a microelectrode is moved in 3 dimensions above a substrate, and a controlled electrochemical stimuli triggers the modification of surfaces [3]. For example, a microelectrode placed close to the substrate will be subjected to a potential step to start an electrochemical reaction [4]. The product of this reaction will diffuse toward the substrate to create local patterns with a resolution determined by the size of the diffusion layer [5,6]. Moreover, SECM can be used to visualize the newly created pattern. In the present work, the electrogeneration of Cu(I) was used to locally trigger a click reaction and to pattern ethynylferrocene molecules on a glassy carbon surface covered by azide moieties. The click reaction is a Cu(I) catalyzed Huisgen 1,3-dipolar cycloaddition of alkynes and azide to form 1,2,3-triazole [7]. To simplify existing procedures, we fabricated a dual gold-copper microelectrode. This configuration obliterate the polishing step

between the modification and imaging steps and the requirement of copper in the starting solution.

Click chemistry combined with SECM was demonstrated for the first time by Bard et al. [8] for the immobilization of a fluorescent molecule on a glass substrate. For this, a gold microelectrode was used to locally generate Cu(I) species by reduction of an initial solution containing Cu(II). Cu(I) catalyzed the reaction between the fluorescent molecules and the azido-terminated self-assembled monolayer. The same principle was used by Hapiot et al. [9], but in this case, a Pt microelectrode was used to pattern gold macroelectrodes previously modified by azido-terminated self-assembled monolayers. Bedioui et al. [10] used a gold microelectrode and click chemistry to covalently immobilize ferrocene on a glassy carbon surface entirely modified by azido-aryl groups via the diazonium approach. The ferrocene was observed by imaging the surface with SECM using the same gold microelectrode and ferricyanide as redox mediator. One disadvantage of this procedure is the electrodeposition of Cu on the Au microelectrode which demands an additional cleaning step, like anodic stripping or mechanical polishing, between the surface writing step and the reading step [10]. Mechanical polishing is not straightforward, firstly the gold electrode is removed, then it is mechanically polished and finally it is repositioned. This procedure is tedious because it requires a perfect repositioning in order to find the spot. In our work we propose a solution to address these limitations.

We decided to work without any Cu(II) initially present in the solution and use the oxidation of a copper microelectrode to locally generate Cu(I). But because it is not possible to achieve approach

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curves and surfaces imaging with a copper microelectrode, we fabricated a dual microelectrode combining gold and copper wires. The gold part was used to fix the distance between the microelectrode and the substrate and also to obtain an SECM image of the modified surface in feedback mode. Other dual electrodes have been used to study the generation of species on one electrode and collection on the other one, or to detect different species at the two different electrodes [11–13]. To the best of our knowledge it is the first time that a dual Au-Cu microelectrode is used to modify and analyze a substrate.

2. Experimental

2.1. Chemicals

All chemicals (4-azidoaniline hydrochloride, sodium nitrite, ethynylferrocene, ascorbic acid, absolute ethanol, hydrochloric acid, potassium ferricyanide, copper sulfate) were purchased from Sigma-Aldrich and used as received. All the solutions were prepared in ultrapure water (resistivity 18.2 M Ω cm at 25 °C).

2.2. Fabrication of dual electrode

A borosilicate theta glass capillary (World Precision Instrument, 1.5 mm O.D. 1.05 mm I.D) was first cleaned in ethanol and then dried in oven at 80 °C for 15 min. Copper and gold wires (diameter 25 μ m from Goodfellow) were introduced in two different compartments and placed in the middle of the capillary. Then a laser puller (Sutter instruments P2000) was used to seal one part of wires in the capillary by melting the glass. The capillary was then manually broken and the sealed end was polished firstly with a sand paper p4000 and then with 0.3 μ m alumina paste to obtain a clean surface (Fig. 1). To avoid misalignment between the two wires the dual microelectrode should be held perfectly at 90° during the polishing step. The electrical connection to the unsealed end of the wires was made with carbon powder to a copper wire (diameter 500 μ m).

2.3. Preparation of modified surfaces

Substrates made of glassy carbon electrode of 3 mm in diameter were obtained from IJ Cambria Scientific Ltd. The glassy carbon electrodes were polished successively with sand paper and with 0.3 μ m alumina paste. The electrodes were thoroughly washed with ultrapure water and put in ultrasonic bath for 5 min to remove the alumina that remained on their surface.

