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Using a Hydrazone-Protected Benzenediazonium Salt to Introduce a Near-Monolayer of Benzaldehyde on Glassy Carbon Surfaces

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Abstract: A methodology is described for introducing a thin layer of covalently attached benzaldehyde on glassy carbon surfaces using aryl diazonium chemistry. Usually the electroreduction of aryl diazonium salts leads to the formation of an ill-defined multilayer because of the involvement of highly reactive aryl radicals that can add to already-grafted aryl groups. However, in this study we used a two-step "formation-degradation" procedure to solve this problem with the first step consisting of an electrografting of an aryl diazonium salt of a long-chain and bulky alkyl hydrazone onto a glassy carbon surface. The design of the hydrazone group serves to minimize multilayer formation by greatly diminishing the grafting rate after the first-layer formation and at the same time preventing radical additions from taking place at the inner aryl ring. Another valuable property of the hydrazone group is that it easily can be deprotected to the corresponding aldehyde by acid hydrolysis (i.e., the degradation step). In this manner, a thin and well-defined film of covalently attached benzaldehyde with an estimated coverage of 4×10^{-10} mol cm^{-2} was formed. The electrochemical responses of benzaldehyde were highly reproducible and largely independent of grafting medium (water or DMSO) and along with that also the thickness of the initially grafted film. AFM and contact angle measurements support the findings. The "formation-degradation" approach thus lays the foundation for carrying out further functionalization reactions in a controlled manner.

Introduction

Since the first electrochemical grafting of aryl diazonium salts on carbon-based surfaces was published,[1] the interest in this area has been growing steadily.[2] One of the most prominent features of this method is that covalent bonds are formed between the carbon substrate and the aryl radicals generated from the reduction of the diazonium salt, thereby ensuing an extraordinarily high thermal,[1a,c,3] chemical,[1a,c,3b] and electrochemical stability[2a,d,j,l] of the modified layer. Over the years, the method has been extended to include other substrates, that is, metals,[4] silicon,[5] and organic materials.[4k,6] Along with this development, new types of grafting agents such as iodonium[7] and sulfonium salts[8] have been introduced.

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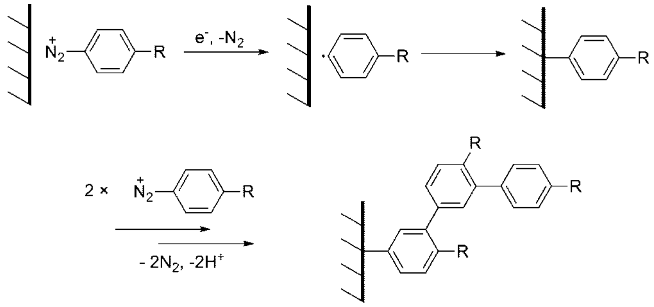
It has also been shown that the grafting may take place spontaneously on conducting materials without the need for an electrochemical activation step.[4d,e,9] Alternatively, ultrasonication[10] or a chemical reductant such as iron powder,[4k] $NaBH_4$,[4k] and hypophosphorous acid[10,11] may be employed having the diazonium salt in a relatively high concentration. Furthermore, if a monomer (typically of the vinylic type) is introduced, a combined aryl radical-initiated grafting and polymerization process can be accomplished. In this manner, relatively thick polymeric coatings can be prepared on both conducting and insulating surfaces.[4k]

The diazonium salt method has now matured to the point where useful coating applications have been developed,[12] but other areas also promise bright applicative prospects. Pinson et al. used covalently modified carbon felt with a high surface area for carrying out solid state synthesis,[13] McCreery et al. developed new types of organic molecularly based junctions,[14] Downard et al. reported on surface patterning,[15] and recently procedures for developing oligonucleotide-functionalized biochips have been outlined.[16]

Although the diazonium salt approach for modifying surfaces offers many advantages compared with, for example, self-assembled monolayers of thiols on gold in terms of high thermal stability, persistency toward chemicals/solvents, and a large accessible potential window, there remains a great disadvantage in that the layer structure is, in general, poorly defined. This is due to the fact that surface derivatization occurs in a process that involves highly reactive aryl radicals (produced from the reduction of diazonium salts and upon expulsion of nitrogen)[17] attacking not only the plain surface but also already-grafted aryl layers to afford multilayers as shown in Scheme 1.[2b,j,m]

Scheme 1. Multilayer Formation Occurring with Diazonium Salts as Grafting Agents



While the process to some extent may be controlled through the applied potential, electrolysis time,[2g,k,4i] and solvent[2e,h] the derivatized surface will seldom be sufficiently well-defined for developing, for example, high-performance sensors or molecular devices or for carrying out quantitative studies of electron transfer (or hopping) phenomena. In specific cases sterically encumbered substituents (i.e., *tert*-butyl) on the aryl ring can be exploited to prevent the polymerization reaction from taking place, thereby allowing the formation of a near-monolayer of chemically inert molecules.[18] However, the disadvantage of these particular systems is that their chemical inertness will prevent them from being used in further functionalization reactions.

In recent work we proposed a so-called "formation-degradation" approach for overcoming the problem associated with the multilayer formation, while at the same time generating a reactive nucleophilic surface suitable for further chemical reactions (Scheme 2).[19] The basic idea consists of preparing diazonium salts containing a pendant functional group serving two purposes. First, it should possess structural and/or electronic shielding properties that enable it to protect the remaining part of the molecule, in particular, toward radical-based reactions. Second, the functional group as now modified with the polymeric film should be cleavable since this would leave essentially a monolayer of a covalently attached substructure of the original molecule on the surface. The first model system successfully demonstrating this methodology was based on diazonium salts of diaryl disulfides which after grafting and reductive degradation provided a near-monolayer of surface-attached and strongly nucleophilic thiophenolates.[19]

In this work, our aim is to extend the scope of the "formation-degradation" approach by including a controlled preparation of a thin reactive layer of benzaldehydes on glassy carbon surfaces. In this manner, pathways for forming a near-monolayer of not only chemically inert molecules[18] and highly reactive nucleophiles[19] but also reactive electrophiles should become available. As a protective and cleavable group for aromatic aldehydes we choose the hydrazone functionality which after the grafting process easily can be hydrolyzed to form the target aldehyde. At the same time the protective group can be designed with the purpose of preventing or at least minimizing the importance of radical reactions taking place at the inner aryl ring and/or the conjugated double bond. It would be this essential feature that

