

Sterically Controlled Functionalization of Carbon Surfaces with $-C_6H_4CH_2X$ ($X = OSO_2Me$ or N_3) Groups for Surface Attachment of Redox-Active Molecules

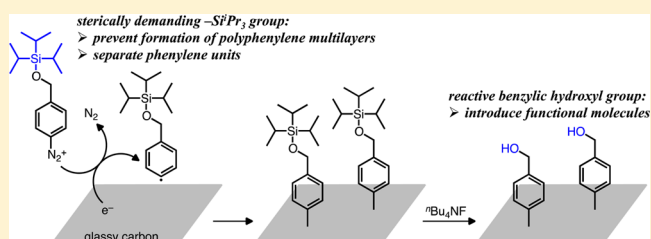
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Supporting Information

ABSTRACT: Glassy carbon electrodes were modified by electrochemical reduction of a diazonium molecule (${}^iPr_3SiOCH_2C_6H_4N_2^+BF_4^-$) featuring a triisopropylsilyl-protected benzylic hydroxyl group. This electrochemical process introduced a monolayer of ${}^iPr_3SiOCH_2C_6H_4-$ groups onto the surface of the electrode. The bulky $-Si^iPr_3$ protecting group not only prevents the uncontrolled growth of structurally ill-defined and electronically blocking polyphenylene multilayers, but also separates the phenyl groups in the monolayer. Thus, the void spaces between these aryl units should allow a better accommodation of sizable molecules. Removal of the $-Si^iPr_3$ protecting groups by nBu_4NF exposed the reactive benzylic hydroxyl functionalities that can undergo further transformations to anchor functional molecules. As an example, redox-active ferrocene molecules were grafted onto the modified electrode via a sequence of mesylation, azidation, and copper-catalyzed [3 + 2] cycloaddition reactions. The presence of ferrocenyl groups on the surface was confirmed by X-ray photoelectron spectroscopic and electrochemical studies. The resulting ferrocene-modified glassy carbon electrode exhibits cyclic voltammograms typical of surface-bound redox active species and remarkable electrochemical stability in an acidic aqueous environment.



INTRODUCTION

Chemical functionalization of stable, conductive, carbon-based electrodes with functional molecules¹ produces molecule–carbon interfaces for applications in molecular electronics,² sensing,³ and catalysis.⁴ Although a variety of strategies^{5–9} have been developed to modify carbon surfaces with well-defined layers of molecules, further improvements that allow more precise control of the structure, morphology, thickness, and density of such layers are highly desired. For example, a widely used strategy pioneered by Pinson and Savéant^{8–10} involves electrochemical reduction of diazonium molecules using a carbon-based electrode to generate aryl radicals, which react with the proximate carbon surface to form stable molecule–surface bonds (C–C bonds combined with some azo linkages of the C–N=N–C type^{11,12}). The in situ generated aryl radicals at the electrode–solution interface can react further with the aryl groups that have already added to the surface, resulting in the uncontrolled growth of a thick, structurally ill-defined, polyphenylene-based molecular layer on the surface^{10,13} (referred to as multilayers to emphasize the presence of more than one phenylene monomeric unit along the direction perpendicular to the electrode). To limit the formation of such multilayers, improvements to the original method have been introduced, such as modification of the deposition conditions,^{13,14} structural changes to the diazonium

molecules,^{15–20} use of an ionic liquid as the solvent,²¹ and addition of a radical scavenger.²²

In addition to optimization of known surface modifications, there is also interest in expansion of the types of reactive functionalities that can be introduced onto the surface. Studies in the latter area also promote the use of chemically modified carbon electrodes for various applications. For example, a rapidly growing interest in energy-related catalysis entails covalent attachment of molecular proton or carbon dioxide reduction catalysts onto carbon electrodes,^{23–26} to provide assemblies that provide opportunities for fundamental mechanistic understanding, or integration into practical devices. The general strategy for addressing this challenging task involves modification of both the carbon electrode surface and the catalyst with groups that can react^{23–25} or interact²⁶ to establish stable surface–catalyst linkages.

