

# Effect of Applied Potential on Arylmethyl Films Oxidatively Grafted to Carbon Surfaces

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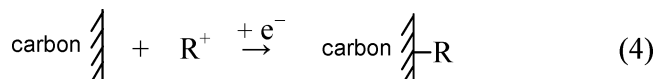
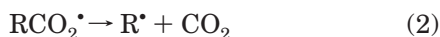
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Arylmethyl films have been grafted to glassy carbon surfaces and to pyrolyzed photoresist films (PPFs) by electrochemical oxidation of 1-naphthylmethylcarboxylate and 4-methoxybenzylcarboxylate. Atomic force microscopy (AFM) and electrochemistry were used to characterize the as-prepared films and to monitor changes induced by post-preparation treatments. Film thickness was measured by depth profiling using an AFM tip to remove film from the PPF surface. Surface coverage of electroactive modifiers was estimated from cyclic voltammetry, and monitoring the response of a solution-based redox probe at grafted surfaces gave a qualitative indication of changes in film properties. For preparation of the films, the maximum film thickness increased with the potential applied during grafting, and all films were of multilayer thickness. The apparent rate of electron transfer for the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  couple was very low at as-prepared films. After film-grafted electrodes were transferred to pure acetonitrile-electrolyte solution and subjected to negative potential excursions, the response of the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  couple changed and was consistent with faster electron-transfer kinetics, the film thickness decreased and the surface roughness increased substantially. Applying a positive potential to the treated film reversed changes in film thickness, but the voltammetric response of the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  couple remained kinetically fast. After as-prepared films were subjected to positive applied potentials in acetonitrile-electrolyte solution, the apparent rate of electron transfer for the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  couple remained very slow and the measured film thickness was the same or greater than that before treatment at positive potentials. Mechanisms are considered to explain the observed effects of applied potential on film characteristics.

## Introduction

The covalent grafting of molecular species to carbon surfaces by the electrochemical generation of aryl-based radicals was first reported more than 10 years ago.<sup>1</sup> Most attention has been focused on the reduction of aryl diazonium salts, in particular the mechanism for covalent grafting, the structure of the resultant layers, their stability to physical, chemical, and electrochemical treatments, and potential applications.<sup>2,3</sup> The electrochemical oxidation of arylcarboxylates at carbon electrodes also results in the formation of surface films.<sup>4–7</sup> Detailed studies of the mechanism of the electrochemical oxidative decarboxylation reaction have been reported,<sup>8</sup> and mechanism shown in eqs 1–4 has been proposed for the grafting of arylcarboxylates to carbon surfaces.<sup>4,8</sup>



The films have been characterized by spectroscopy, scanning tunneling microscopy (STM), and electrochem-

istry,<sup>4,5,7</sup> and the reaction has been used to generate modified carbon felts with potential applications in combinatorial synthesis and electrocatalysis.<sup>5–7</sup>

The initial report of carbon surface derivatization by this method describes some intriguing aspects of film behavior.<sup>4</sup> For film preparation, a two-step grafting process was shown to give films with higher surface coverage than those prepared with a single grafting. Films were first grafted using potential scans just encompassing the carboxylate oxidation peak. After disappearance of the oxidation peak, a new peak was observed at a potential between the initial peak, and the peak for oxidation of the surface film itself. Oxidation at the potential of this new peak (in modifier solution) led to further grafting. Voltammetry of surface-attached groups on GC confirmed an increase in modifier surface coverage and STM images showed a denser film on highly ordered pyrolytic graphite (HOPG) after the second grafting than after a single grafting.

A second interesting finding from the same study is that the films could be removed from the surface (erased) by an electrochemical treatment in blank acetonitrile-electrolyte solution. Erasing was achieved by holding the potential of the grafted glassy carbon (GC) electrode slightly positive of the peak for irreversible oxidation of the attached groups. After this treatment, electrodes were found to exhibit the same behavior as a clean GC electrode,

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toward solution redox species. Hence, it was concluded that the surface film had been removed.

The work described here was prompted by the reports of second grafting and erasing processes for films formed by oxidation of arylcarboxylates at carbon surfaces. We have recently demonstrated that film thickness measurements using the atomic force microscope (AFM) and film surface coverage measurements using electrochemistry are a powerful combination for investigating layers grafted to carbon substrates.<sup>9,10</sup> Here we apply these techniques to a detailed examination of films grafted on glassy carbon and pyrolyzed photoresist films (PPFs) by electrochemical oxidation of arylcarboxylates. In particular, we have monitored the changes in film thickness, surface coverage of electroactive groups, and ability of the film to inhibit electron transfer to a solution redox probe, after subjecting preformed films to potential excursions (beyond  $\pm 1.5$  V vs Ag/Ag<sup>+</sup>) in 0.1 M [Bu<sub>4</sub>N]BF<sub>4</sub>-acetonitrile solution.

## Experimental Section

**Chemicals and Materials.** Potassium ferricyanide (Riedel De Haën AG), tetrabutylammonium hydroxide (TBAOH), 1 M in methanol (Aldrich), and KCl (AnalaR, BDH) were used as received. Aryl acetic acids [1-naphthalene acetic acid (Sigma), *p*-nitrophenyl acetic acid (Aldrich), and *p*-methoxyphenyl acetic acid (Koch-Light laboratories)] were converted to the corresponding carboxylate in the electrochemical cell by dissolving the aryl acetic acid in acetonitrile and slowly adding 0.9 M equivalents of TBAOH in methanol. Acetonitrile (HPLC grade) was dried over CaH<sub>2</sub> for 2 days and refluxed under N<sub>2</sub> for 2 h prior to distilling in an N<sub>2</sub> atmosphere. Milli-Q water, >18 M $\Omega$ , was used for all aqueous solutions. Tetrabutylammonium tetrafluoroborate ([Bu<sub>4</sub>N]BF<sub>4</sub>) was prepared by standard methods and dried under vacuum at 80 °C for 2 days. All glassware and electrochemical cells were dried and stored at 45 °C.

