Diazonium Chemistry

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# In Situ Formation of Diazonium Salts from Nitro Precursors for Scanning Electrochemical Microscopy Patterning of Surfaces**

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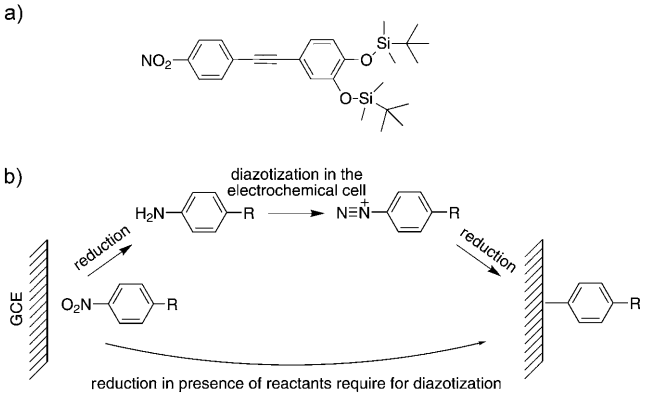
Carbon and metal surfaces derivatized with organic moieties by electrogenerated aryl radicals derived from diazonium salts have been thoroughly studied.[1–3] The wide range of aryldiazonium salts[4] that can be reduced onto samples ranging from bulk solids[5] to nanosized substrates[6,7] allows direct introduction of functional groups at surfaces while avoiding oxidative conditions. Recently, a simpler procedure consisting of the in situ generation of a diazonium salt from an amine by standard diazotization procedures[8,9] eliminated the purification step and improved the inherent instability of selected diazonium salts.

Herein, we derivatize surfaces by the reduction of a diazonium salt produced in situ from the nitro compound (Scheme 1). In a first procedure, a sequential approach completely reduces the nitro precursor to the corresponding amine, which is subsequently diazotized in the electrochemical cell. In a second procedure, a "one-pot" reaction produces the diazonium salt in situ from the nitro precursor in the presence of all reagents used in the sequential approach. The latter procedure can be directly used for microelectrochemical patterning of surfaces by application of scanning electrochemical microscopy (SECM) in tip-generation/sample-collection (TG/SC) mode.[10]

In the sequential approach, a preparative electrochemical reduction of the nitro group is achieved, and sodium nitrite is added in a subsequent step. A typical cyclic voltammetry (CV) pattern shows an irreversible cathodic wave at 0.2 V assigned to the reduction of the diazonium salt produced in situ from the electrogenerated amine.

In the one-pot approach, we postulated that in the presence of $NaNO_2$, the reduction of the nitro group would derivatize the electrode surface by diazotization of the electrogenerated amine. In Figure 1, the cathodic wave at




***Scheme 1.*** a) Structure of the nitro precursor. b) Reaction system for the derivatization of a glassy carbon electrode (GCE) by reduction of diazonium salts produced in situ from nitro precursor.

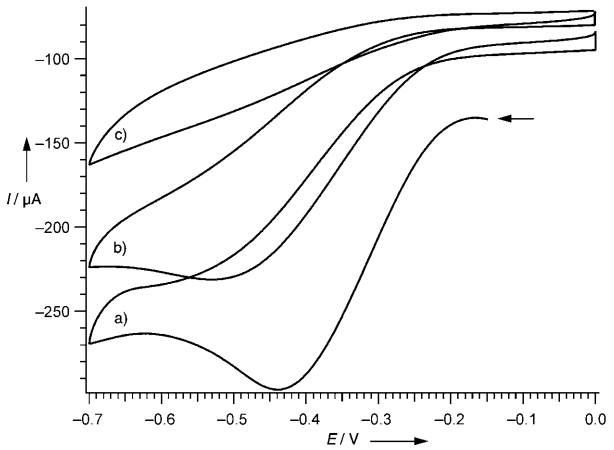



***Figure 1.*** a) First, b) fourth, and c) eighth CV cycles recorded with a GCE. Conditions: acetonitrile/1 M HCl (96:4), 0.1 M $Bu_4NPF_6$, 5 mM nitro precursor, three equivalents $NaNO_2$. Sweep rate: 50 $mV s^{-1}$.

−0.43 V corresponds to the standard reduction of the nitro group to an amine. With successive cyclic voltammograms, the reduction of the diazonium salt generated in situ shifts the peak potential cathodically and decreases the peak height until permanent passivation of the glassy carbon electrode (GCE) is achieved. Given the fast kinetics of diazotation,[11] the conversion of the amine into the diazonium cation is expected to occur in the vicinity of the electrode surface, as confirmed by CV at high sweep rates (Figure 2).