In this paper we describe modification of glassy carbon (GC) electrodes with a layer of chemically well-defined $-C_6H_4CH_2X$ ($X = OSO_2Me$ or N_3) groups. This functionalization is initiated by electroreduction of a triisopropylsilyl ($-Si^iPr_3$)-protected diazonium molecule ${}^iPr_3SiOCH_2C_6H_4N_2^+BF_4^-$. The sterically

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demanding $-\text{Si}^i\text{Pr}_3$ group is then removed to expose a benzylic hydroxyl group in a controlled fashion. Reactions of this hydroxyl group may then be used to introduce mesylate ($-\text{OSO}_2\text{Me}$) and azide ($-\text{N}_3$) functionalities, which should be useful for grafting a variety of functional molecules (e.g., catalysts) onto the electrode surface.

EXPERIMENTAL SECTION

General Considerations. All chemicals were purchased from commercial suppliers and used as received unless otherwise noted. The diazonium salt **1**,²⁷ the aniline 4-(((triisopropylsilyloxy)methyl)aniline,²⁸ and the ligand tris(benzyltriazolylmethyl)amine²⁹ were prepared according to literature procedures. All air-sensitive manipulations were conducted under an inert atmosphere using standard Schlenk techniques or in a nitrogen-filled drybox. ¹H NMR spectra were recorded on a Bruker Ascend 500 MHz spectrometer at room temperature and referenced to the residual protonated solvent. FT-IR spectra were collected on a Bruker VERTEX 70 spectrometer.

Synthesis of the Diazonium Salt 2. The compound 4-(((triisopropylsilyloxy)methyl)aniline (0.398 g, 1.42 mmol) was dissolved in MeCN (2 mL) to form a clear solution. In a nitrogen-filled drybox, NOBF_4 (0.166 g, 1.42 mmol) was dissolved/dispersed in MeCN (5 mL) in a Schlenk flask, which was brought out of the drybox and cooled to -78°C in a dry ice/acetone bath. To this frozen solution of NOBF_4 was added the solution of 4-(((triisopropylsilyloxy)methyl)aniline. The reaction mixture was removed from the dry ice/acetone bath, and it began to slowly thaw. The reaction mixture was allowed to warm to 0°C with stirring, and was stirred for an additional 1.5 h in an ice/water bath. The reaction mixture was concentrated to dryness under reduced pressure. The residual material was extracted with CH_2Cl_2 (5 mL \times 3), and the combined extracts were filtered through Celite into another Schlenk flask under a nitrogen atmosphere. Volatile fractions of the filtrate were removed under reduced pressure. The residual material was triturated with Et_2O to afford a heterogeneous mixture. The dark brown filtrate was removed by cannula filtration under a nitrogen atmosphere. The remaining yellow solid was washed with Et_2O (5 mL \times 3) and hexanes (5 mL), and dried under vacuum to afford 0.191 g (36%) of **2** as a yellow solid. ¹H NMR (CD_3CN , 500 MHz): δ 8.41 (d, $J = 9.0$ Hz, 2H), 7.91 (d, $J = 9.0$ Hz, 2H), 5.10 (s, 2H, CH_2O), 1.23 (septet, $J = 7.4$ Hz, 3H, CHMe_2), 1.10 (d, $J = 7.4$ Hz, 18H, CHMe_2). IR (KBr): $\nu_{\text{NN}} = 2266\text{ cm}^{-1}$. This compound is moderately hygroscopic in air, and slowly decomposes in solution at room temperature, as indicated by the changes observed in the ¹H NMR spectrum after 1 day. This compound is, however, stable as a solid for at least 2 weeks when stored in a -30°C refrigerator.

Electrochemistry. Electrochemical studies, including electrochemical modifications of glassy carbon electrodes and scans of the cyclic voltammograms of the modified electrodes, were conducted on a BioLogic SP-200 potentiostat in a standard three-electrode setup. The bare and modified glassy carbon electrodes were used as the working electrode, and a platinum wire was used as the counter electrode. A Ag/Ag^+ (0.01 M of AgNO_3 in MeCN with 0.1 M of $^t\text{Bu}_4\text{NPF}_6$) reference electrode was used for nonaqueous measurements, and a Ag/AgCl (in 3 M of NaCl) reference electrode was used for aqueous measurements. For reductive scans during which the dissolved oxygen can be reduced, the electrolyte solution was purged with nitrogen for 3 min before measurements, and measurements were performed with a constant stream of nitrogen flowing through the headspace of the electrochemical cell.

