Combining Aryltriazenes and Electrogenerated Acids To Create Well-Defined Aryl-Tethered Films and Patterns on Surfaces

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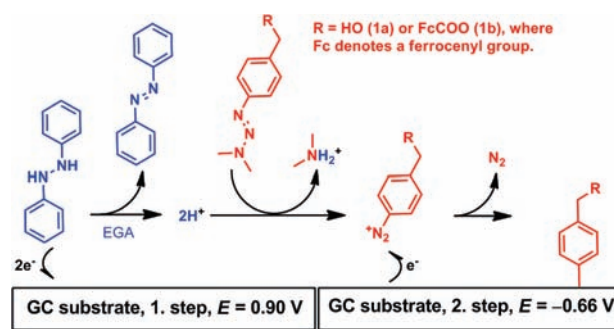
S Supporting Information

ABSTRACT: Immobilization of submonolayers to 4−5 multilayers of organic molecules on carbon surfaces can be performed by in situ generation of aryl radicals from aryltriazenes. The central idea consists of oxidatively forming an electrogenerated acid of N,N'-diphenylhydrazine to convert the aryltriazene to the corresponding diazonium salt in the diffusion layer of the electrode. In a second step, the diazonium salt is reduced at the same electrode to give a surface of covalently attached aryl groups. In this manner, various moieties tethered to the aryl groups can be immobilized on the surface. Here a ferrocenyl group was introduced as redox marker, the electrochemical signal of which is extraordinarily well-defined. This behavior is independent of film thickness, the latter being easily controlled by the number of repetitive cycles performed. It is also demonstrated that the new approach is suitable for patterning of surfaces using scanning electrochemical microscopy.

Scheme 1. Mechanism Suggested for Electrografting of Aryl Groups on Carbon Surfaces by Exploiting the Reaction of Aryltriazenes with an Electrogenerated Acid (EGA)

Electrografting using aryldiazonium salts is a recognized method for covalently tethering aryl groups to various conducting materials.[1] Spontaneous grafting[2] or chemically induced grafting under reductive conditions can also be achieved, even on nonconducting surfaces.[3−5] The chemisorbed films most often consist of inhomogeneous organic multilayers,[6,7] although methods for generating near-monolayers have been developed.[8−11]

The high reactivity of aryldiazonium salts often limits the synthetic possibility of constructing complex molecules. Many functional groups (nucleophilic or reducing) are incompatible with diazonium salts or the acidic conditions under which they usually are formed. Biomolecules are therefore very often covalently attached to surfaces via postmodification or in situ diazotization of aniline precursors.[12,13]

One way to circumvent the problem related to the high reactivity of diazonium salts would be to use a protecting group for the diazonium functionality, e.g., an aryltriazene formed by reaction of the aryldiazonium salt with a secondary amine. Aryltriazenes have high stability toward bases, nucleophiles, and reductants. Furthermore, they are less polar and much easier to handle in organic synthesis. Importantly, an aryltriazene may be deprotected at any point simply by adding an acid to give the corresponding diazonium salt. This nice approach was first reported by Tour and co-workers,[14−16] who synthesized complex aryltriazenes that were converted to diazonium salts just prior to grafting. A similar method was recently employed by us in the modification of a carbon electrode with single-stranded DNA.[17]

The use of aryltriazenes for these purposes could be made even more versatile if the conversion to the corresponding diazonium salt could be made to take place essentially during grafting. Such an approach would require in situ generation of the acid, preferentially only in the vicinity of the substrate. In the early 1980s, Torii and Uneyama developed the concept of an electrogenerated acid (EGA).[18] Recently, Maurer and co-workers used this approach to remove t-BOC protecting groups from immobilized peptides[19] and later to generate reactive N-acyliminium ion intermediates on a microelectrode array.[20] Specifically, the EGA was formed by oxidizing N,N'-diphenylhydrazine in acetonitrile (MeCN).