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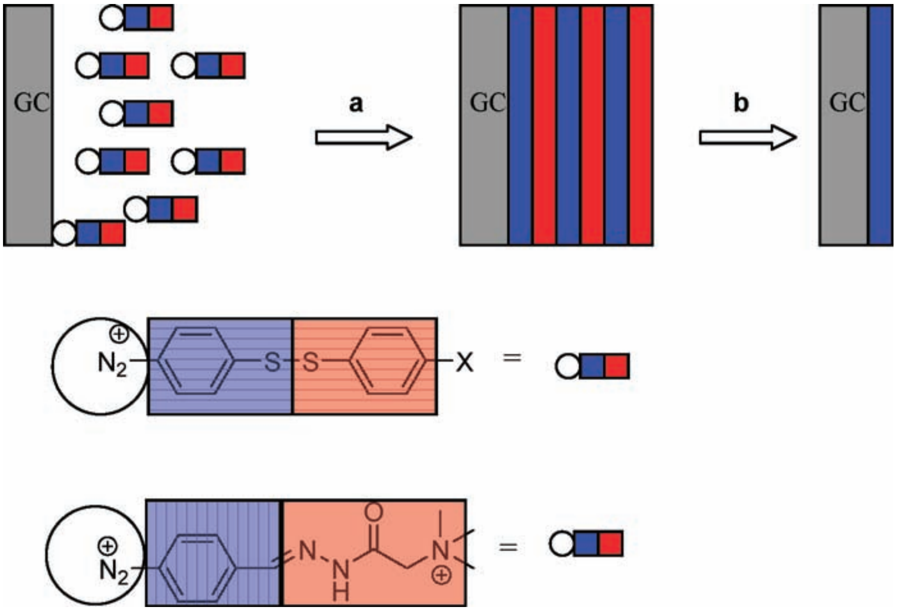
Scheme 2. Illustration of the "Formation-Degradation" Approach for Obtaining a Near-Monolayer of Covalently-Attached Molecules[a]



[a] (a) Formation (through grafting of aryl diazonium salts); (b) degradation (through electrochemical or chemical processes). Diazonium salts of diaryl disulfides[19] and alkyl aryl hydrazones (this work) are suggested as model compounds for forming strongly nucleophilic (i.e., thiophenolates) and electrophilic (i.e. benzaldehydes) surfaces, respectively.

allows the formation of a thin layer of surface-attached benzaldehyde upon hydrolysis. The modified surfaces are analyzed and characterized by means of cyclic voltammetry, atomic force microscopy (AFM), and contact angle measurements.

Experimental Section

Chemicals. The synthesis of (*E*)-4-((2-(2-(trimethylammonio)-acetyl)hydrazono)methyl)benzenediazonium tetrafluoroborate (**1**) followed the general procedure outlined elsewhere;[20a] a detailed description is provided in the Supporting Information. The formylbenzenediazonium salt (**2**)[20b] and the dediazotized product of **1**, that is, (*E*)-2-(2-benzylidenehydrazinyl)-*N*,*N*,*N*-trimethyl-2-oxoethanaminium chloride (**3**),[20c] were synthesized according to the literature cited. Acetonitrile (anhydrous, 99.9%) purchased from Laboratory-Scan, dimethyl sulfoxide (DMSO) from Fluka, and ethanol from Kemityl were used as received. Tetrabutylammonium hydroxide (Bu_4NOH; 1.5 M aqueous solution) was obtained from Fluka, whereas Bu_4NBF_4 was prepared using standard procedures. Water was triple distilled. All other compounds were commercial and used in the highest grade available.

Electrodes and Instrumentation. Glassy carbon (GC) rods (Sigradur G, HTW, $\phi = 1$ mm) imbedded in epoxy resin or GC plates (Sigradur G, HTW, 10 × 10 × 1 mm) were employed as working electrodes, while a platinum wire was used as counter electrode. An Ag/AgI electrode (silver wire immersed in a Pyrex tube containing 0.1 M Bu_4NBF_4 + 0.01 M Bu_4NI in acetonitrile or DMSO) separated from the main solution by a ceramic frit served as reference electrode in acetonitrile or DMSO while a saturated calomel electrode (SCE) was used in aqueous and ethanolic solution. At the end of each experiment in the aprotic media, the standard potential of the ferrocenium/ferrocene couple, $E^{\circ}_{Fc^+}$, was measured and all potentials were referenced against SCE using a previous determination of $E^{\circ}_{Fc^+} = 0.41$ or 0.43 V vs SCE in acetonitrile or DMSO, respectively.[21] A description of the electrochemical instrumentation[7] and AFM[19a] has been provided previously. The contact angle equipment consisted of a 1/2″ digital video camera (720 × 576 pixels) equipped with a TECHSPEC Silver series Telecentric measuring lens. The contact angle of the drop was obtained with the software program JImage and the plugin DropSnake.[22]

Electrochemical Experiments. Glassy carbon electrodes were carefully polished before any modification by successive treatments with diamond suspensions (Struers, grain size: 9, 3, 1, and 0.25 μm) followed by rinsing with water and ethanol and finally 10 min ultrasonic cleansing in ethanol. The electrochemical modification of both glassy carbon electrodes and plates was performed via potentiostatic electrolysis of a 2 mM solution of the diazonium salt (**1** or **2**) in water, acetonitrile, or DMSO (using in all solutions the diazonium salt as supporting electrolyte) for 300 s. The solutions were prepared just before use. For neither **1** nor **2** in aqueous solutions could distinctive reduction peaks be observed in cyclic voltammetry, so we choose to perform the grafting at a potential located in the plateau-like region, that is, −0.6 V vs SCE. The grafted surface was then thoroughly rinsed and ultrasonicated for 10 min in water and ethanol, respectively, before further analysis.

