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Scanning electrochemical microscopy for the direct patterning of a gold surface with organic moities derived from iodonium salt

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ABSTRACT

The scanning electrochemical microscope (SECM) is used in the direct mode to draw patterns of a thin passivating organic layer on a gold electrode surface and to image them. The patterning is ensured by the local electrografting of the organic moieties obtained by reduction of an aryliodonium salt, as evidenced by XPS and SECM line scans. The resolution of the writing process is controlled by the charge injected.

1. Introduction

The modification of surfaces with specific chemical functionalities results in applications in chemical sensing [1,2], microelectronics [3], corrosion inhibition [4], electrocatalysis and biosensing [5]. For the past decade, the electrochemical reduction of aryldiazonium salts onto conductive surfaces has been widely investigated [6]. This technique allows the covalent attachment on various surfaces of electrogenerated aryl radicals bearing different functionalities. However, the spontaneous grafting of the aryl moieties onto the surface [7] interferes and restricts the patterning of surfaces via diazoniums to the use of micro-contact printing [8] or to local scratching from an electrografted surface [9]. Besides, electrografting of glassy carbon can also be performed by other radical generating species such as diaryliodonium ions [10]. As a result of a lower reduction potential than their diazonium analogues, the iodoniums are less prone to spontaneous grafting of surfaces and are then better candidates for local surface electrografting.

The SECM is a convenient tool for local surface derivatization due to its ability to generate micrometric sources of a broad range of reactive chemical species [11]. Moreover, its slow writing speed can be circumvented by using “stamp” electrodes [12]. In the direct mode, it was used to pattern various conducting surfaces with organic moieties [13–20]. The local introduction of specific chemical or biochemical activity can be obtained either from the local tip-induced desorption of alkanethiols from a thiol-covered gold electrode [13–15] or from the local polymerization of surface with bioactive polymers [16–20], even though the latter strategy requires important efforts to synthesize specific electroactive monomers.

Here, we propose to selectively electrograft a conductive surface with organic moieties using the SECM in the direct mode with a commercially available iodonium species, bis-(4-*tert*-butylphenyl)iodonium *p*-toluenesulfonate (**1**). We examine the electrografting of **1** at a gold surface by cyclic voltammetry (CV) and SECM and then use the SECM to micropattern Au surface with aryl radicals derived from **1**.

2. Experimental

2.1. Chemicals and electrodes

Chemicals were from Aldrich or SDS. Electrografting was conducted either on 1 mm diameter disk gold electrodes or on cm^2 area gold plates surfaces (1000 Å gold coated silicon wafers, Aldrich).

2.2. Electrochemical procedures

The CV investigation was performed on a 1 mm diameter gold electrode in a glass electrochemical cell containing 10 mL of solution (ACN or water), 0.1 M of supporting electrolyte (NBu_4BF_4 in ACN, KCl in water). The SECM investigation was performed on gold plated surfaces with a Pt tip (radius, $a = 12.5$ μm, ratio of glass to

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metallic radius ~5) moved by a home-made SECM. The approach curves were obtained from 4 mM solutions of a redox mediator (potassium ferrocyanide, $Fe(CN)_6^{4-}$, in water, ferrocene, Fc, in ACN under argon) by biasing the tip on the redox mediator oxidation plateau (0.50 vs Ag/AgCl for both probes), the gold substrate was unbiased.

A potentiostat/galvanostat (CH660A, IJ Cambria) was used in a three or two-electrode configuration with a 1 mm diameter platinum wire counter-electrode. For SECM or CV experiments, respectively a 1 mm diameter Ag/AgCl or a SCE was the reference.

For SECM lithography (with **1**) and line scanning (with $Fe(CN)_6^{4-}$), the microelectrode was positioned from approach curves at a distance of 8–10 μm from the substrate and performed by scanning the tip at 5 μm/s above the substrate.

The gold surfaces were cleaned by successive oxidation–reduction until reproducible voltammograms were obtained. The electrografting of entire gold surfaces was obtained from chronoamperometric reduction of a 2 mM ACN solution of **1** by biasing them at −1.1 V vs SCE for 300 s. The surfaces were then ultrasonicated in acetone for 10 min.

2.3. XPS characterization

A Thermo VG Scientific ESCALAB 250 system fitted with a micro-focused, monochromatic Al Kα X-ray source (1486.6 eV) and a magnetic lens was used. An X-ray beam of 650 μm was used at a power of 10 mA × 15 kV. The spectra were acquired in the constant analyzer energy mode (40 eV pass energy for the narrow regions) and calibrated by setting the C–C/C–H C1s peak at 285 eV.

