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Surface Derivatization

Patterning of Surfaces by Oxidation of Amine-Containing Compounds Using Scanning Electrochemical Microscopy**

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The microstructuring of surfaces with organic moieties is important for the development of new analytical tools, but the production of such surfaces by conventional photolithographic procedures remains challenging. Scanning electrochemical microscopy (SECM) has recently emerged as a viable patterning alternative because it can be used both for production and imaging of micro- and nanopatterned surfaces.[1–3] SECM patterning of surfaces can occur either in the direct mode or by using the tip as a source of reactive species.[4,5] The first approach relies on the use of the SECM tip as a microscopic auxiliary electrode, which constrains the current lines near the sample that acts as a working electrode. The faradaic current that flows through the tip-to-sample gap induces an electrochemical reaction, which is restricted to a localized volume beneath the tip. In the second approach, the reactive species are locally electrogenerated at the SECM tip. As the reactive species diffuse to the sample, the species can be either regenerated after modification[6,7] (feedback mode SECM) or consumed[8] (tip-generation/sample-collection mode; TG/SC SECM).

Free-radical grafting methods constitute the more flexible and versatile procedure for direct introduction of organic and biological moieties in order to achieve the permanent derivatization of surfaces.[9] The two main strategies consist of the electrochemical reduction of diazonium salts[10] or oxidation of amine-containing compounds.[11] Nevertheless, free-radical grafting is not amenable to writing procedures since the spontaneous derivatization of the entire surface exposed renders the direct micropatterning of surfaces impossible.[12,13] We recently reported a new procedure that circumvents this problem, and demonstrated the utility of diazonium salts for surface microstructuring (Figure 1 a).[14] This strategy is ideally suited for the writing of single organic micropatterns, but is less adapted for the production of complex organic microstructures because of rapid passivation of the SECM tip. This problem occurs as the diazonium

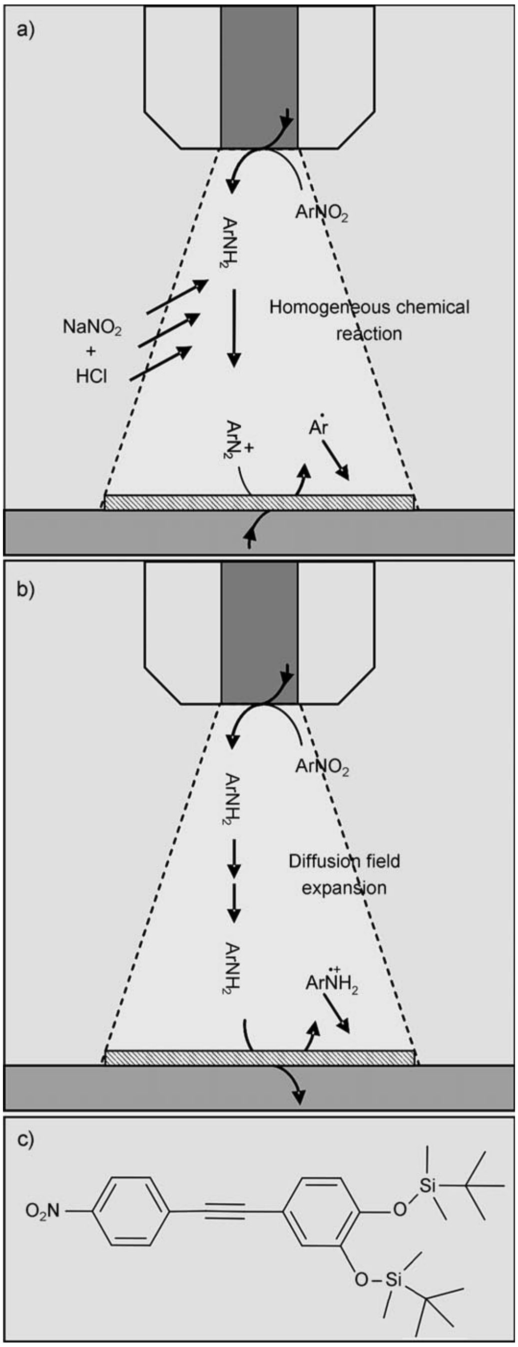

Figure 1. Reaction systems suitable for SECM patterning of surfaces in TG/SC mode based on a) reduction of diazonium salts or b) oxidation of amine-containing compounds. c) Structure of the nitro precursor.