PPF preparation followed general methods described previously.<sup>9,11</sup> Two coats of positive photoresist AZ4620 (Clariant) were spin-coated on pre-cut silicon wafers at 3000 rpm and soft-baked for at least 20 min before pyrolyzing at 1050 °C for 1 h in a forming-gas atmosphere. Sheet resistances of PPF samples were determined using gold conductive wires set in a square arrangement. A spring tension device provided reproducible downward pressure of the gold wires onto the carbon surfaces. Sheet resistances greater than 30  $\Omega \square^{-1}$  were usually found to give poor electrochemical responses to standard redox probes and were discarded. Only PPF samples with sheet resistances <25  $\Omega \square^{-1}$  were used for modification. The mean surface roughness,  $R_a$ , of the PPF surface was determined from AFM data and was typically <0.5 nm. The  $R_a$  value was calculated over lengths between 2 and 10  $\mu\text{m}$  depending on the scan area.

**Electrochemistry.** All electrochemical measurements were performed using computer-controlled EG&G PAR model 273A and model 173 instruments. The electrochemical cell for use with PPF samples has been described in full elsewhere;<sup>9</sup> briefly, the PPF samples were mounted horizontally between an insulated metal base plate and a glass solution cell with a Viton O-ring and four springs that sealed the solution above the PPF while maintaining a copper electrical contact to the PPF external to the solution. The O-ring also defined the geometric area of the PPF working electrode (0.26 cm<sup>2</sup> for electrode modification and 0.12 cm<sup>2</sup> for subsequent scans at the modified surface). A conventional glass cell was used with the glassy carbon (GC) disk electrode (diameter = 3.0 mm). In each case, the secondary electrode was a Pt wire and the reference was either an SCE (for aqueous solutions) or a Ag wire pseudo-reference electrode (for acetonitrile solutions). The ferrocene/ferrocenium couple appeared at  $E_{1/2} = 0.50$  V (vs Ag/Ag<sup>+</sup>) in 0.1 M [Bu<sub>4</sub>N]BF<sub>4</sub> acetonitrile solution. Solutions for electrochemistry were degassed with N<sub>2</sub>,

and all measurements were made at  $22 \pm 2$  °C. All Fe(CN)<sub>6</sub><sup>3-</sup> (3 mM in 0.2 M KCl aqueous solution) voltammetry was obtained with scan rate = 200 mV s<sup>-1</sup>.

Films were prepared on GC and PPF surfaces using controlled potential electrolysis in acetonitrile solutions containing 5.2 mM of the arylcarboxylate and 0.1 M [Bu<sub>4</sub>N]BF<sub>4</sub>. A relatively high carboxylate concentration ensured that film growth was complete in relatively short grafting times (see below). For the standard modification procedure, two voltammetric cycles at 200 mV s<sup>-1</sup> were recorded between 0 and 1.4 V and then the working electrode potential was maintained for the selected time at 100 mV more positive than the modification peak, i.e.,  $E_{\text{app}} = E_{\text{pa}} + 100$  mV. For PPF samples, the modified surface was thoroughly washed with pure acetonitrile and dried with nitrogen gas. Modified GC was ultrasonicated in pure acetonitrile for 30 s and dried with nitrogen gas.

Determination of voltammetric peak areas was performed by curve fitting.<sup>12</sup> Lorentzian, Gaussian, or a mixture of Lorentzian–Gaussian curves were fitted to the voltammetric peaks via the Levenberg–Marquardt algorithm. Polynomial baselines can be fitted during the nonlinear least squares iteration, or they can be solved for and subtracted from the voltammogram prior to the curvefit.

**UV–Visible Spectroscopy.** Spectra were collected with a GBC Scientific UV/vis 920 Spectrometer, using a 500 to 190 nm scan range, 1 nm slit width, 0.067 nm scan interval, and 150 nm/min scan speed. A quartz cuvette with 1 cm path length contained the sample, and all samples were referenced to air from the dual beam. Solutions for UV analysis were prepared by adding aliquots (0–100  $\mu\text{L}$ ) of 0.1 M TBAOH in methanol to a 10 mL solution of 5.9 mM NM-COOH in acetonitrile giving 12 different solution compositions. From each solution, 40  $\mu\text{L}$  was further diluted to 4 cm<sup>3</sup> with methanol–acetonitrile solvent and the UV spectrum recorded.

**Atomic Force Microscopy.** AFM (Digital Instruments Dimension 3100) topographical measurements were performed in noncontact tapping mode with a silicon cantilever (NSC 12 model, Ultrasharp) operating at moderate resonant frequencies (350 kHz). The images were collected with a resolution of either 256 or 512 samples per line and a scan rate of <1 Hz. The data were collected in ambient air conditions, and each scan was duplicated to ensure that any features observed were reproducible. The procedure for film depth profiling using an AFM tip to mechanically remove film from the modified PPF surface has been described previously.<sup>9,10,13</sup> Briefly, the technique of “scratching” the modified PPF surface uses a chip configuration that has three silicon cantilever tips, of different lengths, at one end. As one of the two shorter tips located on either side of the central longest tip approaches the surface to begin a tapping mode scan, the longer tip (not in resonance) imbeds into the surface film and effectively scratches the modifier from the PPF surface. Some of the PPF surface, to an average depth of 0.3 nm, is also removed by scratching and hence film thickness data have been adjusted by this amount. After removing the film from an area 10  $\mu\text{m} \times 1 \mu\text{m}$ , the tips were withdrawn from the PPF surface and the AFM alignment was refocused onto the longer tip which was used in tapping mode to scan the scratch. Loose debris from the scratch was removed by gentle air convection near the AFM tip. The average cross-sectional plot of the AFM image was used to determine the depth of the film. From the cross-sectional plot, at least 8 paired data points were collected where each pair contained one point from within the scratch and one outside. The height differences of the film were recorded, and two new random locations were selected. The estimated error in the in the paired data points is  $\pm 0.2$  nm. After correction for the scratch depth at bare PPF, all quoted film thickness data have an associated uncertainty of  $\pm 0.4$  nm.

Reported surface roughness values ( $R_a$ ) are an arithmetic average of measured mean roughness values obtained from twenty randomly selected areas (each approximately 1  $\mu\text{m} \times 1 \mu\text{m}$ ) of the carboxylate-derived film. Each mean surface roughness value was calculated using the NanoScope software.