The total charge, Q, used for the reduction of surface-grafted electroactive groups was obtained by integration of the background-subtracted electrochemical response recorded in cyclic voltammetry at a sweep rate of 0.1−2 V s^{-1} (in either a phosphate buffer, i.e., 0.1 M $H_2PO_4^-/HPO_4^{2-}$, or 0.05 M Bu_4NOH + 0.1 M Bu_4NBF_4/ethanol). The surface coverage, Γ, was then calculated using Faraday′s law, i.e. $\Gamma = Q/nFA$, where n is the number of electrons transferred, F is Faraday′s constant, and A represents the geometric area of the electrode. A linear background was assumed and manually adjusted under the faradic peak in accordance with our previous studies.[7,8,19] However, it is important to note that for film-coated electrodes there is a large uncertainty associated with establishing an appropriate baseline since the properties of the film

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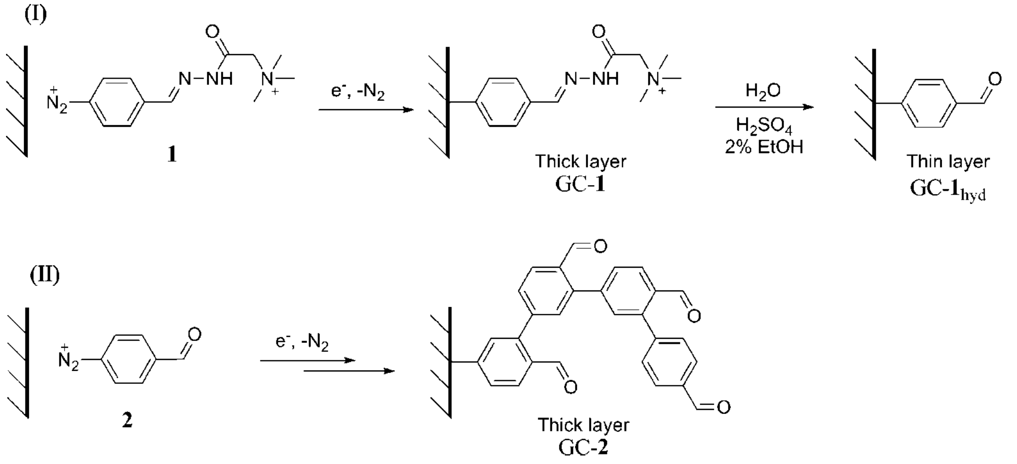
Scheme 3. Electrografting in Aqueous Solution of (I) Benzaldehyde Girard's Reagent T Hydrazone Diazonium Salt (**1**) Followed by an Acidic Hydrolysis to Form a Thin Layer of Surface-Attached Benzaldehyde and (II) Formylbenzenediazonium Salt (**2**)



change during sweeping. In particular, this is true for irreversible processes taking place close to the background discharge. To shed further light on this issue we carried out a few determinations of Γ using polynomial rather than linear baselines. This led to somewhat larger values and showed in line with the conclusion of Yu et al.[21] that for irreversible cases such as those studied herein the uncertainty could be of at least 20%.

The electrochemical blocking properties of the modified surfaces were investigated against two redox probes, that is, ferrocene in 0.1 M Bu_4NBF_4/acetonitrile and $K_3Fe(CN)_6$ in 0.1 M $H_2PO_4^-$/HPO_4^{2-} (pH 7). For the experiments involving immobilization of ferricyanide in films the pertinent modified electrodes were soaked in an aqueous solution containing 5 mM $K_3Fe(CN)_6$ in a test tube for 10 min. The electrodes were rinsed three times with distilled water and then transferred to a phosphate-buffered solution (pH 7) to record the electrochemical response. All solutions were carefully deaerated with argon.

Hydrolysis Conditions. The hydrazone protection group could be hydrolyzed to the corresponding aldehyde[23] by placing the electrodes electrografted by **1** in a test tube containing a mixture of 0.1 mL concentrated sulfuric acid, 0.1 mL ethanol and 4.8 mL water under stirring conditions for 24 h. After the reaction was finished the electrodes were sonicated 10 min in water and ethanol, respectively.

Contact Angle Measurements. Contact angles were measured by introducing a 4 μL water drop onto the surface of the appropriately prepared GC sample plate (10 × 10 × 1 mm) placed on a horizontal stage. The image of the water drop was taken by a digital camera and analyzed to obtain the static contact angle. Measurements were repeated five times with new drops at different positions on the sample.

AFM Measurements. AFM imaging was performed in tapping mode at scan frequencies of 1−2 Hz with minimal loading forces applied and optimized feedback parameters. This ensured minimal sample distortion by tip compression. Silicon nitride cantilevers (NSG01, NT-MDT, Russia) were used with a typical resonance frequency of 150 kHz, a spring constant of 5.5 N m^{-1} and a typical tip radius of 10 nm. The resolution of AFM scans was 512 × 512 pixels. Several images were obtained from separate locations across the surfaces to ensure reproducibility. Silicon nitride cantilevers (NSG01, NT-MDT, Russia) were used to perform scratch measurements. Spring constants were independently calibrated by a thermal tune procedure described in the PicoForce software (Version 6.12).

Molecular Lengths. The PM3 facility in the Chem3D Ultra 10.0 program package (1986−2006 CambridgeSoft) was used for calculating molecular lengths.

Results and Discussion

The two diazonium-based grafting agents used in this study are depicted in Scheme 3. Compound **1** which is the system of main interest is a so-called benzaldehyde Girard's reagent T hydrazone tetrafluoroborate diazonium salt. Numerous Girard reagents have already been developed for synthetic purposes because of their high solubility in aqueous solutions.[24] For this study the pendant group is of particular importance since it should serve the purpose of minimizing multilayer formation.

From that perspective, the relatively long-chain, positively charged, and bulky hydrazone group seems to be ideal [Scheme 3, pathway (I)]. First of all, once the first layer is formed the enhanced blocking effect of a layer consisting of large molecules (molecular length ≈ 1.3 nm) will make multilayer formation less likely simply because the electrode passivation leads to a greatly diminished reduction rate of the grafting agent. Second, the diffusion of **1** toward the electrode surface will be distinctively slowed down by the presence of the positively charged and bulky ammonium group. Third, even if aryl radicals should be generated in the outer part of the first layer, they will most likely dimerize, do hydrogen abstraction from the pendant group, or eventually couple with the thus generated radical species rather than attack the inner ring. Importantly, whichever reactions take place at the pendant group do not really matter, since it will be cleaved anyway in a subsequent hydrolysis step to generate a thin layer of covalently attached benzaldehyde.

The formylbenzenediazonium salt (**2**) is included in the investigation to provide an ill-organized multilayer of benzaldehyde units upon electrografting [Scheme 3; pathway (II)]. Thus, a comparative analysis of the surface layers obtained by the two approaches, that is, the "formation-degradation" approach and the direct grafting should reveal important features about both kinds of layer.

