

Formation of Multilayers on Glassy Carbon Electrodes via the Reduction of Diazonium Salts

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The functionalization of carbon electrodes with aryl films can be achieved via the electrochemical reduction of the corresponding diazonium salt. We have previously shown that this deposition procedure will produce multilayer films on ordered graphite under certain conditions. We examine here the formation of multilayer films on glassy carbon (GC) electrodes by potential step electrolysis of diazonium salts for longer periods of time. The deposition of diethylaniline (DEA) is tracked with the use of infrared reflectance absorption spectroscopy and scanning force microscopy. DEA is continually deposited over a 30 min potential step and the film thickness approaches 20 nm. Phenylacetic acid and nitrophenyl films that are 15–25 nm thick can also be deposited in this way. We also find that, despite the presence of a relatively thick DEA film on a GC electrode, electron transfer to benchmark redox systems is not completely blocked. We attribute the compromised blocking to a high density of defects in the film structure.

Introduction

A significant amount of effort has been put forth recently to develop methods to covalently bind chemical groups to carbon electrodes.¹ A protocol initially examined by Pinson et al. has emerged and involves the grafting of functionalized aryl groups via the electrochemical reduction of diazonium salts.² The acceptance and application of this method by a number of researchers is primarily due to the ease with which diazonium salts bearing a wide range of functional groups can be synthesized, as well as the structure and stability of the resulting layer.³ Functionalized phenyl films have been utilized in a number of fundamental studies at carbon electrodes including investigations of electrochemical reactions of surface bound layers⁴ and long-range electron tunneling studies.⁵ Biological applications include their use as a platform to link biomolecules⁶ and as a layer to control protein adsorption.⁷ The reduction of diazonium salts has also been employed to modify silicon and metal surfaces.⁸ Considering the number of studies exploiting this attachment scheme thus far, it is clear that the use of this method to control the chemistry of carbon surfaces will become more widespread. Thus, a complete understanding of the deposition and structure of these films is required for their successful application.

The binding of aryl groups to carbon electrodes is likely a two-step process. The first step involves the electrochemical reduction of the diazonium salt to generate aryl radicals. This is followed by the reaction of the radicals with the carbon surface. It was initially proposed that a covalently bound monolayer was formed from this pro-

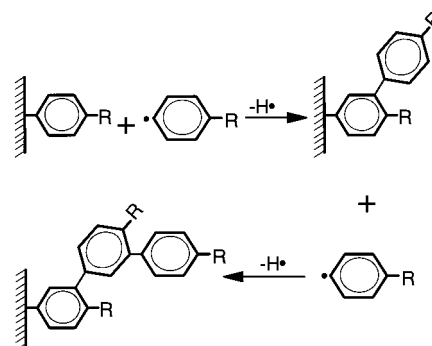


Figure 1. Schematic illustration of the predicted mode of multilayer formation via the attachment of aryl radicals in solution to the aryl moieties bound to the carbon surface. The hydride radicals produced in this mechanism can react with solvent or other aryl radicals.

cedure.² We have previously investigated the binding of diethylaniline (DEA) radicals to highly oriented pyrolytic graphite (HOPG) electrodes.⁹ Our results indicated that aryl *multilayers* can be formed by the reaction of an electrochemically generated radical with a surface-bound phenyl group as illustrated in Figure 1.

The results reported here extend our previous work by identifying the conditions necessary to produce phenyl multilayers on glassy carbon (GC) and probing the resulting films. The structure and thickness of aryl films bound to polished GC electrodes are characterized as a function of deposition time. We employ infrared reflectance absorption spectroscopy (IRRAS) and scanning force microscopy (SFM) to show that the reduction of diazonium salts will lead to the formation of multilayer films on GC under certain conditions; specifically, long periods of deposition time (10–30 min). The electrochemical barrier properties of phenyl multilayers are also explored to provide insights into the structural uniformity of the layers.

Experimental Section

Reagents. 4-Diazo-*N,N*-diethyl aniline tetrafluoroborate (DEA) and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) were

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(1) Downard, A. J. *Electroanalysis* 2000, 12, 1085–1096.