Experimentally, the potential is cycled between 0.8 and −0.8 V. Figure 2 focuses on the reversible system ascribed to

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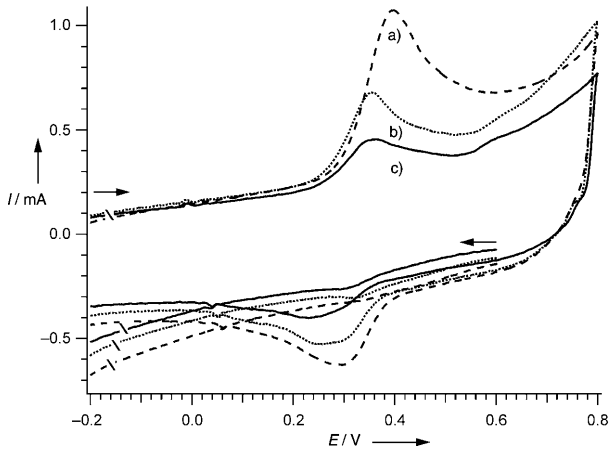


***Figure 2.*** Cyclic voltammograms recorded with a GCE. Conditions: acetonitrile/1 M HCl (96:4), 0.1 M $Bu_4NPF_6$, 5 mM nitro precursor, and a) 1, b) 1.5, or c) 2 equiv sodium nitrite. Sweep rate: 5 $Vs^{-1}$.

the hydroxyaminophenyl/nitrosophenyl couple. Upon addition of one equivalent $NaNO_2$, the reversible system's intensity decreases slightly but remains well-defined compared to that obtained in absence of sodium nitrite (Figure S1 in the Supporting Information). Further increases of the number of equivalents of $NaNO_2$ leads to a decrease in the reversible system's intensity and the appearance of a new cathodic wave at 0.2 V that correlates well with the CV pattern obtained using the sequential approach discussed above.

GCE derivatized by an aryl radical substituted in *para* position with a catechol moiety protected with silyl groups is prepared under potentiostatic conditions at −0.5 V over 5 min in acetonitrile/1M HCl (96:4, 0.1M $Bu_4NPF_6$) containing 5 mM nitrobenzene compound in the presence of three equivalents $NaNO_2$. After deprotection in 1M tetrabutylammonium fluoride (TBAF) solution in THF, the catechol-modified GCE is characterized by cyclic voltammetry. Figure 3 shows typical cyclic voltammograms obtained with a modified GCE before and after deprotection of the hydroxy groups. For comparison, the voltammogram recorded with a GCE derivatized by the sequential approach is superimposed.

After the deprotection step, the modified electrode shows a reversible peak at 0.2 V ascribed to the hydroquinone/quinone couple. Surface confinement of the catechol groups is confirmed by the linear relationship of the anodic and cathodic peak currents with sweep rates over the range 0.005 to 1 $Vs^{-1}$. This finding implies that a GCE can be derivatized by reduction of diazonium salts produced in situ from either amino or nitro precursors.

This original one-pot reaction is suitable for local electrogeneration of diazonium salts and allows us to reconsider the use of diazonium salts for the microstructuring of surfaces using SECM. To date, diazonium salts have not been used for direct electrochemical patterning owing to the spontaneous derivatization of exposed surfaces,[12–14] although alternative strategies to circumvent this problem have been put forth.[15–17]

Herein, the SECM tip acts as a source of diazonium salts by rapid diazotization of the electrogenerated amine as it

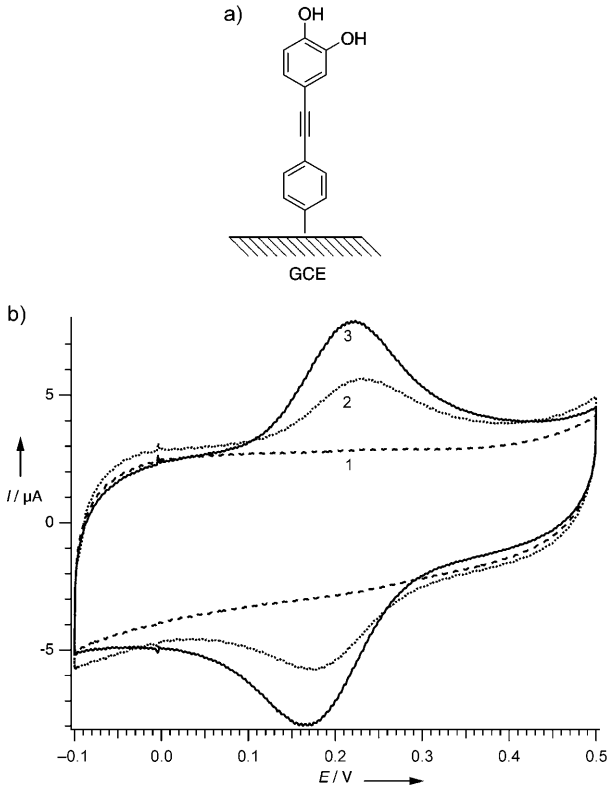


***Figure 3.*** a) Representation of the catechol-modified CGE. b) Cyclic voltammograms recorded in sodium phosphate solution (pH 7.4, 0.1 M KCl) with a GCE derivatized by reduction of diazonium salt produced in situ from the nitro precursor 1) before and 2) after 5 min exposure to 1 M TBAF in THF. 3) Cyclic voltammogram obtained with a GCE derivatized by the sequential procedure (see text for details). Sweep rate: 50 $mVs^{-1}$.