Herein we demonstrate that the combination of aryltriazenes and EGA can be exploited successfully in double potential step cycles to electrograft aryl groups onto surfaces through the local generation of diazonium cations (Scheme 1). We will show that even an aryl-tethered ferrocenyl moiety capable of reducing the diazonium functionality (**1b**)[21,22] can be covalently attached at carbon surfaces using this procedure and that the electrochemical response of the modified electrode is extraordinarily well-defined. In
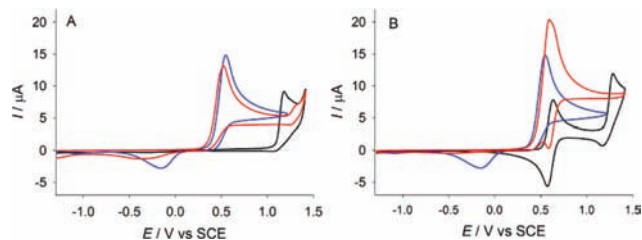
Figure 1. Cyclic voltammograms of 2 mM **1a** and **1b** (black curves in A and B, respectively), 2 mM N,N'-diphenylhydrazine (blue curves), and a mixture of the two (red curves) recorded at a sweep rate of 0.2 V s^{-1} in 0.1 M Bu$_4$NBF$_4$/MeCN.

addition, the surface coverage and thickness of the formed film can be easily controlled by the number of cycles employed. Finally, an interesting application of the technique for patterning of surfaces is presented. Triazene **1a**, a precursor of **1b** in the synthesis of the latter (see the Supporting Information), is also included in the study.

Mechanistic Investigation. Cyclic voltammetry is a powerful tool for elucidating reaction mechanisms. The cyclic voltammogram (CV) recorded for N,N'-diphenylhydrazine in 0.1 M Bu$_4$NBF$_4$/MeCN is shown in Figure 1A (blue curve). It exhibits an irreversible two-electron oxidation wave at 0.55 V vs SCE, while the reduction wave at -0.15 V vs SCE corresponds to the reduction of protons released in the oxidation process. The azobenzene formed is reduced at a lower potential (-1.4 V vs SCE) outside the potential window considered. The corresponding CV of **1a** (black curve) exhibits an irreversible one-electron oxidation wave appearing at a more extreme potential of 1.2 V vs SCE. Finally, the CV recorded for an N,N'-diphenylhydrazine/**1a** mixture (red curve) shows that the oxidation wave for N,N'-diphenylhydrazine is almost unperturbed while the oxidation wave for **1a** and the reduction wave for the released protons are strongly suppressed. The broad and ill-defined reduction wave at -0.4 V vs SCE stems from the reduction of the aryldiazonium cation formed by acid-catalyzed decomposition of **1a**, as confirmed by the CV of an authentic sample of this diazonium salt; the simultaneously generated dimethylammonium ion is not reduced in the potential window considered. Altogether, this indicates that the protons released from the oxidation of N,N'-diphenylhydrazine convert the triazene to the corresponding diazonium cation within the time scale of the experiment.

Similar CVs with a few distinct differences were recorded in the case of **1b** (Figure 1B). The CV for **1b** alone shows a one-electron oxidation wave at 0.64 V vs SCE, which is assigned to the oxidation of the ferrocenyl moiety (in comparison, $E°$ for ferrocenecarboxylic acid = 0.55 V vs SCE). This is followed by a one-electron irreversible oxidation wave pertaining to the triazene group at 1.3 V vs SCE.[23] The CV recorded for an N,N'-diphenylhydrazine/**1b** mixture (red curve) is more complex because the oxidation waves for N,N'-diphenylhydrazine and the ferrocenyl moiety are merged. Again, the oxidation wave for the triazene group and the reduction wave of protons are strongly suppressed. Only a small reduction wave assigned to the reduction of the ferrocenium moiety can be seen at 0.6 V vs SCE. Finally, a very small wave at -0.5 V vs SCE pertaining to the reduction of the generated aryldiazonium cation can be observed.

Reaction Mechanism. Scheme 1 outlines the proposed reaction mechanism for a two-step electrografting procedure in which the grafting agent, the aryldiazonium salt, is liberated from the
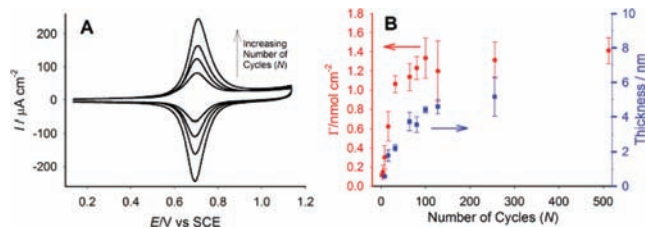