(2) Delamar, M.; Hitmi, R.; Pinson, J.; Saveant, J.-M. *J. Am. Chem. Soc.* 1992, 114, 5883–5884.

(3) Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Saveant, J.-M. *J. Am. Chem. Soc.* 1997, 119, 201–207.

(4) Saby, C.; Ortiz, B.; Champagne, G. Y.; Belanger, D. *Langmuir* 1997, 13, 6805–6813.

(5) Yang, H.-H.; McCreery, R. L. *Anal. Chem.* 1999, 71, 4081–4087.

(6) Bourdillon, C.; Delamar, M.; Demaille, C.; Hitmi, R.; Moiroux, J.; Pinson, J. *J. Electroanal. Chem.* 1992, 336, 113–123.

(7) Downard, A. J.; Roddick, A. D. *Electroanalysis* 1995, 7, 376–378.

(8) Henry de Villeneuve, C.; Pinson, J.; Ozanam, F.; Chazalviel, J. N.; Allongue, P. *Mater. Res. Soc. Symp. Proc.* 1997, 451, 185–195.

(9) Kariuki, J. K.; McDermott, M. T. *Langmuir* 1999, 15, 6534–6540.

purchased from Aldrich. 4-Diazonitrobenzene tetrafluoroborate (NB) was obtained from Sigma. 4-Diazophenylacetic acid tetrafluoroborate (PAA) was synthesized from 4-aminophenylacetic acid (Aldrich) according to a published procedure.¹⁰ Reagent grade acetonitrile (CH_3CN) was purchased from Fisher. The redox systems studied were as follows: $\text{Ru}(\text{NH}_3)_6^{3+}$ (aq) in 1 M KCl ($\text{pH} = 5.7$) and $\text{Fe}(\text{CN})_6^{4-}$ (aq) in 1 M KCl ($\text{pH} = 6.8$) were prepared at 1 mM concentrations from $\text{Ru}(\text{NH}_3)_3\text{Cl}_3$ (Strem Chemicals) and $\text{K}_4\text{Fe}(\text{CN})_6$ (BDH Chemicals), respectively. Eu^{3+} (aq) in 0.2 M HClO_4 ($\text{pH} = 1.3$) was prepared at 5 mM concentrations from $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Aldrich). All reagents were used as received. All solutions were purged with argon prior to use.

Electrode Preparation and Electrochemical Measurements. Square planar GC electrodes were cut from a larger, 3 mm thick plate of GC-20 (Tokai GC-20, Electrosynthesis Corp, NY). For SFM analysis, the electrodes measured $\sim 1 \times 1 \text{ cm}^2$. The GC electrodes used for IRRAS studies were $3 \times 6 \text{ cm}^2$ plates. The backside of these plates was coated with a thick ($\sim 1 \text{ mm}$) film of poly(ethylene)/poly(vinyl acetate) 60:40 (Aldrich) to block electroactivity. All GC electrodes were initially prepared by polishing with successive slurries of 1, 0.3, and $0.05 \mu\text{m}$ alumina in 18 M Ω deionized water on a polishing microcloth (Buehler). The electrodes were sonicated in deionized water for 5 min between polishing steps.

Regions of GC electrodes were blocked by spraying the surface with polystyrene (PS) (Aldrich, $M_w = 45\,000 \text{ D}$) dissolved in CCl_4 . A homemade nebulizer was used. After modification of these "patterned" GC electrodes, the PS mask was removed by rinsing with CCl_4 . Cyclic voltammetric measurements were performed in a standard three-electrode cell in which the electrode area of the GC was defined by an elastomeric O-ring (area = 0.5 cm^2). A platinum auxiliary electrode and a Ag/AgCl reference electrode were used. The scan rate was 100 mV/s for all voltammograms. The cell was connected to either a model CV-27 (Bioanalytical Systems Inc.) or Pine Instruments model AFCBP1 potentiostat. Data were recorded with either an Omnigraphic (Houston Instruments) X-Y recorder or with PineChem (version 2.5.2) software. Phenyl layers were deposited by potential-step electrolysis of the corresponding diazonium salt in CH_3CN (0.1 M Bu_4NBF_4) in the same cell as described above. The cyclic voltammetric peak potentials for each diazonium salt are as follows: DEA, $E_p = -0.75 \text{ V}$ vs Ag/AgCl; PAA, $E_p = -0.20 \text{ V}$; NB, $E_p = 0.2 \text{ V}$. Cyclic voltammetric peak separations (ΔE_p) were used to determine heterogeneous electron-transfer (ET) rate constants (k^0) via the method of Nicholson.¹¹

