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Strategies for fabrication of highly-dense ordered arrays of metal microdisks by the scanning electrochemical microscopy microwriting approach

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ABSTRACT

The microwriting approach of the scanning electrochemical microscopy (SECM) was adapted and optimized for the fabrication of extensive ordered arrays of gold microdisks deposited on conductive supports. This technique uses a SECM tip as a source for the localized delivery of metal ions by well-controlled electro-dissolution of the metal microelectrode. In this work, novel configurations of recessed-microelectrode tips (radii $\leq$ 12.5 μm) were developed to make possible the deposition of a large number of well-defined disks from the same probe by a semi-automatic procedure. A sequence of steps that coordinates tip potential, tip position, and substrate potential values was designed and implemented to improve the repeatability and confinement of the deposited microdisks. The effects of potential and time conditions for gold electro-dissolution and electrodeposition on the morphological properties of gold disks deposited on Pt and glassy carbon were explored. The selective modification of glassy carbon-supported gold arrays with an electrocatalytic material (Pt) for a specific reaction (hydrogen evolution) and their further SECM activity screening were described to illustrate a way to use them as multielectrode platforms.

1. Introduction

Ordered arrays of microelectrodes with varied shapes and sizes are electrode platforms with applications in fundamental and applied areas of chemistry. These are valuable configurations for applications in sensors [1,2–4], micro-batteries [5,6], activity screening of electro- and photo-catalytic materials [7,8], as well as in fundamental studies of mass transport phenomena [9,10] and of synergetic effects in electrocatalysis [11], among many other uses. In these platforms the microelectrodes can be either individually connected [3,4,12,13], or wired by a single connection through a common conductive support [7,8,11,14–16]. Many of the potential applications of these arrays entail a large number (or a high density) of microelectrodes. Thus, most of the methods used for fabrication of arrays rely on lithographic and microfabrication techniques [3–6,12–16] that in most cases require specific facilities.

Microfabrication methods based on localized electrochemical deposition of materials have the advantage to require relatively simple instrumentation. Besides, they have great potentiality to push the resolution of microfabrication techniques to the sub-micrometer and nanometer levels [17,18]. Localized electrodeposition can be attained by coupling electrochemical methods with micro-positioning devices [19–21], for example with the scanning electrochemical microscopy (SECM), which was one of the pioneering techniques of this type [22]. SECM offers nowadays a variety of operation modes to tackle situations with diverse requirements of resolution, size, shape, and material nature [23]. In general, SECM-based patterning methods use the SECM probe to induce localized delivering or etching of materials [23–25]. In most cases the whole substrate is polarized, so localization of the patterning process on the substrate is mainly governed by the radial distribution of tip-generated reactant concentration between the tip and the substrate. Then, not only the tip size but also the distance between the tip and the substrate (absolute value and constancy along the pattern) are critical parameters that limit the resolution and extension of the patterns. Among the different operation modes, the so-called "microwriting" method developed by Meltzer and Mandler [25] is a simple and versatile procedure with potential application in a great number of microfabrication processes. This approach relies on the electrochemical [24–26,27] or chemical [28,29] deposition

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of a metal on the substrate surface from metal ions that are locally electro-dissolved at the metallic tip. When the transfer of material from the tip to the substrate is coordinated with the tip movement, arrays of metallic disks or bands can be obtained [23–29].

While the SECM microwriting approach should be potentially useful for fabrication of microelectrode arrays, its implementation still requires optimization of probes and fabrication conditions that are critical for attaining a proper confinement of the deposited structures, particularly when extensive arrays with high density of microelectrodes are required. For that reason the method was never applied beyond a demonstrative proof of concept with small arrays. Thus, the goal of the present work is to expand the application of the microwriting SECM-based technology to the fabrication of highly-dense arrays of disk microelectrodes, by developing both new types of probes and fabrication programs that assure a proper control of dissolution/deposition potentials, times and confinement. Moreover, in order to exemplify potential uses of these high-density arrays, this work demonstrates a possible way to modify them for their use as platforms supporting an electrocatalytic material with a specific function.

2. Materials and methods

2.1. Chemicals and materials

Analytical grade copper sulphate, sulphuric acid (98%), and hydrochloric acid (35%) from Merck (Germany) and hexachloroplatinic(IV) acid hydrate from Aldrich (USA) were used as received. Water was deionized with an exchange resin, doubly distilled, and treated with a Purelab purifier (Elga Labwater, resistivity ≥18.2 MΩ cm). Array supports were glassy carbon plates (1 mm thick, type I) from Alfa Aesar (USA) and platinum foils (0.3 mm thick) from Vega & Camji (Argentina), which were polished with alumina powder and ultrasonically cleaned in water. High purity wires of Pt from Alfa Aesar (USA) and of Au from Goodfellow (UK), and borosilicate glass capillaries (1.5 mm outer diameter, 0.1 mm thickness) from Paralwall (Argentina) were employed for fabrication of SECM probes.