Modifications of Glassy Carbon Electrodes to Prepare 1-GC and 2-GC. 1-GC and 2-GC were prepared by repeated potential cycling (3 cycles for 1-GC and 5 cycles for 2-GC) between 0.3 and -1.1 V (vs Ag/Ag^+) in solutions of the diazonium salts (1 mM) **1** and **2**, respectively, in MeCN with the electrolyte $^t\text{Bu}_4\text{NPF}_6$ (0.1 M), at a scan rate of 100 mV/s. The modified glassy carbon electrodes were rinsed with MeCN, sonicated in MeCN for 5 min, and dried under a constant flow of nitrogen. Glassy carbon disks with a diameter of 5 mm and a thickness of 4 mm that can be easily mounted to the XPS

sample holder were used and modified for better collections of X-ray photoelectron spectra.

3-GC. Triisopropylsilyl groups on 2-GC were removed by immersing 2-GC in a solution of $^t\text{Bu}_4\text{NF}$ (0.2 M) in THF for 2 h at room temperature under a nitrogen atmosphere. The resulting glassy carbon electrode 3-GC was washed with THF, sonicated in THF for 5 min, and dried under a constant flow of nitrogen.

4-GC. Under a nitrogen atmosphere, methanesulfonic anhydride (20 mg) was dissolved in a mixture of CH_2Cl_2 (10 mL) and NEt_3 (0.5 mL). 3-GC was immersed in this solution cooled in an ice/water bath for 3 h to convert hydroxyl groups on 3-GC to mesylate groups on 4-GC. 4-GC was rinsed with CH_2Cl_2 , sonicated in CH_2Cl_2 for 5 min, and dried under a constant flow of nitrogen.

5-GC. 4-GC was immersed in a hot (80°C), saturated solution of NaN_3 in DMF for 12 h to produce the azide-functionalized glassy carbon electrode 5-GC, which was rinsed with MeOH, sonicated in MeOH for 5 min, and dried under a constant flow of nitrogen.

6-GC. 5-GC was immersed in a solution of ethynylferrocene (2 mM), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.4 mM), sodium ascorbate (8 mM), and tris(benzyltriazolylmethyl)amine (0.4 mM) in DMSO (20 mL) and H_2O (10 mL) under a nitrogen atmosphere for 16 h. The resulting glassy carbon electrode 6-GC was rinsed with H_2O , sonicated in H_2O for 5 min, sonicated in MeOH for 5 min, and dried under a constant flow of nitrogen. A slight contamination of the surface by copper was observed.

Surface Coverage of Ferrocenyl Groups on 6-GC. The surface coverage Γ (mol/cm^2) of the ferrocenyl groups on 6-GC was determined from the cyclic voltammograms of 6-GC shown in Figure 4a, using eq 1.

$$\Gamma = \frac{Q_{\text{wave}}}{e \times n \times N_A \times A_{\text{electrode}}} \quad (1)$$

Q_{wave} (in coulomb (C)) is obtained by integrating the area of a background-subtracted anodic or cathodic wave, n is the number of electrons involved in the electrode reaction and is equal to 1 for the ferrocene/ferrocenium redox pair, the elementary charge $e = 1.60 \times 10^{-19}$ C, Avogadro's number $N_A = 6.02 \times 10^{23}$, and the surface area of a 5 mm glassy carbon disk of $A_{\text{electrode}} = 0.20\text{ cm}^2$.

The surface coverage of ferrocene on 6-GC was reported as an average value obtained from a set of 10 parallel calculations using one of the anodic and cathodic peaks of the cyclic voltammograms measured at scan rates of 100, 200, 300, 400, and 500 mV/s.