SFM Imaging. SFM images were obtained with a Nanoscope III Multimode microscope (Digital Instruments, Santa Barbara, CA). Both contact and tapping-mode SFM were employed. For tapping-mode imaging, Si cantilevers were oscillated at their resonance frequency ($\sim 200\text{--}300 \text{ kHz}$). The parameter in tapping-mode imaging that determines tapping force is the ratio of the set point (or imaging) amplitude, A_{sp} , to the oscillation amplitude, A_0 , where $r_{sp} = A_{sp}/A_0$.¹² All images shown here were collected with r_{sp} between 0.5 and 0.7 (moderate tapping force) at a scan rate of $\sim 1 \text{ Hz}$. Contact-mode imaging was performed with Si_3N_4 cantilevers; $k \sim 0.06 \text{ N/m}$ (Digital Instruments, NanoProbes) at normal forces of $< 10 \text{ nN}$. Images were flattened by the use of software and are otherwise shown unfiltered.

IRRAS Studies. IRRAS spectra were obtained on an ATI Mattson Infinity Series Fourier transform infrared (FTIR) spectrometer equipped with an external sample module and a liquid nitrogen cooled mercury-cadmium telluride (MCT) detector. The IR beam was incident on the GC surface at an angle of 60° with respect to the surface normal.¹³ Spectra were taken at 4 cm^{-1} resolution with an interferometer mirror speed of 50 kHz . Typically, 1000 scans were averaged to yield spectra with an acceptable signal-to-noise ratio. The interferograms were Fourier transformed using triangular apodization. Reference spectra were obtained on an unmodified polished GC electrode.

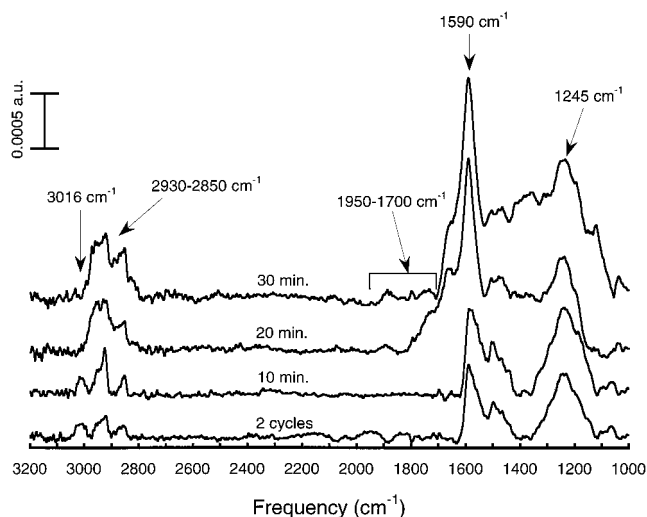


Figure 2. IRRAS spectra of DEA films formed on a GC electrode. The bottom spectrum corresponds to a film produced by 2 cycles in 5 mM DEA (0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$) between -0.1 and -0.9 V vs Ag/AgCl. The remaining spectra correspond to modification by electrolysis at -1.20 V vs Ag/AgCl for different lengths of time.