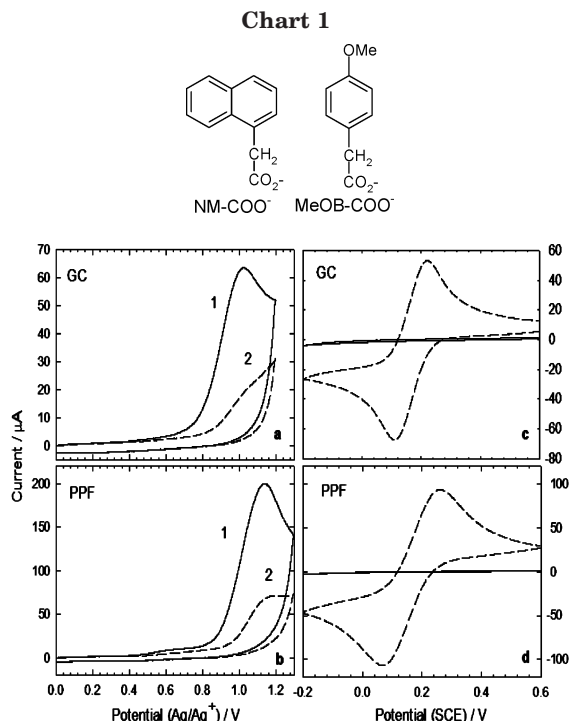
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**Figure 1.** Comparison of cyclic voltammetry at GC (a and c) and PPF (b and d) surfaces. (a and b) First scan (—) and second scan (---) ( $200 \text{ mV s}^{-1}$ ) with stirring between scans, of  $5.2 \text{ mM NM-COO}^-$  in  $0.1 \text{ M [Bu}_4\text{N]BF}_4$ -acetonitrile solution. (c and d) Scans of  $3.1 \text{ mM Fe(CN)}_6^{3-}$  in aqueous  $0.2 \text{ M KCl}$  at bare (—) and  $\text{NM}_T$ -modified (---) surfaces.

## Results and Discussion

**Selection of Carboxylate Modifiers and Measurement of Solution Composition.** Electrochemical and AFM investigations of film formation and film properties were undertaken at GC and PPF surfaces. PPF and GC have previously been shown to have similar characteristics as electrode materials for solution species undergoing simple outer-sphere electron transfer, and as a surface for diazonium coupling reactions.<sup>11</sup> Hence initial experiments were aimed at identifying arylcarboxylates with suitable film-forming properties at GC and PPF surfaces. Chart 1 shows the two arylcarboxylates chosen for this investigation. Their selection was based on previous reports of electrochemical grafting of arylcarboxylates to GC and HOPG electrodes.<sup>4</sup> Thus, 1-naphthylmethylcarboxylate ( $\text{NM-COO}^-$ ) and 4-methoxybenzylcarboxylate ( $\text{MeOB-COO}^-$ ) were reported to readily form passivating films on GC electrodes on repeat cycling through the carboxylate oxidation peak. Further, films prepared from  $\text{NM-COO}^-$  exhibit additional redox chemistry based on the electroactive NM group. This provides a convenient means to examine the film electrochemically.

Figure 1 shows two consecutive voltammetric scans of  $5.2 \text{ mM NM-COO}^-$  in acetonitrile solution at (a) GC and (b) PPF surfaces. The oxidation peak near  $1.1 \text{ V}$  is attributed to the reactions described by eqs 1–4, above.<sup>4</sup> On repeat scans the peak current decreases as oxidation is inhibited by the passivating film forming on the electrode surface.<sup>4</sup> After holding the potential at  $E_{\text{app}} = E_{\text{pa}} + 100 \text{ mV}$  for  $300 \text{ s}$  in the same solution, the electrodes were sonicated and/or rinsed and transferred to an aqueous  $\text{Fe(CN)}_6^{3-}$  solution. Panels c and d of Figure 1 show the response of  $\text{Fe(CN)}_6^{3-}$  before and after the grafting step at the GC and PPF surfaces, respectively. The loss of response of the redox probe at the grafted surfaces provides evidence for a surface film that decreases the apparent

rate of electron transfer to  $\text{Fe(CN)}_6^{3-}$  in solution.<sup>14,15</sup> The similarity of the ratio of peak currents for scans 1 and 2 of the grafting process at GC and PPF (Figure 1, panels a and b), and the passivating effects of the grafted films at each surface (Figure 1, panels c and d) suggest similar rates of film formation and film properties at GC and PPF. Likewise for  $\text{MeOB-COO}^-$ , the grafting process is very similar at both carbon surfaces (see the Supporting Information). Hence these modifiers were used for further experiments.<sup>16</sup> For convenience, experiments involving voltammetric determination of film surface coverage and examination of the  $\text{Fe(CN)}_6^{3-}$  response at the modified surface were carried out only at GC. All film thickness measurements were made with films grafted to PPF, where the low surface roughness of PPF gives more accurate measurements compared to GC.

Carboxylates were generated in the electrochemical cell by addition of methanolic  $[\text{Bu}_4\text{N}]\text{OH}$  to an acetonitrile solution containing the corresponding carboxylic acid. A less than stoichiometric amount of base was added to avoid the presence of unreacted hydroxide ion, which is electrochemically oxidized in the potential range of interest. In the absence of added base, solutions containing only the parent acid, methanol, and water (added to give the same concentrations as in the grafting solutions) showed no redox activity at the grafting potential.

UV spectroscopy was used to examine the neutralization reaction, and to establish the concentration of the carboxylate in grafting solutions. Aliquots of  $0.1 \text{ M TBAOH}$  in methanol were added to  $5.9 \text{ mM NMCOOH}$  in acetonitrile to generate 12 solutions containing  $\text{NM-COOH}$  and  $\text{NM-COO}^-$ , including solutions containing only the acid and only the carboxylate. The UV bands of  $\text{NM-COOH}$  and  $\text{NM-COO}^-$  in the mixed acetonitrile/methanol solvent system were measurably different and hence the ratio of  $\text{NM-COOH}$  to  $\text{NM-COO}^-$  in solution could be determined.<sup>17</sup>

Principal component regression analysis (singular value decomposition, SVD, and linear regression methods) of the measured spectra was completed. One significant advantage of SVD analysis<sup>18</sup> is that the outcome gives the number of species that are present. The SVD results for the region from  $247$  to  $330 \text{ nm}$  for all 12 samples gave two statistically significant spectra that form the basis for all of the measured data. Reducing the data set to those with excess added base gave only one significant spectrum (i.e., the spectrum of  $\text{NM-COO}^-$ ). This confirms that the reaction between  $\text{NM-COOH}$  and  $\text{TBAOH}$  gives  $\text{NM-COO}^-$  as the only product. Using the spectra of  $\text{NM-COOH}$  and  $\text{NM-COO}^-$  in the linear regression analysis of the spectrum of the (diluted) grafting solution showed that the solution contained  $0.7 \text{ mM NM-COOH}$  and  $5.2 \text{ mM NM-COO}^-$  (see the Supporting Information). The same amount of base was added to grafting solutions of  $\text{MeOB-COOH}$ , giving  $5.2 \text{ mM}$  solutions of the corresponding carboxylate.