X-ray Photoelectron Spectroscopy (XPS). XPS measurements were performed using a Kratos Axis Ultra DLD system. The measurements were carried out at a base pressure of $<1 \times 10^{-8}$ Torr. A monochromatic $\text{Al K}\alpha$ (1486.6 eV) X-ray source and a takeoff angle of $\theta = 0^\circ$ (defined as the angle between the vector along which photoelectrons are collected by the detector and the surface normal) were used for the measurements. Survey scans between binding energies of 1200 and 0 eV were taken with a pass energy of 160 eV. High-resolution scans between narrow binding energy windows were taken with a pass energy of 20 eV. Spectral analysis was performed using the Casa XPS processing software. A Shirley background was subtracted from each high-resolution spectrum prior to data fitting.

The atomic ratios of the elements on the electrode surface to the carbon element from the electrode (shown in Table S1 in the Supporting Information) were calculated from the areas of the high-resolution XPS spectra of these elements, which were normalized by the sensitivity factors of the corresponding elements (C 1s, 1.0; Si 2p, 0.82; S 2p, 1.68; N 1s, 1.80; Fe 2p, 16.4). The C 1s peak at a binding energy of 284.5 eV, among the deconvoluted peaks in the C 1s XPS spectrum, was used as a measure of the carbon from the electrode, assuming a negligible contribution of the carbon in the surface layer to this peak.

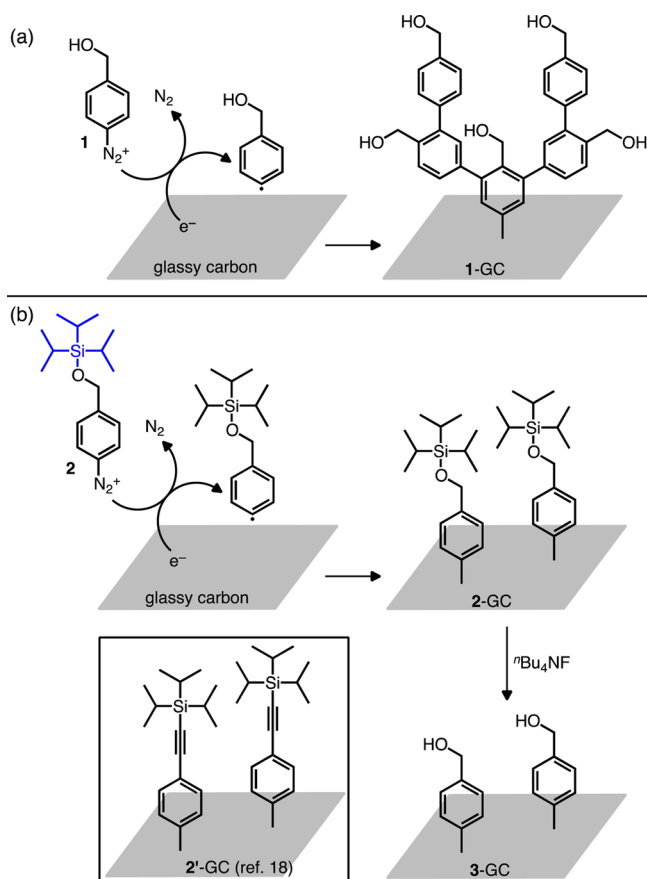
Computational Methods. The geometry of the molecule $^i\text{Pr}_3\text{SiOCH}_2\text{C}_6\text{H}_5$, as a complete molecular model of the phenyl groups ($^i\text{Pr}_3\text{SiOCH}_2\text{C}_6\text{H}_4-$) on 2-GC, was optimized by density functional theory (DFT) calculations using B3LYP functional^{30–32}

with the 6-31G** basis set^{33,34} for all atoms. The calculation was performed with the GAMESS(US) package.³⁵

RESULTS AND DISCUSSION

The diazonium salt **1** (Scheme 1a) was chosen for introduction of reactive benzylic hydroxyl groups onto the surface for

Scheme 1. Formation of (a) Thick, Dendritic Polyphenylene Multilayers and (b) Thin, Isolated Phenyl Monolayer on Surfaces of Glassy Carbon Electrodes, by Electrochemical Reduction of the Diazonium Salts (a) **1** and (b) **2**^a