Results and Discussion

Binding of aryl films to carbon electrodes via the electrochemical reduction of the corresponding diazonium salt can be achieved through either potential cycling or a potential step.³ We have previously shown that films with greater than monolayer thickness can be deposited on ordered graphite.⁹ To investigate possible multilayer formation on GC, aryl films were deposited by potential-step electrolysis for various lengths of time. A deposition procedure commonly reported involves two or three potential cycles at 100 mV/s in 5 mM diazonium salt. We classify this procedure as producing monolayer coverage, and we use films deposited in this way as a starting point for comparison. In the sections below, we investigate the growth and thickness of aryl films deposited on GC electrodes for long periods of time.

Tracking Diethylaniline (DEA) Deposition with IRRAS. Figure 2 contains a series of spectra that tracks DEA film growth as a function of deposition time. Figure 2 contains a spectrum of a film formed on polished GC from two cycles in 5 mM 4-diazo-*N,N*-diethyl aniline tetrafluoroborate as well as spectra from electrodes held at -1.2 V vs Ag/AgCl for 10, 20, and 30 min. A band at $\sim 2300 \text{ cm}^{-1}$ due to the $\text{N}\equiv\text{N}$ stretch of the diazonium salt is absent in all spectra as is expected for films formed by a radical attachment mechanism. Assignments and intensities for the prominent bands are given in Table 1.¹⁴ Generally, the absorbance of each band increases with deposition time, an observation consistent with the continual growth of the DEA film over the time scale of the deposition.

Downard recently suggested that the applied overpotential is an important parameter in determining the structure of phenyl layers on GC.¹⁵ Our results along those lines agree with this claim. The potential used to deposit the films for Figure 2 (-1.2 V) represents an overpotential of -450 mV relative to the cyclic voltammetric peak for DEA deposition. Deposition of DEA at an overpotential of -150 mV (-0.9 V) resulted in IRRAS spectra with bands

(10) Dunker, M. F. W.; Starkey, E. B.; Jenkins, G. L. *J. Am. Chem. Soc.* **1936**, *58*, 2308–2309.

(11) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351–1355.

(12) Magonov, S. N.; Elings, V.; Whangbo, M.-H. *Surf. Sci.* **1997**, *375*, L385.

(13) Porter, M. D.; Bright, T. B.; Allara, D. A. *Anal. Chem.* **1986**, *58*, 2461–2465.

(14) Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Introduction to Organic Spectroscopy*; MacMillan Publishing Co.: New York, 1987.

(15) Downard, A. J. *Langmuir* **2000**, *16*, 9680–9682.

Table 1. Band Assignments and Intensities from the IRRAS Spectra of DEA Films on GC in Figure 2

	assignment				
	aromatic C–H stretch 3016 cm ⁻¹	aliphatic C–H stretch 2930–2850 cm ⁻¹	aromatic C=C stretch 1590 cm ⁻¹	aromatic C=C stretch 1480–1500 cm ⁻¹	phenyl-N stretch 1245 cm ⁻¹
	absorbance $\times 10^{-3}$				
2 cycles	0.13	0.19	0.66	0.32	0.56
10 min	0.15	0.40	0.76	0.48	0.76
20 min		0.46	1.7	0.66	0.81
30 min		0.57	2.0	0.77	1.2

of roughly equal intensity for 10, 20, and 30 min lengths of deposition times. We find that a deposition overpotential of -300 mV is required to observe continued film growth with IRRAS. The higher driving force required is consistent with the self-inhibiting nature of these films.³

Several details from Figure 2 and Table 1 support the mechanism illustrated in Figure 1. A band due to aromatic C–H stretching is observed at 3016 cm^{-1} for films formed for short periods of time. However, films formed for longer periods of time do not exhibit this peak. In this experiment, transition dipoles with a component perpendicular to the GC surface will be preferentially excited due to the IRRAS surface selection rule. The transition dipole of the aromatic C–H bonds in the first monolayer of DEA molecules is likely to contain a major component normal to the surface. The disappearance of the 3016 cm^{-1} band is consistent with these C–H bonds being replaced by phenyl–phenyl bonds during multilayer formation. The second and third layer of phenyl groups may be in an orientation that lessens the perpendicular component of the phenyl C–H transition dipole to a degree below our detection limit.