Azide functional groups were introduced on glassy carbon electrodes by reduction of 4-phenylazide diazonium salt [14]. The

diazonium salt was prepared in-situ in the solution by diazotization of the parent aniline [15]. The initial solution contained 1 mM of 4-azidoaniline in 0.5 M HCl and sodium nitrite was added to a final concentration of 2 mM. The electroreduction of the 4-phenylazide diazonium was achieved by cycling 6 times the working electrode between 0 and -0.9 V vs Ag/AgCl at 50 mV s⁻¹. The characteristic peak corresponding to the diazonium reduction was observed on the first cycle and disappeared on the second cycle.

For the click chemistry on the entire carbon surface, a solution of 5 mM ascorbic acid and 10 mM CuSO₄ was prepared. Ethynylferrocene, initially prepared as 0.1 mg ml⁻¹ in ethanol, was added to a final concentration of 10 μ M. The glassy carbon electrode containing the azide group on the surface was immersed in this solution for 60 min [16].

For the local “electroclick” reaction the same ethynylferrocene solution was used but without CuSO₄ and ascorbic acid. The microelectrode was positioned close to the substrate (\approx 10 μ m) above the azido-modified substrate. A potential of 0.5 V was applied to the copper microelectrode to generate Cu(I) ions that locally triggered the click reaction between the ethynylferrocene and the azide moieties.

2.4. Cycling Voltammetry and SECM experiment

All the electrochemical measurements were performed using a CH instrument (Austin, TX) Model 920C. An Ag/AgCl (KCl 3 M) reference electrode and platinum wire were used in a three-electrode system. All steady state SECM approach curves were recorded at 1 μ m s⁻¹ approach rate. The approach curves and the SECM imaging were recorded by applying -0.1 V on the gold microelectrode to generate ferrocyanide under diffusion limited condition. In all the experiments, a potential of 0.5 V was applied on the substrate.

3. Results and Discussion

Cyclic voltammetry measurements were first recorded on the gold and copper microelectrode to verify that the dual Au-Cu microelectrode works properly before performing the surface modification and the SECM experiments. Afterwards, the gold microelectrode was characterized by realizing approach curves on insulating and conductive substrates in a ferricyanide solution (Fig. 2). These curves are usually represented in dimensionless form by plotting the microelectrode current (I_T) normalized by the current when the microelectrode is far away of the substrate (I_{inf}) as a function of the distance (d) normalized by the microelectrode radius (a). These results showed that the dual electrode functions as well as a normal microelectrode despite the fact that the gold part is not centered and that the diameter of the entire tool is quite large (300 μ m). Therefore, it was important to check whether

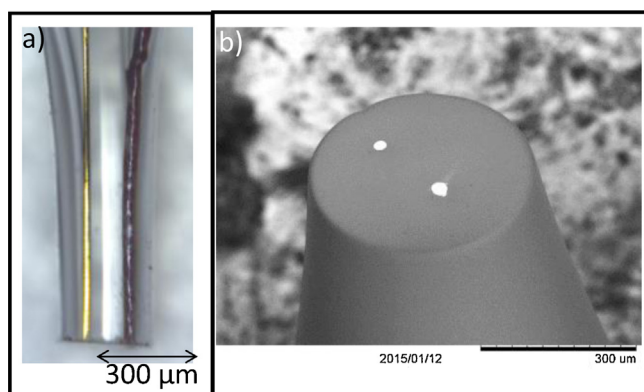


Fig. 1. a) Optical and b) SEM images of the dual gold-copper microelectrode.

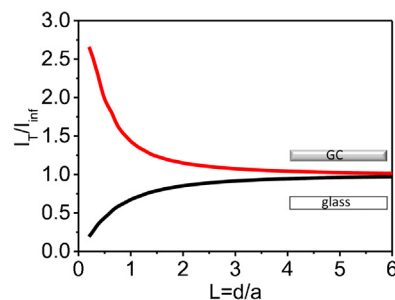


Fig. 2. SECM approach curves in K₃Fe(CN)₆ 2 mmol L⁻¹ as mediator with NaCl 0.1 mol L⁻¹ in aqueous solution. E_{dual-Au} = -0.1 V, E_{substrate} = 0.5 V. (—) On glassy carbon (GC) electrodes, positive feedback. (—) On glass, negative feedback.

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