^a2'-GC was previously prepared¹⁸ and is shown here as a comparison to 2-GC. Deprotection of 2-GC by ^tBu₄NF to produce 3-GC is also shown in part b.

subsequent on-surface reactions. As expected, electrochemical reduction of **1** using a glassy carbon electrode resulted in the formation of polyphenylene multilayers derived from **1** on the electrode surface (Scheme 1a). As shown in Figure S2a (Supporting Information), the cyclic voltammogram of **1** measured with a glassy carbon electrode exhibits an irreversible wave at -0.74 V (vs Fc/Fc⁺), arising from reduction of **1** to N₂ and the phenyl radical (Scheme 1a). This wave is not present in subsequent scans (Supporting Information Figure S2a), indicating passivation of the electrode by a molecular layer formed on the surface during the first scan. Using such a modified glassy carbon electrode, we could not observe a reversible oxidative wave for a solution of ferrocene in MeCN with the electrolyte ^tBu₄NPF₆ (Figure 1a). These observations are consistent with the formation of polyphenylene multilayers (Scheme 1a) on the electrode (**1**-GC). This thick layer effectively blocks electron transfer between the electrode and

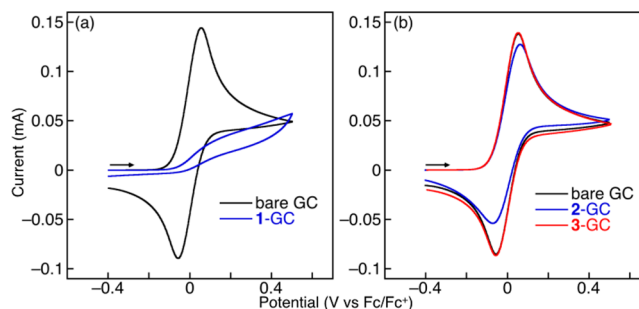


Figure 1. Cyclic voltammograms of ferrocene (4.8 mM) in MeCN with the electrolyte ^tBu₄NPF₆ (0.1 M) at a scan rate of 100 mV/s, measured with (a) the bare GC and 1-GC electrodes and (b) the bare GC, 2-GC, and 3-GC electrodes.

redox-active molecules in solution,^{10,13,36} and would also likely slow, if not entirely inhibit, electron transfer between the electrode and any redox-active molecules attached to the electrode through this layer. Furthermore, reaction of a molecule with the distribution of functionalities associated with the dendritic polyphenylene units on 1-GC would likely yield a carbon surface with a poorly defined molecular-level structure.

A strategy to suppress the growth of multilayers makes use of bulky diazonium salts to prevent bond-forming reactions between the in situ generated radicals and the aryl groups already grafted to the surface,^{16–20} by way of steric repulsion between substituents on the reagents. Sterically demanding groups can be introduced onto an aryl diazonium salt, either permanently as substituents on the phenyl ring¹⁶ or temporarily as cleavable groups that may also be utilized to protect functionalities in the molecule from reactions with aryl radicals.^{17–20} The size of the diazonium salt **1** can be readily expanded by protection of the benzylic hydroxyl group with a triisopropylsilyl (–Si^tPr₃) group, which has been shown to prevent the formation of polyphenylene multilayers in a related system (2'-GC, Scheme 1b).¹⁸ Removal of the –Si^tPr₃ group may then expose the hydroxyl group, opening up the opportunity for subsequent chemical modifications on the electrode surface.