2.2. Instrumentation

For a visual inspection of tips and arrays an optical microscope (Nikon Optiphot with a FX-35DX camera) was used. The morphology and composition of the arrays were characterized by SEM using a benchtop scanning electron microscope PhenomWorld model PROX (Netherlands) equipped with an energy dispersive X-ray spectrometer (EDS), and by AFM in contact mode using a scanning probe microscope Agilent 5400 (USA). The mechanical stability was evaluated by mounting the arrays on the Teflon tip of a rotating disk electrode (RDE) Radiometer EDI 10 K (France). Array fabrication and scanning electrochemical microscopy experiments were carried out using a home-built SECM instrument described elsewhere [30], furnished with a bipotentiostat Heka Elektronik (Germany) model PG340. The tip position was controlled with three motorized translation stages Zaber model T-LS (Canada) with 28 mm travel distance, and a XYZ nanopositioning system Physik Instrumente (Germany) model Nanocube P-611.3S. Both the bipotentiostat and the positioning systems were commanded by the software Potmaster (Heka Elektronik) batch-controlled via LabView programs (National Instruments, USA). The SECM Teflon cell had a typical configuration, with a platinum wire (Vega & Camji) as counter-electrode and a SECM tip as working electrode. The reference electrodes were a saturated calomel electrode (SCE) for experiments in HCl and in Cu-containing solutions, and a reversible hydrogen electrode (RHE) for SECM evaluation of the hydrogen evolution reaction. The SECM cell was supported on a flat platform that allowed tilt correction via two graduated micrometer screws, which is critical for the reproducibility of the tip-substrate distance during the fabrication sequence.

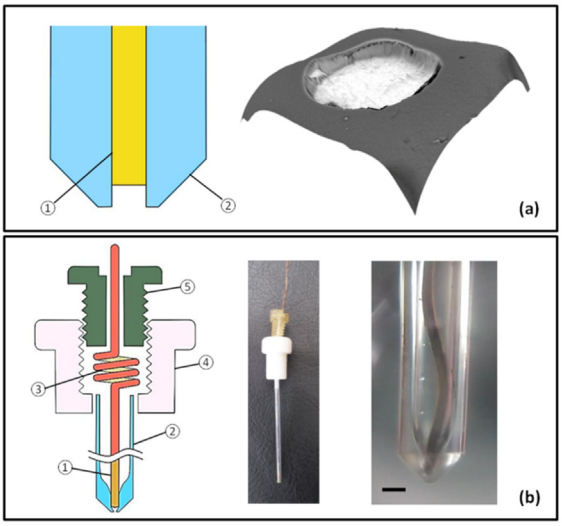

Fig. 1. (a) Scheme (left) and 3D-reconstruction of a SEM image (right) of a 25-μm-diameter Au RDP-A probe. (1) Sealed and etched Au wire leaving a recessed disk; (2) polished and sharpened sealing capillary. (b) Scheme (left) and photograph (center) of the RDP-B probe. (1) Au wire; (2) glass micropipette; (3) copper wire and spring; (4) threaded nipple; (5) pushing screw. The optical micrograph at the right shows the Au wire pushed against the pipette cavity at the bottom (scale bar: 500 μm).

2.3. Fabrication of SECM tips for micro-patterning

The proposed micro-patterning method relies on the ability to transfer a "slice" of metal from the microelectrode to its projected area onto the substrate surface by a mechanism involving electro-dissolution, mass transport and electro-deposition. In order to make this sequence to work efficiently, diffusion of the dissolved metal ions toward the bulk solution must be avoided. This can be attained by confining the transfer sequence into a small gap between microelectrode and substrate surfaces, either by working with a conventional disk microelectrode tip in very close proximity to the substrate [25,27,28] or by using a tip configuration with the microelectrode surface slightly recessed below the glass sheath surface. By following this last way, a recessed tip can be approached until its sheath surface makes contact with the substrate surface, building a cylindrical microcell laterally limited by the glass sheath walls where the metal transfer can proceed in a confined and quasi-isolated environment. Thus, to apply this strategy in this work, recessed-disk gold microelectrodes were used as SECM tip for fabrication of gold microdisk arrays by the microwriting method. Two configurations of recessed-disk probes were evaluated seeking to obtain more extensive and better defined arrays. Simple schemes of these two configurations are shown in Fig. 1.

The recessed-disk probe A (RDP-A), schematized in Fig. 1a, was fabricated by heat-sealing of Au wires into borosilicate glass capillaries, polishing and sharpening [31] to obtain Au disk tips, followed by a short electrochemical etching. First, pieces of 25-μm-diameter Au wires were soldered to copper wires using a micropoint soldering machine (S&H Dental, Argentina) and introduced into borosilicate glass capillaries. Then, their ends were melted by careful heating under a torch flame until the sealing of about 2 mm of the wires was visually verified. The capillaries were polished with coarse sandpaper until the cross section of the wire was exposed. A final polishing with an increasing-grit