**Characterization of As-Prepared Films of NM and MeOB.** GC and PPF surfaces were modified with NM and MeOB using the standard modification conditions.

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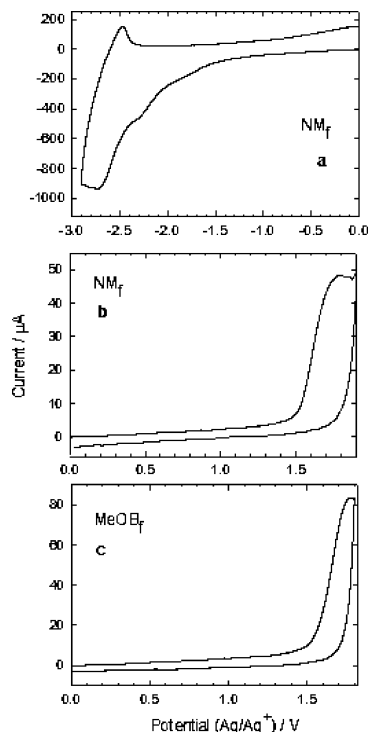
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(16) Grafting of 4-nitrobenzylcarboxylate ( $\text{NB-COO}^-$ ) was also investigated. Although the carboxylate was oxidized at the same potential at both surfaces, and AFM measurements revealed the formation of surface films on PPF, only the film grafted to GC exhibited the expected redox response associated with the nitrobenzyl group. This modifier was not used for further experiments.

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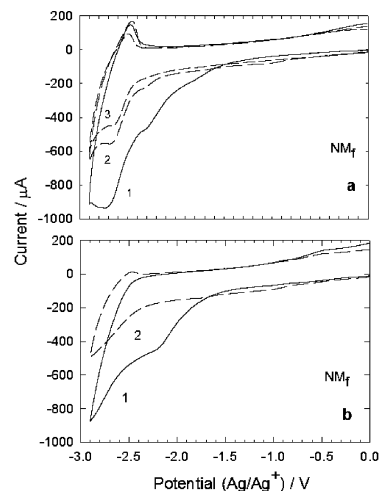




**Figure 2.** Cyclic voltammetry of (a and b)  $\text{NM}_f$ -modified GC and (c)  $\text{MeOB}_f$ -modified GC in 0.1 M  $[\text{Bu}_4\text{N}]\text{BF}_4$ -acetonitrile solution. (a) Scan rate =  $20 \text{ V s}^{-1}$ ; (b and c) Scan rate =  $200 \text{ mV s}^{-1}$ . All scans were recorded on freshly prepared films.

For convenience, grafted films will be referred to as “ $\text{NM}_f$ ” and “ $\text{MeOB}_f$ ”. Electrolysis times were varied from 30 to 300 s. Electrochemical and AFM measurements (see below) revealed no differences between films formed at 30 and 300 s suggesting that film growth is significantly complete within 30 s. Following the grafting step, the modifier solution was removed from the electrochemical cell, and after cleaning, a blank acetonitrile-electrolyte solution was added. Figure 2, panels a–c, shows voltammograms of GC modified with  $\text{NM}_f$  and  $\text{MeOB}_f$ . Scans to negative potentials were obtained at  $20 \text{ V s}^{-1}$  and to positive potentials at  $200 \text{ mV s}^{-1}$ . Each voltammogram was obtained with a freshly prepared film.

On scanning in the negative potential direction,  $\text{NM}_f$  exhibits a redox process centered near  $-2.6 \text{ V}$  (Figure 2a) which can be assigned to a one-electron transfer to surface-attached naphthyl groups.<sup>19</sup> This process is not chemically reversible at scan rates lower than  $20 \text{ V s}^{-1}$ .  $\text{NM}_f$  also undergoes an irreversible oxidation at  $1.8 \text{ V}$  (Figure 2b) that is close to the potential for irreversible oxidation of solution phase 1-methylnaphthalene. Also apparent in Figure 2a are two small prewaves associated with the  $\text{NM}_f/\text{NM}_f^-$  couple. Prewaves have been observed many times in the voltammetry of electroactive films, grafted using both the oxidation of arylcarboxylates and reduction of aryldiazoniums; however, the origin of these prewaves is unknown<sup>2,3,20–22</sup> and was not investigated in this work. For  $\text{MeOB}_f$ , an irreversible oxidation is seen in the voltammograms at  $1.7 \text{ V}$ , (Figure 2c). This peak is also



**Figure 3.** Consecutive scans ( $20 \text{ V s}^{-1}$ ), of  $\text{NM}_f$ -modified GC in 0.1 M  $[\text{Bu}_4\text{N}]\text{BF}_4$ -acetonitrile solution. (a) Film grafted for 300 s at  $E_{\text{app}} = E_{\text{pa}} + 100 \text{ mV}$ ; (b) Film grafted for 300 s at  $E_{\text{app}} = E_{\text{pa}} + 100 \text{ mV}$  followed by 120 s at  $E_{\text{app}} = E_{\text{pa}} + 500 \text{ mV}$ .