The spectra for the films formed for longer periods of time (20 and 30 min) contain several weak bands between 1950 and 1700 cm^{-1} . The positions of these bands (1890 , 1800 , and 1730 cm^{-1}) are consistent with combination and the overtone bands expected for multisubstituted aromatic rings. We note that bands in the region between 900 and 700 cm^{-1} , characteristic of substituted aromatic compounds patterns, are not observed due to the low-frequency cutoff of our MCT-A detector at $\sim 800\text{ cm}^{-1}$. We also note the appearance of a shoulder at $\sim 1660\text{ cm}^{-1}$ on the ring deformation band. We attribute this shoulder to the deformation of multiply substituted rings that comprise the structure of the multilayer. Thus, spectral details from Figure 2 in both the C–H and C=C stretching regions are consistent with the multilayer attachment mechanism depicted in Figure 1.

SFM Measurement of DEA Film Thickness. DEA film thickness can also be tracked with SFM by masking regions of polished GC electrodes with a PS film. Following deposition of DEA, the PS mask is dissolved in CCl_4 . The resulting surface contained regions modified with DEA adjacent to unmodified polished GC. An example of such an electrode is shown in the $30 \times 30\text{ }\mu\text{m}^2$ topographic SFM image in Figure 3A. The regions of higher topography in Figure 3A correspond to the unmasked regions during deposition of DEA. A higher magnification image of the boundary between a modified and an unmodified region is shown in Figure 3B. The thickness measured at the boundaries is plotted vs deposition time in Figure 4. Three conclusions can be drawn from Figure 4. The first is that DEA films thicker than a monolayer can be deposited on GC by employing long periods of electrolysis time. Second, the thickness of the films can be controlled by deposition time. And third, DEA films continue to grow throughout a 30 min deposition. This indicates that aryl radicals are being generated through a 20 nm thick film. We believe

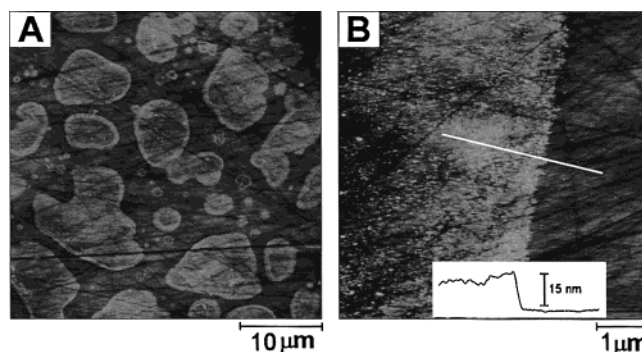


Figure 3. (A) $30 \times 30\text{ }\mu\text{m}^2$ topographic SFM image of a GC electrode modified with DEA through a PS mask. The mask was dissolved in CCl_4 before the image was collected. This procedure produces a surface containing regions modified with DEA (lighter contrast) adjacent to unmodified polished GC (darker contrast). (B) A higher magnification image and cross-sectional profile of the boundary between a modified and unmodified region. The z scale is 40 nm in both images.

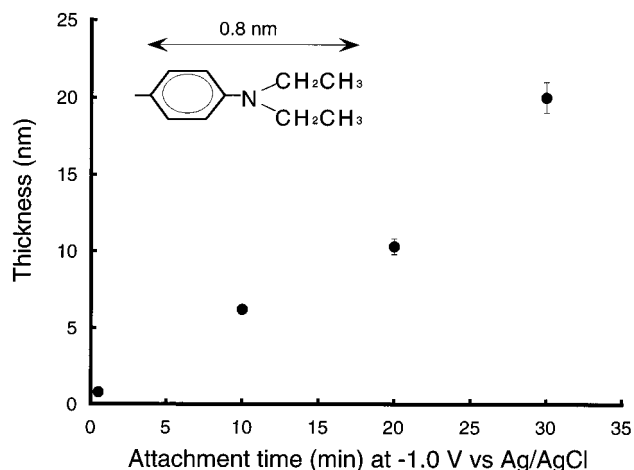


Figure 4. Plot of SFM-measured film thickness against attachment time for DEA films formed on GC via electrolysis of 5 mM DDEA ($0.1\text{ M Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$) at -1.2 V .

that this is due to the defective nature of DEA films formed for long periods of time (vide infra).