Grafting. Figure 1A and B illustrates the repetitive cyclic voltammograms recorded for **1** and **2**, respectively, in aqueous solution. On the initial cycle a broad irreversible wave is observed which diminishes and shifts to more negative values on subsequent cycles, eventually reaching a point of almost complete disappearance. The final voltammogram (d) recorded after 5 min potentiostatic electrolysis at −0.6 V vs SCE (see Experimental Section) is completely featureless. Such behavior

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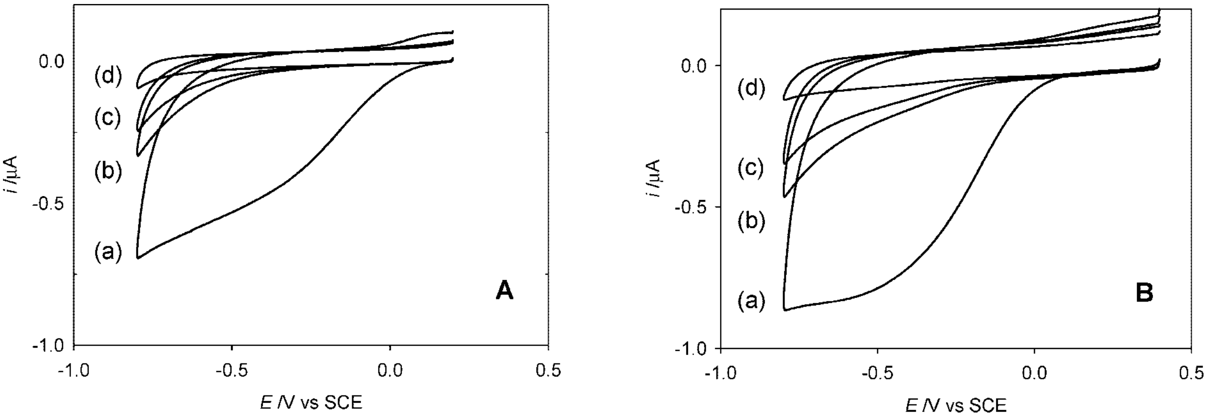

Figure 1. Cyclic voltammograms of 2 mM neutral aqueous solutions of (A) **1** and (B) **2** recorded at a sweep rate of 0.2 V s^{-1} at freshly polished GC electrodes; sweep no. (a) 1, (b) 2, and (c) 3. Solutions were stirred in between cycles. Voltammogram (d) was recorded after potentiostatic electrolysis at −0.6 V vs SCE for 300 s.

is consistent with progressive film formation, i.e., the electrode surface is being modified and passivated by the electrochemical reduction of the grafting agents.[2,7,8] Note also that this behavior is completely different to that of the grafting of the sterically encumbered but relatively small 3,5-bis-*tert*-butylbenzenediazonium ion. In this case there is essentially no decline in the cyclic voltammetric current during the electrografting process because of a limiting formation of a near-monolayer.[18]

The cathodic currents recorded for **1** and **2** on the first sweep are affected by various factors, including diffusion coefficients, transfer coefficients of the pertinent charge transfer processes, preadsorption phenomena, and the grafting efficiency. The resulting ill-defined feature of the waves with relatively large variations in the background currents makes a direct comparison of the two voltammograms meaningless. In general, ill-defined voltammetric waves are a characteristic feature when water is used as the grafting medium.[2e,h] On the other hand, with dipolar aprotic media such as acetonitrile or dimethyl sulfoxide (DMSO) distinct peaks are observable in the cyclic voltammograms (Supporting Information).

Some of the electrodes grafted with **1** were hydrolyzed to convert the hydrazone group to the corresponding aldehyde functionality. The condition used was a strong aqueous acid solution for 24 h which had no affect on the chemically resistant covalent attachment of the molecule to the surface. In the following discussion the glassy carbon electrodes modified directly with **1** and **2** are denoted GC-**1** and GC-**2**, respectively, and the hydrolyzed one GC-$\mathbf{1}_{\mathrm{hyd}}$ (Scheme 3). Unless otherwise noted, all films are assembled in a 5 min potentiostatic electrolysis.

Analysis. Indirect Eletrochemical Detection. One of the most common methodologies used for shedding light on the blocking properties of electrode surfaces is the electrochemical probing of a suitable redox system. In Figure 2 we have collected cyclic voltammograms of ferrocene in acetonitrile recorded for the various electrodes, including a bare GC electrode.

The blocking effect is evident for GC-**1** and, in particular, GC-**2** as interpreted from the appreciable distortion of the otherwise characteristic reversible redox signal of ferrocene obtained at a bare GC electrode. These observations would be in line with the creation of a relatively thicker and/or more compact layer with fewer pinholes on GC-**2** than on GC-**1** due to the smaller size of the grafting agent **2** compared with **1**.

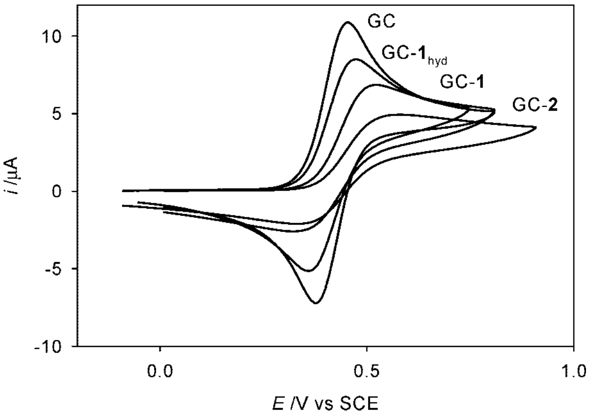

Figure 2. Cyclic voltammograms of 2 mM ferrocene in 0.1 M Bu_4NBF_4/ acetonitrile recorded at a sweep rate of 0.2 V s^{-1} at a freshly polished GC electrode, GC-**1**, GC-**2**, and GC-$\mathbf{1}_{\mathrm{hyd}}$.