**Table 1.**  $\text{NM}_f$  Thickness (nm) and Surface Roughness (nm), before and after Sequential Potential Excursions in 0.1 M  $[\text{Bu}_4\text{N}]\text{BF}_4$ -Acetonitrile, for Films Prepared Using Standard Conditions

film	as prepared		after 2 scans to $-2.9 \text{ V}^a$		after grafting potential, <sup>b</sup> 300 s		after 1.9 V, 120 s	
	<i>d</i>	<i>R<sub>a</sub></i>	<i>d</i>	<i>R<sub>a</sub></i>	<i>d</i>	<i>R<sub>a</sub></i>	<i>d</i>	<i>R<sub>a</sub></i>
$\text{NM}_f$	2.1	0.22	1.6	0.61	2.4	0.35		
$\text{NM}_f$	3.1	0.69	2.1	0.99	2.9	0.77		
$\text{NM}_f$	2.9	0.33	2.2	0.49				
$\text{NM}_f$	2.0	0.26	1.1	0.53	3.0 <sup>c</sup>	0.48		
$\text{NM}_f$	2.0	0.30					2.4	0.36
$\text{NM}_f$	2.0	0.35						
$\text{NM}_f$	2.1	0.29						

<sup>a</sup> Scan rate =  $20 \text{ V s}^{-1}$ . <sup>b</sup>  $E_{\text{app}} = E_{\text{pa}} + 100 \text{ mV}$ ; potential applied after 2 scans to  $-2.9 \text{ V}$ . <sup>c</sup> Potential applied in the presence of  $5.2 \text{ mM NM-COO}^-$ .

present for solution-phase  $\text{MeOB-COOH}$  and provides evidence for surface modification.

The surface coverage of NM groups was estimated for a series of  $\text{NM}_f$  prepared on GC using electrolysis times between 60 and 300 s. Figure 3a shows that, on the first voltammetric scan, overlapping of the prepeaks with the main  $\text{NM}_f$  reduction peak gives a significantly larger area for the cathodic peaks than the corresponding anodic peak. However, the second and subsequent scans have approximately equal areas for the cathodic and anodic peaks, and hence, the area of the second scan cathodic peak was used to determine the absolute charge associated with the  $\text{NM}_f/\text{NM}_f^-$  redox reaction. Assuming a one-electron transfer,<sup>19</sup> the surface concentration,  $\Gamma$ , of electroactive  $\text{NM}_f$  groups was estimated to be  $\Gamma = (1.6 \pm 0.4) \times 10^{-10} \text{ mol cm}^{-2}$  (11 films analyzed). This value is in good agreement with that reported by Savéant and co-workers who determined a surface concentration of  $1.5 \times 10^{-10} \text{ mol cm}^{-2}$  for the same modifier grafted to GC.<sup>4</sup>

Thickness measurements of  $\text{NM}_f$  and  $\text{MeOB}_f$  were undertaken using AFM depth profiling. Tables 1 and 2 show the film thickness for seven  $\text{NM}_f$  and four  $\text{MeOB}_f$  samples prepared using standard conditions. The as-prepared films have thicknesses ranging between 2.0 and 3.1 nm for  $\text{NM}_f$  and 3.3 and 4.7 nm for  $\text{MeOB}_f$ . These films are clearly greater than one molecular layer thick. The lengths of the NM and MeOB modifiers from the carbon surface atom to the outermost atomic radii are 0.72 and

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**Table 2. MeOB<sub>f</sub> Thickness (nm) and Surface Roughness (nm), before and after Potential Excursions in 0.1 M [Bu<sub>4</sub>N]BF<sub>4</sub>-Acetonitrile, for Films Prepared Using Standard conditions**

film	as prepared		after -1.8 V, 300 s		after 2.0 V, 120 s	
	<i>d</i>	<i>R<sub>a</sub></i>	<i>d</i>	<i>R<sub>a</sub></i>	<i>d</i>	<i>R<sub>a</sub></i>
MeOB <sub>f</sub>	3.3	0.51	3.0	0.83		
MeOB <sub>f</sub>	4.7	0.57	3.3	1.1 <sup>a</sup>		
MeOB <sub>f</sub>	3.7	0.52			6.1	0.73
MeOB <sub>f</sub>	4.1	0.44			6.2	0.52

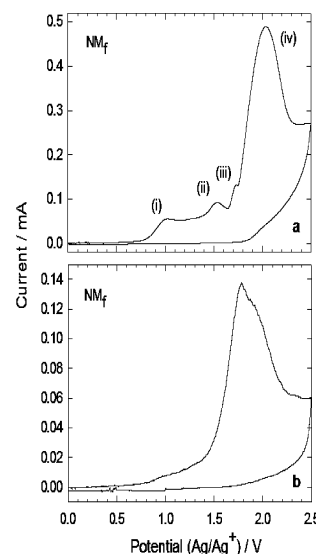
<sup>a</sup> Value obtained from arithmetic average of 10 areas.

0.82 nm respectively (based on optimization of the structures using Spartan). Assuming that the average molecular orientation of the film is perpendicular to the surface, the measured thickness for NM<sub>f</sub> is in the region of 3–4 molecular layers and for MeOB<sub>f</sub> 4–6 molecular layers; that is, the films are multilayered.

Formation of multilayers by oxidation of arylcarboxylates has not previously been reported but is well-established for films prepared by reduction of aryldiazoniums.<sup>3,9,10,13,23–25</sup> In this work, we have not investigated the mechanism by which multilayers may form but assume that the reaction must proceed via grafting of arylmethyl groups to the surface-attached film.

**Two-Step Grafting of NM<sub>f</sub> and Effect of Grafting Potential on NM<sub>f</sub> and MeOB<sub>f</sub>.** Beginning with an NM film that had reached its maximum thickness during the initial grafting step ( $E_{\text{app}} = E_{\text{pa}} + 100$  mV), incrementing  $E_{\text{app}}$  to a more positive potential was found to lead to further film growth. Figure 3 shows consecutive cyclic voltammograms of NM<sub>f</sub> in 0.1 M [Bu<sub>4</sub>N]BF<sub>4</sub>-acetonitrile solution. The scans of Figure 3a were obtained at a film grafted for 300 s at  $E_{\text{app}} = E_{\text{pa}} + 100$  mV, and those of Figure 3b were obtained at a film grafted for 300 s at  $E_{\text{app}} = E_{\text{pa}} + 100$  mV followed by 120 s at  $E_{\text{app}} = E_{\text{pa}} + 500$  mV. After the second grafting step, the first scan shows the peak associated with reduction of NM<sub>f</sub> merged with the solvent limit. The second scan shows reduction and oxidation of the NM<sub>f</sub> groups, although less well-defined than for single-grafted films. It is not possible to obtain a reliable estimate of the surface coverage from the voltammograms of the two-step grafted films; however, a visual inspection of Figure 3, panels a and b, indicates the peak areas, and hence surface concentrations, of electroactive groups, are not greatly different. On the other hand, film thickness measurements (Table 3) gave values ranging from 11.6 to 13.4 nm for the films formed by the two-step procedure, compared with 2.0–3.1 nm for films formed at  $E_{\text{app}} = E_{\text{pa}} + 100$  mV (Table 1). The apparent similarity of voltammetric peak areas for reduction of NM<sub>f</sub> groups for films with thicknesses ranging from 2 to 13 nm provides clear evidence that not all surface groups are electroactive (or survive the grafting process). Hence, voltammetrically determined surface coverage does not accurately represent the amount of material incorporated in the surface film; a similar conclusion has recently been reached for films prepared by diazonium reduction.<sup>10,25</sup>