We have also examined the thickness of films formed for other precursors. For example, 4-diazophenylacetic acid fluoroborate was used to produce films of PAA on a PS-masked GC surface. Figure 5A is a $20 \times 20\text{ }\mu\text{m}^2$ contact-mode topographic image of a PAA film deposited at -1.0 V for 30 min. The PS mask was removed by dissolving in CCl_4 . The cross-sectional profile in the inset of Figure 5A illustrates that a 30 min deposition yields a 25 nm thick PAA film. Figure 5B is a $15 \times 15\text{ }\mu\text{m}^2$ image of a NB film formed at a PS-masked electrode with a thickness of 15 nm . Thus, multilayer aryl films with a range of functional groups can be deposited on GC by reducing the corresponding diazonium salt for time scales greater than 10 min.

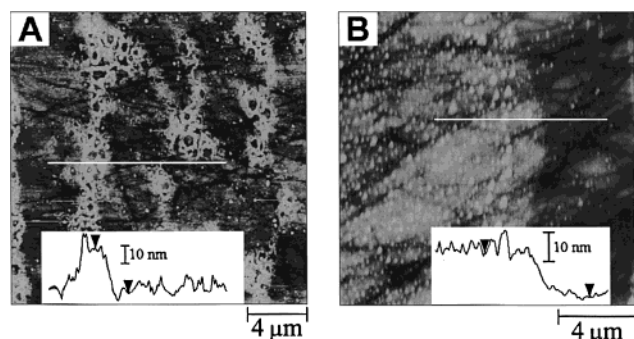


Figure 5. (A) $20 \times 20 \mu\text{m}^2$ SFM image of a PAA film deposited on a PS-masked GC electrode at -1.0 V for 30 min. For PAA deposition, the cyclic voltammetric peak potential is -0.2 V vs Ag/AgCl. The cross-sectional profile corresponds to the line scan through the image. (B) $15 \times 15 \mu\text{m}^2$ SFM image of a NB film deposited on a PS-masked GC electrode at -0.5 V for 30 min. For NB deposition, the cyclic voltammetric peak potential is 0.2 V vs Ag/AgCl. The cross-sectional profile corresponds to the line scan through the image. The PS mask was dissolved in CCl_4 before the collection of both images. The z scale is 40 nm for both images.

Table 2. Cyclic Voltammetric Peak Separations for Three Redox Systems at DEA-Modified GC Electrodes

depn time	ΔE_p (mV) for $\nu = 100$ mV/s			SFM measured thickness (nm)
	$\text{Fe}(\text{CN})_6^{3-/4-}$	$\text{Ru}(\text{NH}_3)_6^{3+/2+}$	$\text{Eu}^{3+/2+}$	
polished GC	78 ± 10	80 ± 9	203 ± 21	0
2 cycles	115 ± 6	88 ± 3	408 ± 15	0.8 ± 0.1
10 min	170 ± 5	110 ± 4	>1200	6.2 ± 0.4
20 min	200 ± 9	115 ± 14	>1200	10.3 ± 0.9
30 min	230 ± 5	120 ± 4	>1200	20.0 ± 0.6

Electrochemical Properties of Thick DEA Films.