Upon hydrolysis of the hydrazone-containing GC-**1** to form GC-$\mathbf{1}_{\mathrm{hyd}}$ a close to complete reestablishment of the characteristic ferrocene signal is found. This lends strong support to our proposition that a chemical degradation reaction produces a thin layer of benzaldehyde [Scheme 3; pathway (I)] with rather poor blocking abilities toward ferrocene. The same overall development is also seen for the ferricyanide redox probe in aqueous solution, although the effect of the surface films in that case appears somewhat larger because of the smaller standard heterogeneous rate constant of ferricyanide (Supporting Information).

The effectiveness of the hydrolysis process can be illustrated even more convincingly for this particular hydrazone simply by soaking GC-**1** and GC-$\mathbf{1}_{\mathrm{hyd}}$ in a ferricyanide solution followed by recording of cyclic voltammograms in the potential range of the $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$ redox pair in a pure electrolyte solution.[25] As seen in Figure 3 distinct signals of ferricyanide are evident for GC-**1** but not GC-$\mathbf{1}_{\mathrm{hyd}}$. This is due to the fact that the GC-**1** film with its positively charged ammonium group is able to electrostatically bind the negatively charged ferricyanide ion in contrast to the neutral aldehyde-containing GC-$\mathbf{1}_{\mathrm{hyd}}$ film. Thus, it may be concluded that the hydrolysis conditions used are adequate for accomplishing a complete removal of the hydrazone protection group.

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(25) (a) Marwan, J.; Addou, T.; Bélanger, D. *Chem. Mater.* **2005**, *17*, 2395–2403. (b) Creager, S. E.; Liu, B.; Mei, H.; DesMarteau, D. *Langmuir* **2006**, *22*, 10747–10753. (c) Choi, E.-Y.; Azzaroni, O.; Cheng, N.; Zhou, F.; Kelby, T.; Huck, W. T. S. *Langmuir* **2007**, *23*, 10389–10394.

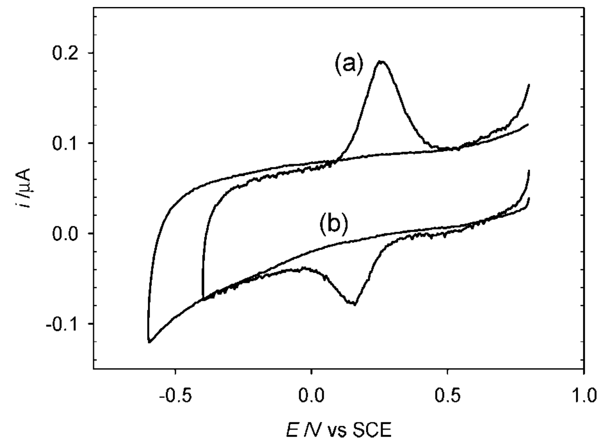

Figure 3. Cyclic voltammograms of (a) GC-**1** and (b) GC-$\mathbf{1}_{\mathrm{hyd}}$ recorded in phosphate buffer (0.1 M $H_2PO_4^-/HPO_4^{2-}$, pH 7) at a sweep rate of 1 V s^{-1} after 10 min immersion in a 5 mM $K_3Fe(CN)_6$ solution.

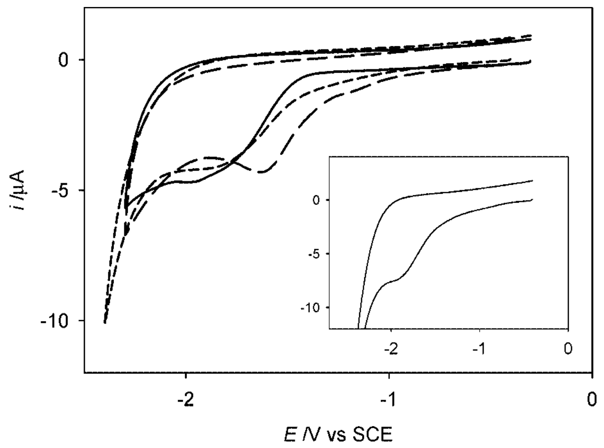

Figure 4. Cyclic voltammograms of GC-$\mathbf{1}_{\mathrm{hyd}}$ (long dashed line), GC-**2** formed either by electrolysis (solid line) or one cyclic voltammetric scan (short dashed line), and GC-**1** (inset) recorded in 0.05 M Bu_4NOH + 0.1 M Bu_4NBF_4/ethanol at a sweep rate of 1 V s^{-1}.

In addition, integration of the current signals for GC-**1** in Figure 3 shows that 0.9×10^{-10} mol cm^{-2} of ferricyanide is immobilized on the film. This number may serve as a lower limit for the surface coverage, Γ, of hydrazones on GC-**1**, considering that a given ammonium group may not necessarily be associated with exactly one of the trivalent ferricyanide ions but may either share it with other ammonium groups or even be uncoordinated. A more precise way of determining Γ will be presented below.

Direct Electrochemical Detection. The electrodes GC-**1**, GC-$\mathbf{1}_{\mathrm{hyd}}$, and GC-**2** contain electrochemically active groups which may be detected directly in cyclic voltammetry in a pure electrolyte solution (Figure 4). The voltammogram pertaining to GC-**1** exhibits an irreversible wave close to the background signal with an estimated cathodic peak potential, E_p of −1.85 V vs SCE (determined after background subtraction). This value is in reasonable agreement with the $E_p = -2.0$ V vs SCE obtained in solution for the reduction wave of compound **3**, i.e. the dediazotized compound of **1** (Supporting Information).

For the GC-$\mathbf{1}_{\mathrm{hyd}}$ film, a reduction peak appears at −1.60 V vs SCE which is completely in line with the electrochemical characteristics of benzaldehyde in solution.[26] Although the exact environment of surface- and solution-based species differs and thus may affect the potential measurements, these results nevertheless provide strong evidence that **1** has been successfully grafted onto the GC surface and that the hydrolysis of the hydrazone functionality generates surface-attached benzaldehyde.

Table 1. Peak Potential, E_p, the Total Width at Half-Height, $\Delta E_{p,1/2}$, the Surface Coverage, Γ, and the Thickness of the Modified Films, *d*, for GC-**1**, GC-$\mathbf{1}_{\mathrm{hyd}}$, and GC-**2**

film	E_p (V vs SCE)[a]	$\Delta E_{p,1/2}$ (mV)[a]	$10^{10}\Gamma_{exp}$ (mol cm^{-2})[a]	*d* (nm)
GC-**1**[b]	−1.85	270	4.0	1.9 ± 0.6
GC-$\mathbf{1}_{\mathrm{hyd}}$[b]	−1.60	220	3.9	1.2 ± 0.4
GC-**2**[b]	−1.80	400	7.2	2.2 ± 0.7
GC-**2**[c]	−1.80	400	4.0	2.1 ± 0.5

[a] In 0.05 M Bu_4NOH + 0.1 M Bu_4NBF_4/ethanol. [b] Electografted by potentiostatic electrolysis. [c] Electografted by a single voltammetric sweep.