To investigate the significance of the second grafting step, voltammetric scans were recorded over a wider potential range (0–2.5 V) in the NM-COO<sup>−</sup> modifier solution. In the first cycle, Figure 4a, there are four peaks labeled i–iv. Peak i is oxidation of the carboxylate, and

**Figure 4.** Cyclic voltammograms (200 mV s<sup>−1</sup>) at GC of 5.2 mM NM-COO<sup>−</sup> in 0.1 M [Bu<sub>4</sub>N]BF<sub>4</sub>-acetonitrile solution. (a) First scan and (b) second scan, with solution stirring between scans.**Table 3. Films Prepared by Two-Step Grafting and by Single Grafting at  $E_{\text{app}} > E_{\text{pa}} + 100$** 

film	$E_{\text{app}} = E_{\text{pa}} + x$		
	<i>x</i> , mV	time, s	<i>d</i> (nm)
NM <sub>f</sub>	100	300	12.5
	500	30	
NM <sub>f</sub>	100	300	11.6
	500	30	
NM <sub>f</sub>	100	300	13.4
	500	300	
NM <sub>f</sub>	100	300	13.3
	500	300	
NM <sub>f</sub>	300	300	5.0
NM <sub>f</sub>	500	300	21.6
NM <sub>f</sub>	500	300	17.4
MeOB <sub>f</sub>	500	300	14.3
MeOB <sub>f</sub>	800	300	16.7
MeOB <sub>f</sub>	800	300	18.4

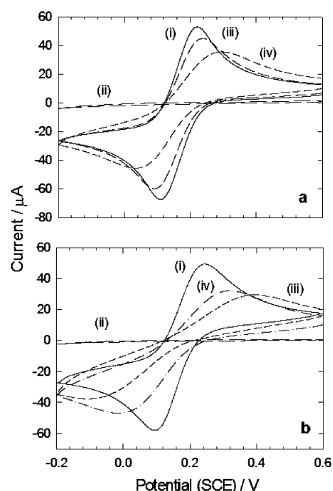
peak iii is assigned to oxidation of surface-attached NM groups. Peak iv appears at the potential where the naphthylmethyl-based oxidation of NM-COOH is observed (in the same medium, NM-COOH exhibits a single, broad irreversible oxidation peak at 2 V), and hence, peak iv is tentatively assigned to oxidation of NM-COO<sup>−</sup> and NM-COOH in solution. The peak current for this process is consistent with that assignment; however, the shape of the peak is not consistent with a simple diffusion-controlled process. We are unable to account for this observation but note that the oxidation process giving rise to peak (iv) does not appear to be involved in the grafting process, nor does it appear in the voltammetry of NM<sub>f</sub>. Peak ii corresponds to that previously assigned to oxidation of adsorbed carboxylate, and it is this process that was proposed to be responsible for the second (distinct) grafting step.<sup>4</sup> In the second cyclic scan, Figure 4b, only a broad oxidation peak is observed that is assumed to arise from merging of the processes giving peaks i–iv in the first scan.

The voltammograms of Figure 4 show significant anodic current at potentials positive of ~0.8 V, and it is not possible to associate the current at 1.3 V, for example, exclusively with peak i or ii. Under the conditions used here, the role of peak ii and the significance of the second grafting process are unclear. Single graftings (300 s)

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**Figure 5.** Cyclic voltammetry in 0.2 M KCl of (a) 3.7 mM  $\text{Fe}(\text{CN})_6^{3-}$  at (i) polished GC, (ii)  $\text{NM}_f$ -modified GC, (iii)  $\text{NM}_f$ -modified GC after 2 scans to  $-2.9$  V at  $20 \text{ V s}^{-1}$ , (iv)  $\text{NM}_f$  after 30 scans to  $-1.8$  V at  $200 \text{ mV s}^{-1}$  followed by holding the potential at  $-1.8$  V for 120 s; (b) 3.1 mM  $\text{Fe}(\text{CN})_6^{3-}$  at (i) a polished GC, (ii)  $\text{MeOBF}_f$ -modified GC (300 s), (iii)  $\text{MeOBF}_f$ -modified GC after 2 scans to  $-2.9$  V at  $20 \text{ V s}^{-1}$ , (iv)  $\text{MeOBF}_f$ -modified GC after holding the potential at  $-1.8$  V at for 300 s.

undertaken at higher potentials (300 and 500 mV more positive than  $E_{\text{pa}}$ ) generated films of similar thickness and properties to those prepared by two individual step grafting (Table 3). Experiments undertaken with  $\text{MeOBF}_f\text{-COO}^-$  gave qualitatively similar results (Table 3). Single step grafting at  $E_{\text{app}} = E_{\text{pa}} + 500 \text{ mV}$  and  $+800 \text{ mV}$  generated films with thicknesses of 14.3 and 17.4 nm, respectively, considerably thicker than the films prepared under standard (single step) conditions ( $\sim 4 \text{ nm}$ ). It is clear that the final film thickness increases with the potential used for grafting. Similar behavior has been reported for diazonium-grafted films and can be explained by the self-inhibiting nature of the films; that is, increasing over-potentials are required for film growth to greater thickness.<sup>24,26–28</sup>

**Film Changes Induced by Scans to Negative Potentials.** Changes in film thickness and  $\text{Fe}(\text{CN})_6^{3-}$  redox response at  $\text{NM}_f$  and  $\text{MeOBF}_f$  grafted surfaces were monitored to establish the effects of negative potential excursions on the properties of the films. Films were grafted to GC and PPF surfaces using standard conditions. After measuring the film thickness and surface roughness and recording the voltammetric response of  $\text{Fe}(\text{CN})_6^{3-}$ , the films were transferred to acetonitrile-electrolyte solution and treated to negative potential excursions. After treatment, the film thickness and surface roughness were again measured, and voltammograms of  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{NM-COO}^-$  were obtained at the treated surface.