The diazonium molecule **2**, a bulky version of **1**, was prepared by oxidation of the corresponding triisopropylsilyl-protected aniline (^tPr₃SiOCH₂C₆H₄NH₂) with NOBF₄ (Scheme S1 and Figure S1, Supporting Information). The conventional preparation of diazonium molecules using sodium or isopentyl nitrite under acidic conditions resulted in cleavage of the –Si^tPr₃ group (Supporting Information Scheme S1). The cyclic voltammogram of **2** exhibits an irreversible wave at -0.79 V (vs Fc/Fc⁺; Supporting Information Figure S2b), but gradually becomes featureless in subsequent scans. This spectral change is similar to that of **1**, thus suggesting modification of the glassy carbon electrode with a 2-derived molecular layer (2-GC). Whereas a surface elemental analysis of 1-GC is less informative because of the background carbon, nitrogen, and oxygen signals from the glassy carbon electrode, the XPS spectrum of 2-GC (Figure 2a and Supporting Information Figure S3) exhibits the Si 2s and Si 2p signals, assigned to the –Si^tPr₃ groups on the surface. These silyl groups can be removed to afford 3-GC by treatment with ^tBu₄NF (Scheme 1b). The successful deprotection was confirmed by the absence of silicon-related signals in the XPS spectra of 3-GC (Figure 2a and Supporting Information Figure S3). The increased atomic

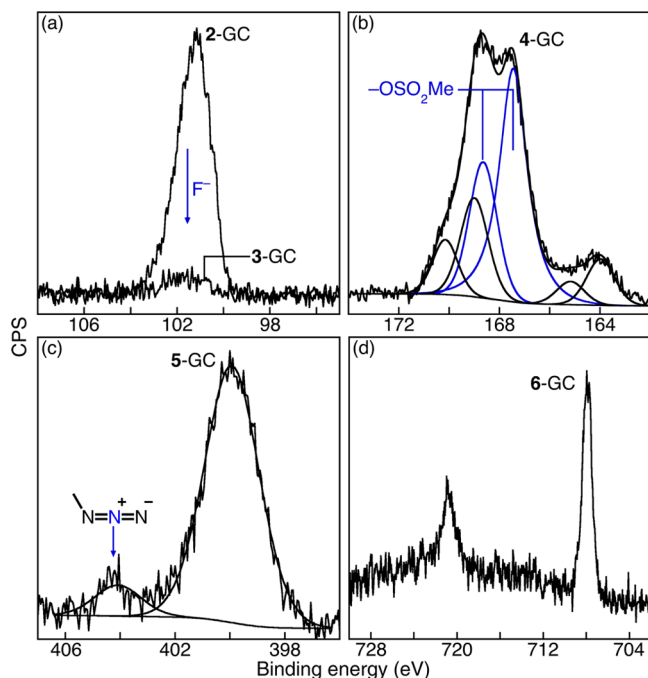


Figure 2. Selected high-resolution XPS spectra of the modified glassy carbon electrodes: (a) Si 2p spectra of 2-GC and 3-GC, (b) S 2p spectrum of 4-GC, (c) N 1s spectrum of 5-GC, and (d) Fe 2p spectrum of 6-GC.

ratios of the nitrogen element on the surface to the carbon element from the electrode (N/C) for 2-GC and 3-GC, relative to that for a bare glassy carbon electrode (Table S1, Supporting Information), suggest incorporation of some azo-type (C=N=N—C) molecule–surface bonds (*vide supra*) onto 2-GC and 3-GC, accompanying the formation of C—C bonds.^{11,12}

The cyclic voltammogram of ferrocene measured with the 2-GC electrode, in marked contrast to that obtained with 1-GC and exhibiting no waves (Figure 1a), contains a quasireversible wave with clearly discernible anodic and cathodic peaks (Figure 1b). This wave is distorted from that obtained with a bare glassy carbon electrode, by having slightly decreased anodic and cathodic peak currents and increased peak-to-peak separation (Figure 1b). Nevertheless, the positive electrochemical response given by 2-GC is consistent with a minimal growth of *multilayers* on the surface. Note that the oxidation of ferrocene was completely inhibited on 2'-GC, which was believed to be modified with *bilayers* of linear, rigid ${}^i\text{Pr}_3\text{SiC}\equiv\text{CC}_6\text{H}_4-$ groups.¹⁸ Thus, a thin, phenyl (${}^i\text{Pr}_3\text{SiOCH}_2\text{C}_6\text{H}_4-$) *monolayer*, across which electrons can tunnel between the electrode and ferrocene at a reasonable rate, was likely formed on 2-GC (Scheme 1b). Removal of the flexible $-\text{Si}^i\text{Pr}_3$ groups on 2-GC further decreases the thickness of this monolayer, and hence decreases the barrier for electron tunneling. As a consequence, the cyclic voltammogram of ferrocene measured with 3-GC is now superimposable with that measured with a bare glassy carbon electrode (Figure 1b).