diffuses through the tip-to-sample gap (Figure 4). A micropattern of aryl moieties is deposited on a gold substrate by application of SECM in TG/SC mode. First, to perform local electrografting by SECM, a platinum tip (25 μm diameter; the ratio of the radii of the insulating sheath over the conducting disc (RG) is 6) is positioned 6 μm from the sample surface using conventional feedback mode in aqueous 1 mM $K_4Fe(CN)_6$/0.1M KCl. After rinsing with nanopure water and acetonitrile, a solution containing 1 mM nitro precursor and 0.1M $Bu_4NPF_6$ in acetonitrile is introduced. After addition of one equivalent sodium nitrite, the nitrobenzene derivative is converted into the amine at the tip under potentiostatic conditions at −0.4 V for 5 s. Concomitantly, the diazonium moieties produced in situ in the interelectrode space are reduced at the sample polarized at −0.1 V.

The efficiency of this strategy strongly depends on the kinetics of the diazotization reaction, as the reduction of the diazonium salt can also occur at the SECM tip. Addition of one equivalent $NaNO_2$ into the cell allows the expansion of the diffusion field of the electrogenerated amine and limits the reduction of the diazonium salt at the tip. With these appropriate conditions, sample derivatization is restricted to a local area beneath the tip. Figure 4 shows the SECM line scans recorded with $K_4Fe(CN)_6$ before (curve 1; unfiltered

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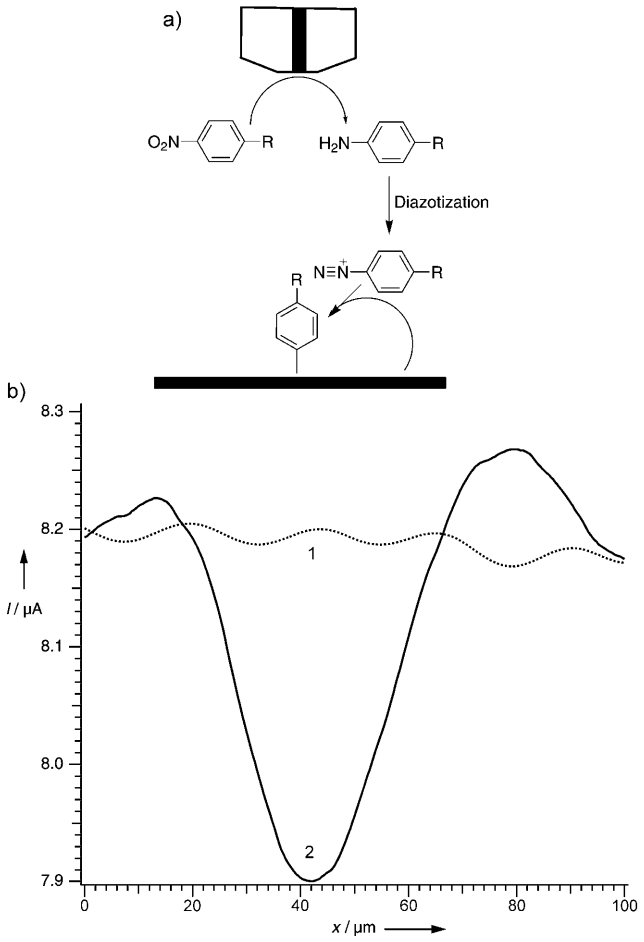


***Figure 4.*** a) Schematic description of the new reaction system suitable for the microelectrochemical structuring of surface by grafting of aryl moieties derived from diazonium salts. b) SECM line scan with $K_4Fe(CN)_6$ 1) before and 2) after local modification of the sample.

signal) and after (curve 2) the local derivatization. The current decrease is consistent with the formation of a 40 µm wide organic pattern that passivates the sample surface. These results confirm that the simpler procedure proposed for the in situ production of aryldiazonium moieties from nitro precursors constitutes a novel reaction system suitable for microelectrochemical patterning of surfaces with organic moieties by application of SECM in TG/SC mode.

## *Experimental Section*

Electrochemical measurements were performed in a three-electrode cell where the working electrode was a GCE (Bioanalytical Systems, 3 mm diameter; model MF-2012), the counter electrode was 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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