Figure 5 shows voltammograms of  $\text{Fe}(\text{CN})_6^{3-}$  obtained at (a)  $\text{NM}_f$  and (b)  $\text{MeOBF}_f$  modified surfaces. Scan ii is at the as-prepared films, and scan iii at the grafted surfaces after two repeat scans between 0 and  $-2.9$  V at  $20 \text{ V s}^{-1}$ . Scan (i), obtained at bare GC, is shown for comparison. For both films, the apparent rate of electron transfer to  $\text{Fe}(\text{CN})_6^{3-}$  is greatly increased at the grafted surface after scans to  $-2.9$  V. When a grafted electrode which has been treated to negative potential scans is returned an acetonitrile solution of the carboxylate modifier, oxidation of

the carboxylate is observed, with a peak current 30% that obtained at a freshly polished electrode (data not shown). For  $\text{NM}_f$ , AFM measurements (Table 1) revealed a 30% reduction in film thickness and a significant increase in surface roughness after scanning to  $-2.9$  V. Topographical images of the films do not show any new or altered features. The effects of applying less negative potentials were also examined. Curve iv in Figure 5a is the voltammogram of  $\text{Fe}(\text{CN})_6^{3-}$  obtained at a  $\text{NM}_f$ -grafted electrode after 30 scans between 0 and  $-1.8$  V in acetonitrile-electrolyte solution at  $200 \text{ mV s}^{-1}$ , followed by 120 s at  $E_{\text{app}} = -1.8$  V. Curve iv in Figure 5b is the voltammogram of  $\text{Fe}(\text{CN})_6^{3-}$  obtained at  $\text{MeOBF}_f$  after applying a potential of  $-1.8$  V to the electrode in acetonitrile-electrolyte solution for 300 s. AFM monitoring of  $\text{MeOBF}_f$  showed that film thickness is decreased and roughness increased by treatment at  $-1.8$  V (Table 2). Evidently, similar changes are induced in the films when the less negative potential is applied but for a longer time. Hence, cycling through film redox couples is not a key factor underlying changes in film characteristics.

To probe the reversibility of film changes,  $\text{NM}_f$ -grafted surfaces that had been cycled twice to  $-2.9$  V and examined using electrochemistry and AFM were returned to 0.1 M  $[\text{Bu}_4\text{N}]\text{BF}_4$ -acetonitrile solution and the potential used for film preparation, i.e.,  $E_{\text{app}} = E_{\text{pa}} + 100 \text{ mV}$ , was reapplied for 300 s. After this treatment, the film thickness returned to the same value (within experimental uncertainty) as the as-prepared films and the surface roughness decreased to close to the value initially measured (Table 1). However, there was no further change to  $\text{Fe}(\text{CN})_6^{3-}$  voltammetry, i.e., the response was indistinguishable to that shown in Figure 5a, scan iii. Clearly, there is no significant cleavage of layers from the film during potential excursions to negative potentials. The changes in film thickness are consistent with potential-induced swelling and shrinking processes, similar to those we recently reported for nitroazobenzene films.<sup>10</sup> For those films, the thickness decreased during reduction in aqueous acid and then increased when more positive potentials were applied in 0.1 M  $[\text{Bu}_4\text{N}]\text{BF}_4$ -acetonitrile solution. The present results cannot be attributed to the effects of different solvents and, hence, must arise from potential-induced changes in film solvation or the concentration of electrolyte ions entrained within the films. Structural changes to the film, such as orientation and packing of groups, cannot be discounted as a contributing factor in the film height changes.

In another experiment,  $\text{NM}_f$ -grafted surfaces which had been cycled twice to  $-2.9$  V were returned to the grafting solution and grafted at  $E_{\text{app}} = E_{\text{pa}} + 100 \text{ mV}$  for 300 s. The film thickness was 2.0 nm after the initial grafting, 1.1 nm after negative potential excursions, and after re-grafting the measured thickness was 3.0 nm (Table 1). Considering the magnitude of potential-dependent film swelling and the experimental uncertainties, it is unclear whether there is further film growth on top of the existing film during the re-grafting step. On the other hand, there were dramatic changes in the  $\text{Fe}(\text{CN})_6^{3-}$  response after re-grafting; the voltammograms showed no features associated with  $\text{Fe}(\text{CN})_6^{3-}$  reduction and were indistinguishable to that shown in Figure 5a, scan i.

The observation that two potential scans to  $-2.9$  V significantly increases the apparent rate of electron transfer to  $\text{Fe}(\text{CN})_6^{3-}$  at all film-grafted surfaces indicates there are additional changes to the films that are unrelated to film shrinkage. Studies of films grafted via diazonium reduction have revealed similar changes in the apparent barrier properties of the films after application of suf-

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ficiently extreme potentials, and it is instructive to consider the proposed origin of those changes. Bélanger and D'Amours covalently grafted multilayer organic films to GC electrodes using the diazonium reduction method and examined the stability of the layers at various potentials in aqueous media.<sup>29</sup> Solution redox probes exhibited significantly increased apparent rates of electron transfer at film-modified surfaces after the films had been subjected to high positive and negative potentials. The authors proposed that desorption of noncovalently grafted modifiers accompanied hydrogen, oxygen, or chlorine evolution at very negative and positive potentials, leaving close to a monolayer of covalently attached modifier on the surface. A different explanation was advanced by McCreery and co-workers to account for an increase in the apparent rate of electron transfer for probe species at diazonium-generated monolayer films, after negative potential scans in acetonitrile solution. Those workers described a conductance switching mechanism in which potential-induced structural changes lead to increased rates of electron tunneling.<sup>30</sup> They proposed that electron injection from the GC substrate into monolayers of biphenyl and nitrobiphenyl may produce a quinoid structure in the film, giving a smaller HOMO–LUMO gap and higher electronic conductance.