3. Results and discussion

3.1. CV and SECM examination of surfaces

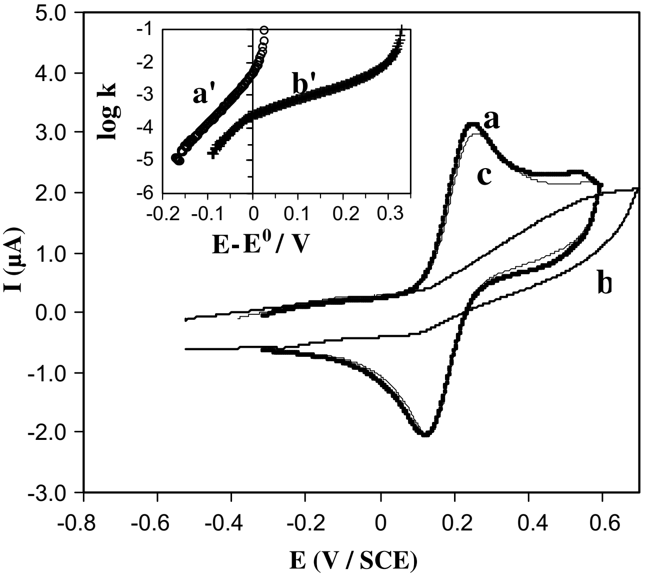


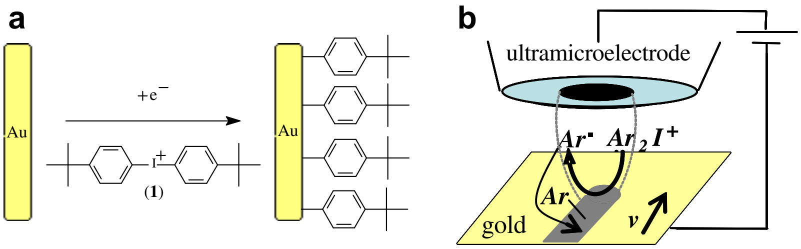
Fig. 1. Cyclic voltammetry of a gold disk (1 mm diameter) in H_2O + 0.1 M KCl + 4 mM $Fe(CN)_6^{4-}$. (a) Bare, (b) electrografted by 2 mM of **1**, and (c) immersed 10 min into a 2 mM solution of **1**. Scan rate = 0.2 V/s. Inset: Tafel analysis of the CV (Eq. (1)) for (a′) bare and (b′) electrografted electrodes.

On a 1 mm gold disk electrode, the reduction of **1** shows a broad irreversible wave (peak potential: $Ep = -0.9$ V vs SCE) which has vanished after the third scan. This is typical of the blocking of the electrode by the aryl moiety that grafts the electrode (Scheme 1a). Entire surfaces of Au electrodes were electrografted by chronoamperometric reduction of **1** at −1.1 V vs SCE. The extent of grafting of the aryl moiety derived from the reduction of **1** has been investigated by CV and SECM. Fig. 1 presents the CV of $Fe(CN)_6^{4-}$ oxidation on a 1 mm gold electrode, which has been submitted to either cleaning only (Fig. 1a) or electrochemical reduction of **1** (Fig. 1b) or immersion into the same solution (Fig. 1c). The reduction of **1** induces the grafting of a layer that blocks the electron transfer from the Au electrode to $Fe(CN)_6^{4-}$ [21]. A Tafel analysis of the CV allows comparison of the apparent standard electron transfer rate constants, k^0_{app}. For a quasireversible process, the variation of the electron transfer rate, k, with the potential, E, is given from the current, $i(E)$, by [22–25]

$$k(E) \approx \frac{i(E)\sqrt{D}}{I_{\lim} - I(E)(1 + \exp(-nF/RT(E - E^0)))} \qquad (1)$$

where $I_{\lim}$ is the diffusion limiting current of the sigmoidal convoluted current, $I(E)$, and D is the probe diffusion coefficient ($D = 7 \times 10^{-6}$ cm^2/s). The extrapolation of log $k(E)$ to $E = E^0$ (Fig. 1) leads to k^0_{app}. For the oxidation of $Fe(CN)_6^{4-}$, k^0_{app} decreases from 5.5×10^{-3} cm/s at an uncovered Au electrode to 2.5×10^{-4} cm/s once electrografted. When the gold electrode is immersed into the iodonium solution without potential application, the oxidation of $Fe(CN)_6^{4-}$ is unchanged, meaning that the surface is uncovered. This is in stark contrast with diazonium salts that spontaneously graft various surfaces, because the radical generation is more endothermic for iodoniums as they are more difficult to reduce than diazoniums [10]. Owing to the dissociative nature of the reduction of these onium salts, this behaviour is a consequence of an I–aryl bond stronger than the N–aryl one [26].

On large Au substrates, the CV analysis was not possible owing to ohmic drop limitations. These surfaces were investigated by SECM in the feedback mode. The SECM approach curves (AC) of the grafted surfaces (Fig. 2) confirm the trends observed on smaller electrodes by CV: the grafting reduces the regeneration of the redox probe at the substrate. A more quantitative analysis could be provided according to Mirkin model for slow heterogeneous kinetics [27,28] at covered substrates, which gives the normalized tip current, I_T ($I_T = i/i_{T,\infty}$ with $i_{T,\infty}$ the current measured at infinite dis-



Scheme 1. (a) Reductive electrografting of diaryliodonium ions **1** onto gold. (b) SECM local electrografting: the microanode tip held at constant distance from a gold macrocathode.