In this respect it is interesting to note that for the benzaldehyde-grafted electrode GC-**2**, $E_{p,c}$ is equal to −1.80 V vs SCE (determined after background subtraction) or 200 mV negative to that of GC-$\mathbf{1}_{\mathrm{hyd}}$. At the same time the GC-**2** wave is considerably broader with a total width at half-height, $\Delta E_{p,1/2}$, = 400 mV compared with 220 mV for GC-$\mathbf{1}_{\mathrm{hyd}}$. A negative potential shift along with a broadening of the current signal as observed for GC-**2** is interpreted as a slow-down of the associated charge transfer process because of multilayer formation. For the GC-$\mathbf{1}_{\mathrm{hyd}}$ film, on the other hand, the benzaldehyde layer formed upon hydrolysis is so thin that the resulting charge transfer process still is sufficiently fast to give an electrochemical response consistent with that of the solution analogue.

An important point to consider is to which extent the electrografting of **2** might be controlled to form a near monolayer of benzaldehyde through either the use of a short electrolysis time or a single cyclic voltammetric sweep. This simple approach has been applied with success for specific diazonium salts such as those of 4-nitroazobenzene,[2c] 4-nitrobiphenyl,[2c,k] and 4-nitrophenyl[4i] and certainly it could undermine the justification of using the two-step “formation-degradation” approach proposed herein.

However, we found that for **2** it was impossible to generate a film having as well a defined electrochemical response as GC-$\mathbf{1}_{\mathrm{hyd}}$, no matter which grafting approach was chosen. A typical voltammogram of a GC-**2** film assembled by just one cyclic voltammetric sweep is included in Figure 4. As seen the electrochemical properties are quite similar to those obtained in the electrolyzed approach, indicating that the direct grafting of **2** must be a very efficient but also uncontrollable process.[19]

In Table 1 all relevant values of E_p and $\Delta E_{p,1/2}$ are collected along with the experimentally determined surface coverage, Γ_{exp}, and the thickness of the modified layers, *d*. The values of Γ_{exp} determined from an integration of the electrochemical signal (as an average of signals recorded at sweep rates ranging from 0.2−2 V s^{-1}) and *d* measured by AFM[27] (Supporting Information) provide additional important information about the two-step “formation-degradation” approach. The Γ_{exp} values are calculated on the assumption that the electrochemical reductions of both the hydrazone and the aldehyde functionalities follows irreversible one-electron processes (in basic medium).[26]

Surface Coverage. With $\Gamma_{exp} \sim 4 \times 10^{-10}$ mol cm^{-2} for both GC-**1** and GC-$\mathbf{1}_{\mathrm{hyd}}$ we may conclude that the hydrolysis process proceeds by almost 100% efficiency without affecting the strong

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(26) Andrieux, C. P.; Grzeszczuk, M.; Savéant, J.-M. *J. Electroanal. Chem.* **1991**, *318*, 369–372.

(27) Anariba, F.; Duvall, S. H.; McCreery, R. L. *Anal. Chem.* **2003**, *75*, 3837–3844.

covalent bonding of the surface-attached molecules. At the same time this also suggests that no aryl groups have been chemically coupled to the pendant hydrazone functionality during the grafting of **1** since such groups would have been removed during the subsequent hydrolysis process, thus giving a decrease in Γ_{exp} going from GC-**1** to GC-$\mathbf{1}_{hyd}$. As an aside it might be mentioned that the 0.9×10^{-10} mol cm^{-2} of ferricyanide we were able to immobilize on the GC-**1** film as suspected would only represent a lower limit for the actual hydrazone coverage. On the basis of the above results we may now state that the hydrazone groups outnumber the ferricyanide molecules by a factor of 4.5.

A calculation of the theoretical coverage, Γ_{theo}, for GC-**1** (close packing case), is not straightforward because of the flexibility of the pendant hydrazone group. Still, limiting values may be obtained. On the assumption that the pendant group is straightened out a calculation of the molecular dimensions using the Chem3D Ultra program leads to a surface molecular area of 18 Å^2 corresponding to $\Gamma_{theo} = 9 \times 10^{-10}$ mol cm^{-2}. On the other hand, if the outer group is stretched in a parallel direction with respect to the surface the molecular area increases to 35 Å^2 and Γ_{theo} decreases to 5×10^{-10} mol cm^{-2}. Actually, this value is close to Γ_{exp} for GC-**1** suggesting that the grafting of a molecule as large as **1** using the diazonium salt approach can be quite efficient. This is not to say that it will leave the surface free of pinholes, the presence of which is confirmed experimentally by the appearance of a more sigmoidal shape of the ferrocene signal in the blocking experiments described above (Figure 2, voltammogram denoted GC-**1**).

For the GC-**2** film $\Gamma_{exp} = 7.2 \times 10^{-10}$ mol cm^{-2} is approximately twice as large as that for the GC-$\mathbf{1}_{hyd}$ film. While it is not surprising that the coverage is higher for a multilayer compared to a supposedly near-monolayered film the difference might have been predicted to be even larger. In particular, this becomes evident if one considers that Γ_{theo} for the ideal close packing of simple para-substituted phenyl rings is as high as 1.2×10^{-9} mol cm^{-2}.[1b] This shows that for a compact multilayer not all of the otherwise electrochemically active groups will be detectable because of electrolyte inaccessibility and/or ion transport limitations in the film as already discussed in detail by Downard and co-workers.[2h,l]

In this context, it is interesting to note that if the GC-**2** film is assembled by means of a single cyclic voltammetric sweep rather than the 5 min potentiostatic electrolysis the grafting is very efficient giving $\Gamma_{exp} = 4.0 \times 10^{-10}$ mol cm^{-2}, i.e. essentially the same as for the GC-$\mathbf{1}_{hyd}$ film. However, the layer structure is ill-defined (most probably consisting of multilayers) as evidenced by the broad signals recorded of the film in cyclic voltammetry (Figure 4).[28]