In addition to thickness, the molecular packing in an electrode-confined layer also governs the blocking property of the functionalized electrode. The latter aspects of the molecular layers on 2-GC and 3-GC were investigated using the inner-sphere probe complex potassium ferrocyanide $\text{K}_4\text{Fe}(\text{CN})_6$. The heterogeneous electron-transfer reaction of an inner-sphere redox-active molecule on a modified electrode requires

permeation of the molecule through pinholes in the molecular layer to the electrode surface, and can therefore help elucidate the presence and size of void spaces in the layer.^{36,37} As shown in Figure 3, the reversible wave associated with the $\text{Fe}(\text{CN})_6^{4-}/$

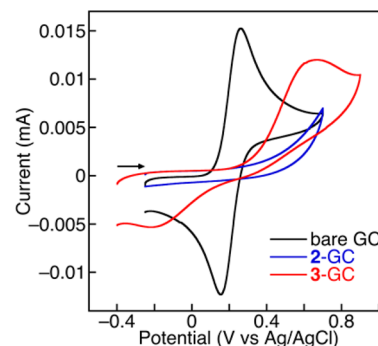
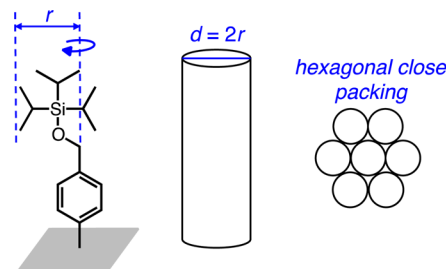


Figure 3. Cyclic voltammograms of potassium ferrocyanide (1.0 mM) in an aqueous solution of KCl (0.1 M) at a scan rate of 100 mV/s, measured with the bare GC, 2-GC, and 3-GC electrodes.

$\text{Fe}(\text{CN})_6^{3-}$ using a bare glassy carbon electrode is not observed with 2-GC, implying that 2-GC is free of pinholes. In contrast, the voltammogram measured with 3-GC displays a broad, quasireversible wave with significantly increased peak-to-peak separation and decreased anodic and cathodic peak currents (Figure 3). This “S-shaped” electrochemical signal is a consequence of diffusion of redox species to or from the electrode through void spaces on 3-GC.³⁸ These vacancies were likely created by removal of the bulky $-\text{Si}^i\text{Pr}_3$ groups from 2-GC, and should have a molecular dimension larger than the size of ferrocyanide (the hydrated diameter of which is ca. 6.0 \AA).³⁶ This notion is also supported by the reported, similar voltammogram of $\text{Fe}(\text{CN})_6^{4-}$ acquired with a glassy carbon electrode prepared by electroreduction of an analogous, silyl-protected diazonium salt (${}^i\text{Pr}_3\text{SiC}\equiv\text{CC}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$ or $\text{Et}_3\text{SiC}\equiv\text{CC}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$) followed by deprotection of the silyl group.¹⁹

The molecular packing of phenyl groups on 2-GC and 3-GC, controlled mainly by the size of the $-\text{Si}^i\text{Pr}_3$ protecting group, was further studied with the assistance of DFT calculations. As shown in Scheme 2, the area occupied by a ${}^i\text{Pr}_3\text{SiOCH}_2\text{C}_6\text{H}_4-$ fragment may be approximated by considering rotation of the $-\text{OSi}^i\text{Pr}_3$ group along the phenyl— CH_2 bond, which defines a cylindrical space on the surface. Geometry optimization of ${}^i\text{Pr}_3\text{SiOCH}_2\text{C}_6\text{H}_5$, as a molecular model of this fragment, gives a diameter of the cylinder of $d = 11 \text{ \AA}$. Assuming a hexagonal close packing of these cylinders on an absolutely flat surface,

Scheme 2. Simplified Illustration of the Molecular Packing of ${}^i\text{Pr}_3\text{SiOCH}_2\text{C}_6\text{H}_4-$ Fragments on the Surface with the Sterically Allowed Maximum Packing Density