In the present work, the reversibility of changes in film thickness is not consistent with large-scale loss of film during negative potential scans. However, modifiers may be desorbed to leave nanometer-sized bare areas. The lateral resolution of the AFM instrument is on the order of 10 nm, and hence, areas on this length-scale or smaller cannot be imaged successfully. The increase in surface roughness of films after scanning to  $-2.9$  V is not inconsistent with such changes in the film. When electron transfer occurs at a surface partially covered with an insulating film, with bare areas that are small and closely spaced, relative to the diffusion layer thickness, the standard heterogeneous rate constant for electron transfer appears to increase as surface coverage decreases.<sup>31</sup> The changes in electrochemical response of  $\text{Fe}(\text{CN})_6^{3-}$  at the modified electrodes, particularly at  $\text{NM}_f$  treated with repetitive scans to  $-1.8$  V, are in qualitative agreement with this model. Similarly, the restoration of the barrier properties of the film after re-grafting at the initial grafting potential can be accounted for by “filling in” of bare areas, created during negative potential excursions.

A mechanism involving electrostatically driven physisorption and desorption of modifiers can account for the creation of nanometer-sized holes in the films. During grafting of the layer, the positive charge of the electrode would promote simple physisorption of the carboxylate, in addition to the covalent coupling. Subsequent treatment of the film-coated electrode at negative potentials will have the opposite effect with electrostatic repulsions removing physisorbed material. The stability of the films during positive potential excursions is consistent with this mechanism (see below).

Considering conductance-switching as an alternative explanation for the effects of scans to negative potentials, this phenomenon cannot be definitively discounted, but several observations suggest it is unlikely for these films. Measurements of surface coverage and film thickness for  $\text{NM}_f$  provide convincing evidence that, at least for thick

films grafted by a two-step procedure, a large proportion of the film is nonelectroactive. This observation would be difficult to reconcile if the film itself was conducting. Further, after scans to negative potentials, applying a potential more positive than the peak for irreversible oxidation of the film does not change the  $\text{Fe}(\text{CN})_6^{3-}$  response; that is, there is no evidence for switching the conductivity off, even after irreversible oxidation of attached groups. Nevertheless, the origin of the effects seen after applying negative potentials remains unresolved, and further experiments are planned to address these questions.

**Film Changes Induced by Applying Positive Potentials.**  $\text{NM}_f$  and  $\text{MeOB}_f$  can be irreversibly oxidized between 1.7 and 1.8 V (Figure 2, panels b and d). In earlier work, it was reported that carboxylate-derived films can be erased by applying a potential a little beyond the irreversible oxidation peak for the film.<sup>4</sup> Thus, the effect of oxidation of  $\text{NM}_f$  and  $\text{MeOB}_f$  on film properties was examined in a series of experiments similar to those described above. After applying a potential of 1.9 V (120 s) and 2.0 V (300 s) to freshly prepared  $\text{NM}_f$  and  $\text{MeOB}_f$ , respectively, the voltammetric response of  $\text{Fe}(\text{CN})_6^{3-}$  was the same as that at the as-prepared films; that is, the apparent rate of electron transfer was very slow. Oxidation of  $\text{NM}-\text{COO}^-$  could not be detected when the  $\text{NM}_f$ -grafted electrode was replaced in modifier solution (5.2 mM  $\text{NM}-\text{COO}^-$  in 0.1 M  $[\text{Bu}_4\text{N}]\text{BF}_4$ -acetonitrile). When oxidized  $\text{NM}_f$  was scanned to  $-2.9$  V (scan rate =  $20 \text{ V s}^{-1}$ ) in acetonitrile solution, the reversible  $\text{NM}_f / \text{NM}_f^-$  couple was found to be absent. Oxidation of naphthyl groups in the presence of low concentrations of adventitious water is expected to yield naphthaquinyl derivatives;<sup>19</sup> however, voltammetry revealed no new redox features that could be attributed to such species. Oxidizing  $\text{NM}_f$  at 1.8 V led to the same changes, whereas 120 s at 1.7 V diminished but did not lead to complete loss of the  $\text{NM}_f / \text{NM}_f^-$  couple.

AFM measurements confirmed that the films remained at least largely intact after oxidative treatment. Table 1 shows that the thickness of an  $\text{NM}_f$  sample was unchanged (within experimental uncertainty) after 120 s at 1.9 V, whereas there was a significant increase in film thickness for  $\text{MeOB}_f$  after 300 s at 2.0 V (Table 2).

Under the conditions used in this work, there is no evidence that grafted films can be removed by irreversible oxidation of electroactive groups in the films. The observed swelling of  $\text{MeOB}_f$  after oxidative treatment is assumed to be related to the applied potential, as discussed above, rather than film redox chemistry. Although irreversible oxidation of aryl groups must change the molecular structure of the films to some extent, the grafted layers exhibit excellent stability to positive applied potentials in acetonitrile-electrolyte solutions.

## Conclusions

Multilayer organic films can be grafted to GC and PPF via oxidation of arylcarboxylates. As-prepared films dramatically reduce the apparent rate constant for electron transfer to solution species. Although the grafted groups can be electrochemically oxidized, the films maintain their integrity after treatment at 1.9 or 2.0 V in acetonitrile solution. This conclusion is based on film thickness measurements and the voltammetric response of solution species. On the other hand, voltammetric scans to potentials more negative than  $-1.8$  V in the same medium lead to significant changes in film properties. The apparent rate constant for electron transfer to solution species increases to close to that for a bare, polished electrode.

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There is a small decrease in film thickness, but for thin films, this can be reversed by application of positive potentials. Hence, films are not substantially removed by this treatment, and the results are consistent with desorption of physisorbed, rather than covalently coupled, modifier, leading to a film with nanometer-sized holes.

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**Supporting Information Available:** Voltammograms showing grafting of MeOB-COO<sup>-</sup> at GC and PPF, representative AFM images of a scratch through an NM film on PPF, and UV-vis spectra of NM-COOH, NM-COO<sup>-</sup>, and the solution used for grafting. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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