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moieties produced in the tip-to-sample gap can be reduced both at the sample and at the SECM tip. To overcome this problem, we have devised a simpler procedure based on the oxidation of amine-containing compounds (Figure 1 b). In this strategy, an amine is generated at the SECM tip by reduction of a nitro-containing compound (Figure 1 c) and the substrate is locally derivatized by oxidation of the electrogenerated amine after diffusion in the interelectrode space.

This novel approach avoids tip passivation since the generation of the amine and the derivatization of the substrate occur by reduction and oxidation, respectively. This procedure is expected to be suitable for complex microstructuring of surfaces and would constitute an electrochemical alternative to the standard lithographic procedures.

The feasibility of producing organic micropatterns on surfaces using the proposed amine-tip-generation/amine-sample-collection sequence was investigated by thin-layer cyclic voltammetry (CV). In the thin-layer configuration, the starting nitro compound and all the electrogenerated species are confined to a thin solution layer at the working electrode, thus mimicking the conventional SECM setup. Figure 2 shows typical thin-layer CV patterns recorded at a glassy carbon (GC) disk. The cathodic peak located at −0.8 V versus Ag/AgCl corresponds to the conversion of the nitro group into the amino group and the first anodic peak at −0.3 V recorded on the reverse potential sweep corresponds to the oxidation of the arylhydroxylamine confined in the thin-layer solution.[15] The second anodic wave at 0.5 V, which appears only when scanning the potential range in which the nitro reduction occurs, correlates well with the anodic peak obtained in conventional CV for the solubilized amine-containing compound. In subsequent cyclic voltammograms, and in accordance with passivation of the electrode, the anodic peak current decreases and the peak potential shifts in the anodic direction.

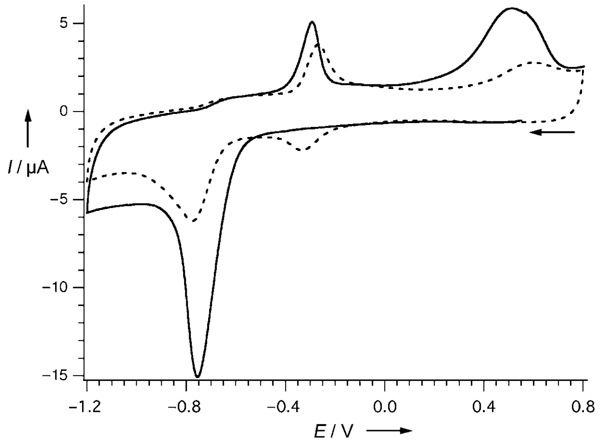

Figure 2. Thin-layer cyclic voltammograms recorded with a GC electrode. Conditions: methanol, 0.1 M $LiClO_4$ and 2 mM nitro precursor. Potential was scanned from 0.8 to −1.2 V for the first (——) and fifth (-----) CV cycle. Sweep rate: 10 mV s^{-1}.

In light of recent studies that addressed surface derivatization by oxidation of primary amines,[16,17] we postulated that the electrogenerated amine confined in the thin-layer solution is oxidized to produce the derivatized surface. Importantly, previous reports have shown that only aliphatic amines bind to the surface. The mechanism for surface derivatization by oxidation of an aromatic amine is beyond the scope of this work and further studies are required for a better understanding of this process. After derivatization by successive potential sweeps over the range from 0.8 to −1.2 V, the GC electrode was investigated by conventional CV after sonication in methanol for 10 minutes. After exposure to 1 M TBAF/THF solution for 5 minutes in order to deprotect the silyl group, CV in sodium phosphate solution shows the redox waves of the catechol functionality (Figure 3). The linear relationship between the anodic and cathodic peak currents with scan rate over 0.005–0.5 V s^{-1} range indicates that the catechol groups are confined to the electrode surface and can be designated as a diffusionless system. Hence, with this procedure, the GC electrode was successfully derivatized by oxidation of the electrogenerated amine that is trapped against the GC disk.