Layer Thickness. For GC-**1** and GC-$\mathbf{1}_{hyd}$ the layer thickness *d* was measured to be 1.9 ± 0.6 nm and 1.2 ± 0.4 nm, respectively. Clearly, the uncertainty in these measurements does not allow for a quantitative description of the layer structure, considering also that all AFM measurements were carried out on dried samples. Still, the results can be used, at least in a relative manner, to substantiate the view that molecular moieties of the originally derivatized surface have been cleaved off. Perhaps somewhat fortuitous is the fact that the difference between the layer thickness of GC-**1** and GC-$\mathbf{1}_{hyd}$ is 0.7 nm, exactly the same as the calculated length of the pendant hydrazone group in **1**. Such a result would imply that GC-**1** essentially consists of a monolayer film, i.e. no extension of the hydrazone group has taken place as a result of aryl radical attack during the grafting process. The already mentioned observation that Γ_{exp} is the same for GC-**1** and GC-$\mathbf{1}_{hyd}$ is in line with this view.

Admittedly, the calculated thicknesses of a monolayer on GC-**1** and GC-$\mathbf{1}_{hyd}$ of 1.3 and 0.6 nm, respectively, are smaller than the corresponding values obtained from the AFM experiments, even if the experimental uncertainties are taking into account. On one side this might suggest that the grafting of **1** followed by the subsequent hydrolysis leads to the formation of molecular structures slightly larger than a monolayer. In such a context one could easily imagine that bis(formylphenyl)-like structures are formed during the grafting process because of aryl radicals adding to an already-grafted phenyl ring rather than the pendant hydrazone group of GC-**1**. On the other side, it should be considered that the thickness determined for GC-$\mathbf{1}_{hyd}$ is essentially the same as that obtained for a near-monolayer of a degraded thiophenolate film[19] and from the electrografting of the sterically encumbered 3,5-bis-*tert*-butylbenzenediazonium on Cu, Au, and SiH.[18]

Obviously, in future studies a flat material such as pyrolyzed photoresist carbon films would be much more suitable for carrying out reliable AFM studies rather than GC plates with their higher surface roughness. Nevertheless, for the thicker and electrochemically blocking GC-**2** film (*d* = 2.2 ± 0.7 nm) it is safe to conclude that a multilayer is present consisting of 3−5 benzaldehyde units as evaluated from the pertinent molecular length (~ 0.6 nm). The fact that essentially the same (limiting) thickness is measured if the GC-**2** film is electrografted through just a single cyclic voltammetric sweep (*d* = 2.1 ± 0.5 nm) shows that the grafting process is extremely effective.

With respect to the above discussion of surface coverages we advocated for the possibility that only a certain fraction of the directly electrografted benzaldehyde groups in GC-**2** would be detectable in cyclic voltammetry, depending on the layer compactness and solvent accessibility.[2h,l] In principle, with the information on *d* now available a calculation of this fraction would have been possible had it not been because of the high uncertainties. However, at least for the limiting scenario, in which GC-**2** has four times as many benzaldehyde groups as GC-$\mathbf{1}_{hyd}$ but only twice the electrochemically determined coverage, we may conclude that half of the aldehyde groups in GC-**2** are not detected electrochemically. Obviously, this calculation is based on the assumption that all aldehyde groups in GC-$\mathbf{1}_{hyd}$ are able to respond electrochemically.

Solvent Effects. With **1** having a double positive charge water became the first solvent choice herein. However, it leaves the important question as to what extent the grafting medium may affect the properties of the films prepared. The picture developed by Brooksby and Downard on the influence of solvents on aryl-based films is that layers formed in water are compact and relatively thin, while in acetonitrile the film thickness becomes larger due to the swelling ability of aryl layers in organic media.[2e,h,29] Unfortunately, acetonitrile was excluded from these

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(28) Measurement of static water contact angles, θ, strongly supports the proposed scheme. For a bare GC electrode $\theta = 77°$. Upon modification with **1**, θ decreases to 37° which points to the formation of a more hydrophilic surface. This corresponds well to the fact that GC-**1** contains the positively charged ammonium group. For GC-$\mathbf{1}_{hyd}$, that is, after hydrolysis and the formation of benzaldehyde, θ increases to 61° which is still lower than the 77° obtained for the bare electrode. Importantly, the value for GC-$\mathbf{1}_{hyd}$ is in agreement with the 63° obtained for GC-**2**. Hysteresis effects were not considered in this work since the purpose was only to show the relative changes that would occur in θ as a response to the modification carried out.

Table 2. Coverage, Γ, and Thickness, *d*, of Films Electrografted by Potentiostatic Electrolysis in Water or DMSO

film	grafting medium	$10^{10}\Gamma_{\mathrm{exp}}$ (mol cm^{-2})[a]	*d* (nm)
GC-**1**	Water	4.0	1.9 ± 0.6
GC-$\mathbf{1}_{\mathrm{hyd}}$	Water	3.9	1.2 ± 0.4
GC-**2**	Water	7.2	2.2 ± 0.7
GC-**1**	DMSO	[b]	3.7 ± 0.5
GC-$\mathbf{1}_{\mathrm{hyd}}$	DMSO	4.0	1.8 ± 0.5
GC-**2**	DMSO	<1.0	3.3 ± 0.5

[a] In 0.05 M Bu_4NOH + 0.1 M Bu_4NBF_4/ethanol. [b] Too close to the background to be determined.

studies because **1** was found to be insoluble. In general, the use of acetonitrile as organic medium is attractive because of its relatively poor H-atom-donating abilities toward the intermediate aryl radicals.[30] Considering that dimethyl sulfoxide (DMSO) would have similar H-atom-donating properties as acetonitrile,[30] we selected this solvent as our organic grafting medium to study solvent effects on the grafting process.

In line with the literature results we find that a GC-**1** film formed by electrografting in DMSO is thicker than the one formed in water by more than 2 nm ($d = 3.7 \pm 0.5$ nm in DMSO). This would be consistent with the formation of about three molecular layers, taking into account that the theoretically calculated thickness of a monolayer on GC-**1** is 1.3 nm. Nevertheless, upon hydrolysis the layer thickness decreases to 1.8 ± 0.5 nm, meaning that ~2 nm of the molecular structure (corresponding to three hydrazone groups) has been cleaved off during hydrolysis.