The blocking ability of DEA films on GC was assessed by cyclic voltammetry of several redox systems. The $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple is a common benchmark system with an (ET) rate that is very sensitive to the state of the GC surface.¹⁶ The ET rate of $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ is relatively insensitive to the GC surface state,¹⁶ and $\text{Eu}^{2+/3+}$ is a system dependent on the presence of surface carbonyl groups.¹⁷ Table 2 lists the cyclic voltammetric peak separation (ΔE_p) for the three systems on polished GC and DEA-modified GC. Also listed is the SFM-determined DEA film thickness. All three systems show an increase in ΔE_p as the deposition time increases, consistent with the IRRAS and SFM results that indicate DEA deposition continues with time. For $\text{Eu}^{2+/3+}$, any deposition more extensive than two cycles completely blocks ET indicating that the attachment of DEA quickly and completely obstructs surface carbonyl sites. However, the other two redox systems do not become completely blocked, even at 20 nm thick DEA films. In fact, the heterogeneous ET rate constants (k°) for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ are much higher than expected for the thicker DEA films. Electrostatic interactions with a partially protonated DEA layer can be discounted because both a positively and negatively charged redox species display similar behavior. For example, we do not observe any significant change in peak current of the cyclic voltammograms for the three redox systems. Hence, there does not appear to be any significant preconcentration of the redox species in the grafted film.

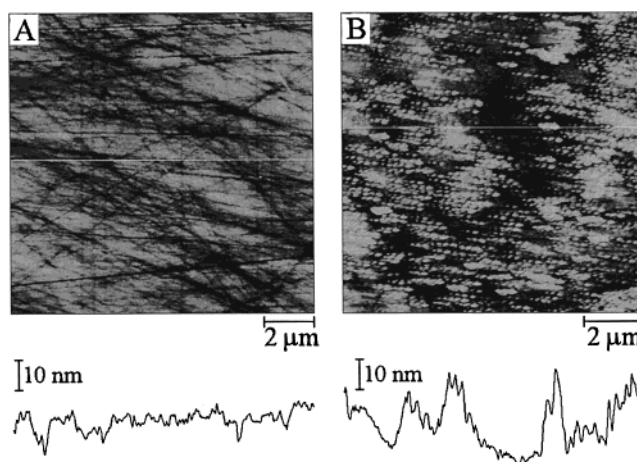


Figure 6. (A) $12 \times 12 \mu\text{m}^2$ topographic image of a polished GC electrode. Analysis of the cross-sectional profile yields rms = 1.3 nm and maximum height = 5.2 nm. (B) $10 \times 10 \mu\text{m}^2$ topographic image of a GC electrode modified with a DEA film for 30 min. Analysis of the cross-sectional profile yields rms = 9.0 nm and maximum height = 16.0 nm. The z scale is 20 nm for both images.

From long-range ET studies at metal/monolayer interfaces, the apparent (k°_{app}) should exponentially decrease with the thickness of the layer, d , via

$$k^\circ_{\text{app}} = k^\circ \exp(-\beta d) \quad (1)$$

where β is the tunneling parameter and k° is the heterogeneous rate constant. Yang and McCreery determined a β of 0.20 \AA^{-1} for through-bond tunneling at functionalized aryl monolayers on GC.⁵ Assuming a similar tunneling mechanism and using k° of 0.012 cm/s for $\text{Fe}(\text{CN})_6^{3-/4-}$ at a polished GC surface, a 20 nm thick DEA film should yield a k°_{app} of $\sim 10^{-20}$ cm/s. The ΔE_p of 230 mV for $\text{Fe}(\text{CN})_6^{3-/4-}$ on the 20 nm thick DEA film (30 min electrolysis), however, corresponds to a k° of 7.3×10^{-4} cm/s. It is clear that ET pathways other than through-bond tunneling are operative at DEA multilayers.

An alternative ET pathway to through-bond tunneling in thin organic films on electrodes is through defects. We investigated the possibility of this mechanism by probing the uniformity of DEA multilayers on GC with SFM. Figure 6 compares the topography of a polished GC electrode (Figure 6A) with that of a 30 min DEA film (Figure 6B). Scratches resulting from the polishing procedure characterize the topography of Figure 6A. The DEA film topography in Figure 6B is composed of groupings of clusterlike structures with a diameter of 100 – 200 nm. Visually, the overall morphology of the DEA film appears less uniform than the original polished GC surface, and it is apparent that the topography in Figure 6B is not governed by the underlying GC substrate. Quantitative descriptions of the topography are obtained from the analysis of cross-sectional profiles. The profile of Figure 6B exhibits a root mean square (rms) value of 9.0 nm and a maximum deviation of 19 nm in the z direction. Similar results are obtained from roughness analysis of the image as a whole. Thus, while the average thickness of a DEA film deposited for 30 min is 20 nm, the local topography varies over a length scale comparable with the thickness.