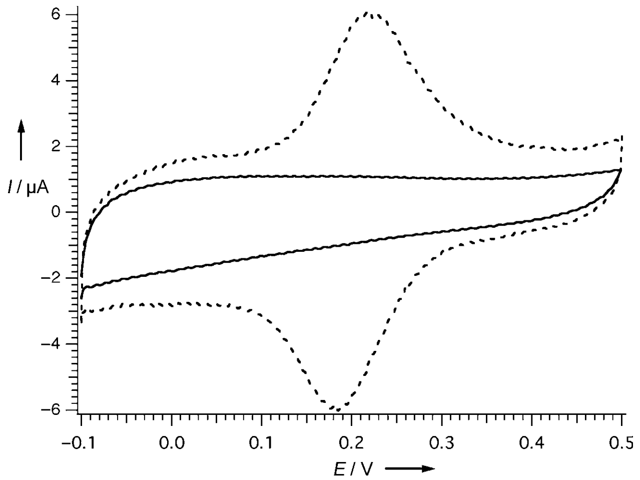

Figure 3. Cyclic voltammograms recorded with a GC electrode derivatized by oxidation of the amine that was electrogenerated in a thin-layer cell. Conditions: sodium phosphate solution (pH 7.4) and 0.1 M KCl. Cyclic voltammograms were recorded before (——) and after (-----) exposure to 1 M TBAF in THF for 5 min. Sweep rate: 50 mV s^{-1}.

Based on the thin-layer CV results, it was expected that similar surface derivatization with the SECM setup would occur at short tip-to-sample distance (Figure S1 in the Supporting Information). As such, the writing of organic micropatterns with the SECM setup is achieved by generation of an amine at a 7 µm diameter carbon tip (the ratio RG of the radii of the insulating sheath over the conducting disc is 10), which is oxidized at a gold sample after diffusion in the interelectrode space. In the experimental setup, the SECM tip was positioned 1 µm away from the substrate using conventional feedback mode in nanopure water containing ferrocene methanol (1 mM) and KCl (0.1 M). After rinsing with nanopure water and methanol, a solution of the nitro precursor (2 mM) and $LiClO_4$ (0.1 M) in methanol was introduced without retraction of the SECM tip. The potential of the SECM tip was set to $E_T = -0.8$ V for 5 seconds and the sample concomitantly was polarized at $E_S = 0.8$ V. Under these conditions, the electrogenerated amine is oxidized just beneath the SECM tip, and produces the local derivatization of the gold sample. Following the SECM patterning of the gold surface, the microstructure was imaged with a 10 µm diameter platinum tip (RG = 5) in a solution of $K_4Fe(CN)_6$ (1 mM) and KCl (0.1M) in nanopure water.

The SECM image in Figure 4 shows a well-defined structure, which is consistent with the formation of a 15 µm wide pattern of organic moieties that passivates the sample. An SECM line scan provides a better estimation of the lateral resolution of the deposit (see Figure S2 in the Supporting Information).

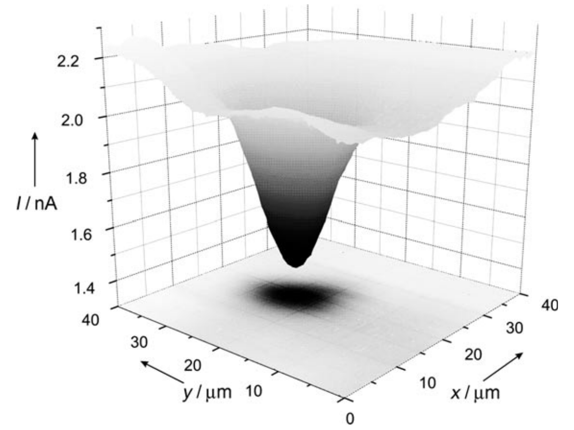

Figure 4. SECM image of a micropattern of organic moieties deposited on a gold sample by oxidation of an amine electrogenerated at the tip. Microstructure imaging conditions: $E_T = 0.5$ V, $E_S = -0.1$ V, tip-to-sample distance = 3 µm, translation speed = 5 µm s^{-1}.

These results demonstrate that the SECM patterning of surfaces by oxidation of amine-containing compounds electrogenerated at the SECM tip constitutes a novel procedure for the writing of organic microstructures, and has potential for the complex organic micropatterning of surfaces.

Experimental Section

Electrochemical measurements were performed in a three-electrode cell where the working electrode was a GC electrode (Bioanalytical Systems, 3 mm diameter; model MF-2012), the counter electrode was a platinum wire and the reference electrode was Ag | AgCl (saturated KCl). A potentiostat/galvanostat model VMP3 (Bio-Logic) monitored by ECLab software was used for the electrochemical experiments. TG/SC SECM measurements were performed with a 100 nm ELPro Scan system (HEKA; model PG 340).

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