Accordingly, it may be concluded that even for a relatively thick film electrogenerated in DMSO the degradation step to form GC-$\mathbf{1}_{\mathrm{hyd}}$ works well. This result would further imply that a reasonably large fraction of the aryl radicals generated during the grafting process have reacted with the pendant hydrazone group (presumably through radical abstraction and coupling reactions) of already-grafted molecules. Still, the shielding of the inner ring provided by the large hydrazone group toward radical attack during the grafting is not as efficient in DMSO as in water, considering that the film after hydrolysis is thicker by 0.6 nm in the former case.[29] In fact, this increase of the thickness would correspond to the assembly of one additional benzaldehyde layer in DMSO, yet without affecting the well-defined electrochemical response of the hydrolyzed films ($E_p = -1.60$ V vs SCE and $\Gamma_{\mathrm{exp}} = 4 \times 10^{-10}$ mol cm^{-2} for DMSO against −1.60 V vs SCE and $\Gamma_{\mathrm{exp}} = 3.9 \times 10^{-10}$ mol cm^{-2} for water) as illustrated in Figure 5.

On this basis we may state that essentially independent of the thickness and/or compactness of the initial grafted layer (~3 layers of the hydrazone in DMSO against 1−2 molecular layers in water) a hydrolyzed film consists of 1−2 layers of benzaldehyde showing the same well-defined reproducible electrochemical properties. In this sense the effect of the grafting medium on the final outcome, that is, GC-$\mathbf{1}_{\mathrm{hyd}}$, is small, the reason of which ultimately can be ascribed to the design of the grafting agent **1** with its bulky and long-chain hydrazone group.

In comparison, the solvent effect is much higher if the benzaldehyde film is formed directly from a grafting (electrolysis or voltammetric scans) of the formylbenzenediazonium salt. While the grafting in water leads to the formation of relatively thin but compact GC-**2** films with a high surface coverage, only broad and poorly defined voltammetric waves with an estimated Γ_{exp} of less than 10^{-10} mol cm^{-2} could be observed for the DMSO-grafted films (Supporting Information). This low electrochemical activity of the grafted benzaldehyde group can be attributed to the presence of a thick, dense and insulating film ($d = 3.3 \pm 0.5$ nm) formed in a highly uncontrolled grafting process.

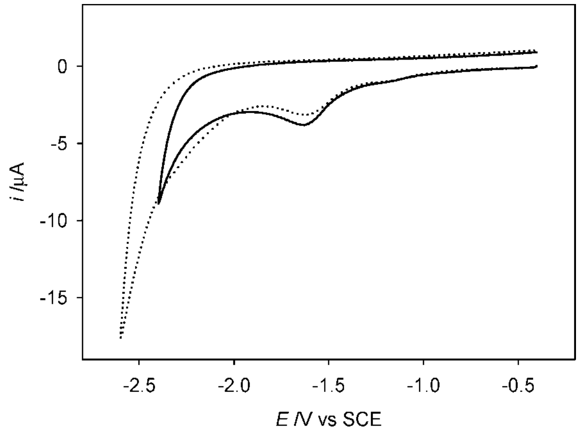

Figure 5. Cyclic voltammograms of GC-$\mathbf{1}_{\mathrm{hyd}}$ in 0.05 M Bu_4NOH + 0.1 M Bu_4NBF_4/ethanol (sweep rate = 1 V s^{-1}) obtained by electrografting of **1** either in water (—) or DMSO (dotted line) followed by acidic hydrolysis.

In conclusion, these studies validate the cartoon presentation in Scheme 2, in that the outer layer—essentially independent of grafting medium, grafting method and film thickness—can be cleaved off to a thin and more well-defined layer in a subsequent degradation step. The chemical rationale behind this observation is that the sterically encumbered hydrazone substituent to a large extent hinders the addition of aryl radicals to aryl rings present in an already-grafted layer. It is even possible that the charge of the ammonium group adds to this behavior by hindering the diffusion of the positively charged diazonium salts toward the positively charged film. The thin-film formation is highly reproducible, thus underlining the validity of the proposed "formation-degradation" principle for the hydrazone/aldehyde system.

Summary

We have extended the so-called "formation-degradation" approach to include the creation of a thin near-monolayer of benzaldehyde on glassy carbon surfaces through the initial grafting of a hydrazone-substituted benzenediazonium salt. The long-chain and bulky hydrazone group was designed with the purpose of minimizing multilayer formation by diminishing greatly the grafting rate upon first-layer formation and at the same time prevent radical additions from taking place at the inner aryl ring. In addition, we have exploited the fact that the chemically resistant covalent attachment of the aryl hydrazone to the surface allows the use of relatively strong acidic conditions for generating a thin layer of benzaldehyde in a hydrolysis step.

The resulting thin film of surface-attached benzaldehyde groups with an estimated coverage of 4×10^{-10} mol cm^{-2} gives well-defined and reproducible electrochemical responses, independent of grafting medium (water or DMSO) and along with this also the thickness of the initially grafted film. This high

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(29) It has previously been shown that exposing films to different solvents upon grafting may lead to easily measurable, reversible changes in film thickness.[2h] However, this effect should not be an issue in our discussion of the grafting medium because all films prepared are treated in the same manner before the AFM measurements (i.e., ultrasonic rinsing for 10 min in water, ethanol, and hexane, respectively).

(30) M′Halla, F.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1980**, *102*, 4120–4127.

reproducibility underlines the validity and generality of the proposed "formation-degradation" principle, at least for the hydrazone/aldehyde system. In contrast, for a multilayered film obtained from a direct grafting of the formylbenzenediazonium salt in either water or DMSO broad and potential-shifted cyclic voltammetric waves are seen.

This study therefore completes the picture in the sense that surface properties of grafted near-monolayers now can be varied from nucleophilic[19] over inert[18] to electrophilic, laying the foundation for carrying out further functionalization reactions in a controlled manner. In future work we intend not only to address such reactions but also to investigate the extent by which the reactivity of surface-assembled benzaldehydes are influenced by the exact layer composition. It will also be of major concern to increase even further the versatility of the "formation-degradation" approach by developing new kinds of electrophilic and nucleophilic surfaces.

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Supporting Information Available: Synthesis of **1**, electrografting and blocking experiments, electrochemical detection and AFM procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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