Figure 2. (A) Cyclic voltammograms of **1b**-modified GC electrodes (obtained using N = 8, 16, 32, and 64 electrografting cycles), recorded at a sweep rate of 0.2 V s^{-1} in 0.1 M Bu$_4$NBF$_4$/MeCN. (B) Surface coverage of electrochemically active ferrocene units (red, left axis) and film thickness measured by ellipsometry (blue, right axis) as functions of N.

aryltriazene with the help of an EGA formed by oxidation at the electrode surface. Specifically, during the first step, the oxidation of N,N'-diphenylhydrazine (at 0.90 V vs SCE for 0.5 s) generates a diffusion layer containing protons that can cleave the aryltriazene upon protonation to give the corresponding aryldiazonium cation along with a dialkylammonium (here dimethylammonium) ion. Although ferrocenyl moieties would be able to reduce the diazonium groups, this does not have time to occur in step experiments.[21,22] In contrast, during the second reductive step (at -0.66 V vs SCE for 0.5 s), the aryldiazonium cation is reduced to the aryl radical, which is capable of reacting with the electrode surface to form a covalently tethered aryl film. The two potential steps are followed by a short 3 s stirring interval to complete the cycle, which further can be repeated N times.

Modified Electrodes. In Figure 2A, we present four CVs recorded at glassy carbon (GC) electrodes already electrografted using the two-step potential procedure on **1b** with N = 8, 16, 32, or 64, respectively. First of all, a distinct signal from a surface-attached ferrocene redox couple with $E°$ = 0.70 V vs SCE is evident; its total width at half-height is equal to the ideal 90.6 mV for Nernstian behavior.[24] For the usually disordered diazonium-based films, such well-defined behavior is seldom seen. Moreover, a plot of $\log I_p$ versus $\log \nu$, where I_p is the peak oxidation current and ν is the sweep rate, gives a slope of unity (Figure S1 in the Supporting Information). The peak potential separation is equal to 9 ± 4 mV, where the small deviation from 0 V can be ascribed to nonideal solvation of the ferrocenyl groups in the film. On this basis, it may be concluded that **1b** was successfully immobilized on the surface. This was also strongly supported by X-ray photoelectron spectroscopy measurements on a film prepared using N = 64, which showed 1.3 atom % Fe originating from the ferrocene part.

In Figure 2B, the electrochemically determined surface coverage, Γ, is plotted versus N (red data). It can be seen that Γ increases linearly for $N \leq 30$, with $\partial\Gamma/\partial N$ = 32.5 pmol cm^{-2} cycle^{-1}. As N continues to increase, Γ approaches a limiting value of 1.4 nmol cm^{-2}, which is in the same range as that found for aryldiazonium electrograftings.[6] Also included in Figure 2B is a plot of the ellipsometrically measured thickness of the dry film, d, versus N (blue data). Interestingly, d evolves in the same manner as Γ ($\partial d/\partial N$ = 0.08 nm cycle^{-1} for $N \leq 30$ with d reaching 5.2 nm as limiting value for larger N), which indicates that all of the ferrocene units are electroactive, even for the thicker films, and that the grafting is a self-inhibiting process. Importantly, the film growth can be controlled by the number of cycles employed, yielding films consisting of submonolayers to 4–5 layers.[25]
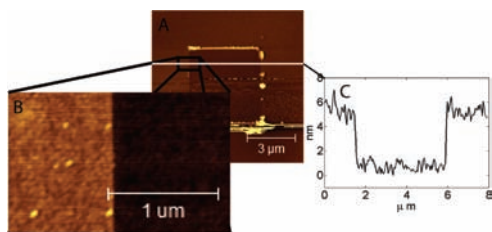
Figure 3. (A) AFM image of a surface grafted using $N = 128$, showing a scratched area made with the AFM tip. (B) Close-up image of the edge between the untouched and scratched areas. (C) Profile showing the height variation in a line scan across the scratched area.

To create what would correspond to a monolayer ($d \sim 1$ nm), 13 cycles were required, indicating a Γ value of ~ 0.4 nmol cm^{-2} according to Figure 2B. This value is in agreement with a previous calculation in which the coverage of ferrocene units was estimated to be 0.45 nmol cm^{-2} on the basis of hexagonal closest-packing.[26] In addition, Hapiot and co-workers[9] obtained an experimental value of 0.44 nmol cm^{-2} for ferrocene units attached to a monolayer of phenylacetylene using click chemistry.