Studies have shown that molecular scale defects can govern ET at organic monolayers adsorbed to metal

(16) Chen, P.; McCreery, R. L. *Anal. Chem.* **1996**, *68*, 3958–3965.

(17) McDermott, C. A.; Kneten, K. R.; McCreery, R. L. *J. Electrochem. Soc.* **1993**, *140*, 2593–2599.

electrodes.¹⁸ Figure 6B shows that the structure of DEA films deposited for longer periods of time exhibits non-uniformity at micron length scales. It is likely that a significant number of molecular scale defects exist in the film as well. The electrochemical barrier properties of these films will be severely compromised by these defects. The low level of electrochemical blocking for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ listed in Table 2 is consistent with a defective film structure. In addition, the prolonged film growth shown in Figure 3 implies that aryl radicals are continually generated. If the radicals are generated at defects, it is surprising that the defects do not "heal" during the 30 min time scale. We speculate that the defect sites may be efficient ET sites for radical production but may not be favorable sites for binding and that more favorable binding sites exist at the film terminus.

It is important, at this point, to compare our results for the blocking capabilities of DEA films with those reported for phenyl films bearing other functionalities. Saby et al. observed complete blocking of $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ at a nitrophenyl film formed for 4 min.⁴ Downard¹⁵ recently reported that an unsubstituted phenyl film, formed for 10 min at sufficient overpotential, also completely blocks $\text{Ru}(\text{NH}_3)_6^{2+/3+}$. A direct comparison of these and our observations is difficult because of differences in materials and the electrode preparation procedure from laboratory to laboratory. For example, Saby et al. and Downard used GC-10 from different manufacturers (Saby, AIMCORE; Downard, Atomergic), while we use Tokai GC-20. It is known that the processing temperature (GC-10, 1000 °C; GC-20, 2000 °C) greatly influences the electrochemical reactivity of GC.¹⁹ Despite these procedural inconsistencies, we believe that the results reported by Saby et al. and Downard are consistent with multilayer formation. A monolayer of phenyl or nitrophenyl groups (0.59 and 0.68 nm thick, respectively³) would not be expected to completely block $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ ET. For example, using

our observed $k^0 = 0.01$ cm/s for $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ at polished GC and $\beta = 0.2$ Å⁻¹, k_{app}^0 at a complete nitrophenyl monolayer would be 0.0026 cm/s. This translates into a ΔE_p of 153 mV for $\nu = 200$ mV/s.

Chen and McCreery noted a slight increase in ΔE_p (12 mV at 20 V/s) for $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ relative to a polished GC surface, at a nitrophenyl film formed under monolayer-producing conditions.¹⁶ Considering all of these results combined, it appears that the blocking capabilities and thus the structure of functionalized phenyl films on carbon electrodes depend on both the precursor molecule and the deposition procedure. Our continuing studies, to be reported separately, indicate that the thickness and blocking ability of multilayer films prepared from para-substituted diazonium salts depend on the functional group.

Conclusions

We report here that multilayer films of substituted phenyl moieties can be formed by the electrolysis of diazonium salts. We find that DEA films continue to grow throughout a 30 min electrolysis at an overpotential of -250 mV. SFM images show that this procedure can produce DEA films with an average thickness of 20 nm. We also show that 15–25 nm thick PAA and NB films can also be produced by 30 min electrolysis. The DEA films produced with long periods of electrolysis time do not display ET-blocking abilities that are characteristic of their thickness. SFM analysis reveals that the topography of these films is nonuniform implying a defective structure. This defective structure compromises the blocking ability of the films.

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(18) Finklea, H. O.; Avery, S.; Lynch, M. *Langmuir* **1987**, *3*, 409–413.

(19) McCreery, R. L. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1991; Vol. 17, pp 221–375.