Atomic Force Microscopy (AFM). In this part, pyrolyzed photoresist films (PPFs) were used as substrates because of their low surface roughness in comparison with GC; otherwise the two materials possess comparable features.[9] A PPF plate grafted with **1b** employing $N = 128$ was analyzed as shown in Figure 3. The modified plate showed surface structures with the same sizes as for the bare PPF plate, indicating a uniform grafting of the whole surface. In fact, the surface roughness increased only slightly upon grafting (~ 4.5 Å) in comparison with the bare PPF surface (~ 3.8 Å).

The AFM tip was used in contact mode to scratch a rectangular area with a pressure sufficiently strong to remove the film without affecting the harder PPF surface. From a scan across this area in noncontact mode (along the white line drawn in Figure 3A), the thickness could be determined from the profile (Figure 3C) as described by Anariba et al.[27] The calculated thickness was 3.75 ± 0.70 nm, in excellent agreement with the value of 3.67 ± 0.17 nm determined using ellipsometry.

Scanning Electrochemical Microscopy (SECM). The ability of aryltriazenes to resist spontaneous grafting stands in contrast to that of aryldiazonium ions.[2] This property, along with the possibility of using EGA to generate diazonium salts locally, opens the possibility of patterning surfaces. SECM is a suitable technique for accomplishing this because the tip electrode can be used to generate the acid/diazonium salt at positive potentials, the use of which should disfavor a spontaneous reaction taking place at the tip itself.[28] On the other hand, the substrate electrode is kept at a negative potential to enable the electrografting of the diazonium salt, which diffuses toward it because of the flux of material created at the tip electrode. It should be mentioned that a similar kind of in situ patterning has been accomplished through the reduction of nitro compounds at the tip electrode followed by diazotization of the thus-formed amine.[29]

In a proof-of-concept experiment, patterning consisting of two rings was created, as imaged in Figure 4. The creation of rings rather than spots can be explained as follows: Oxidation of N,N'-diphenylhydrazine at the tip creates a diffusion layer of high acidity between the tip and substrate. Any aryltriazene entering from the edges of the tip undergoes fast protonation and subsequent deprotection to form the diazonium salt mainly in the periphery of the acidic layer between the tip and the substrate. Notably, the
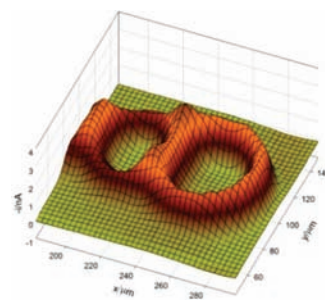

Figure 4. SECM image obtained at a 10 μm Pt tip electrode in 0.1 M Bu$_4$NBF$_4$/MeCN containing 2 mM ferrocene ($E_{tip} = 0.65$ V, $E_{substrate} = -0.15$ V vs SCE). Localized modification of the substrate was carried out by electrolyzing for 200 s a mixture of 2 mM **1b** and 2 mM N,N'-diphenylhydrazine simultaneously at the tip and substrate electrodes ($E_{tip} = 0.9$ V, $E_{substrate} = -0.7$ V vs SCE). The distance between the two electrodes was 3.3 μm (see the Supporting Information).

exact shape of the rings/spots can be altered, depending on the tip–substrate distance, the dimension of the tip electrode, the applied potentials, and the reagent concentrations. Hence, it may be stated that SECM using this method can be employed to create small arrays (e.g., to make biochips).

In summary, we conclude that aryltriazenes can be successfully electrografted to GC and PPF surfaces via a simple electrochemical two-step potential cycle. The method involves the generation of an electrogenerated acid at the electrode to enable the conversion of the aryltriazene to the corresponding aryldiazonium salt, which is the actual grafting agent. The generation of aryldiazonium salts occurs locally for a short time in the diffusion layer of the electrode to be modified (and not in bulk solution), and for this reason, it is possible to anchor directly molecules containing functionalities that otherwise would be capable of reacting with the diazonium group. The surface coverage and the film thickness (submonolayers to 4–5 multilayers) are easily controlled by the number of cycles employed. Finally, the approach is also suitable for patterning surfaces using SECM.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Experimental procedures, synthesis of **1a** and **1b**, plot of log I_p vs log ν, and AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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