Scheme 3. Surface Reactions on 3-GC to Attach Ferrocene onto the Glassy Carbon Electrode

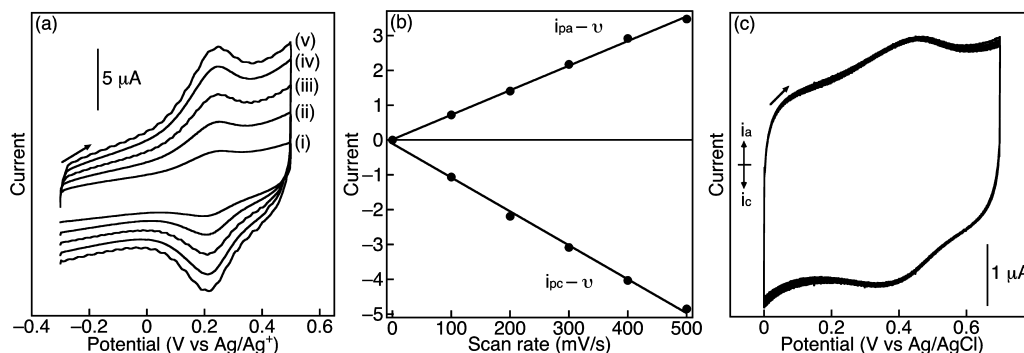
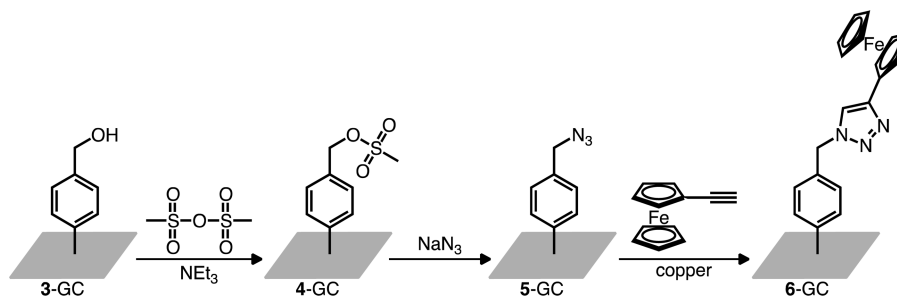


Figure 4. (a) Cyclic voltammograms of 6-GC in MeCN with the electrolyte Bu_4NPF_6 (0.1 M) at scan rates of (i) 100, (ii) 200, (iii) 300, (iv) 400, and (v) 500 mV/s; the anodic and cathodic peak currents versus scan rate plots were shown in part b. (c) Repetitive potential cycling (200 scans, scan rate = 200 mV/s) of 6-GC in a H_2SO_4 (1.0 M) aqueous solution.

the maximum surface coverage was estimated to be 1.6×10^{-10} mol/cm², using eq 2,³⁹ where d is in Å.

$$\Gamma \approx \frac{1.92 \times 10^{-8}}{d^2} \quad (2)$$

Considering a typical roughness factor (1.5–2.5⁴⁰) for a polished glassy carbon surface, the surface coverage of the phenyl groups on 2-GC and 3-GC should be approximately 3.0×10^{-10} mol/cm².

The modified glassy carbon electrode 3-GC provides reactive benzylic hydroxyl groups on the surface, and therefore serves as an ideal platform for attachment of different functional molecules. As an example, a procedure was developed for anchoring redox-active ferrocene molecules onto 3-GC. As shown in Scheme 3, the first step involves a reaction of 3-GC with methanesulfonyl anhydride to convert the hydroxyl group to the mesylate group. This reaction produced 4-GC exhibiting the expected S 2s and S 2p signals in its XPS spectrum (Supporting Information Figure S3). Deconvolution of the broad S 2p core-level spectrum, however, reveals three sets of spin-orbit-coupled doublets (Figure 2b). The largest doublet at binding energies of 168.6 (2p_{1/2}) and 167.4 (2p_{3/2}) eV is consistent with the sulfur being sulfonate ($-\text{OSO}_2\text{R}$).⁴¹ The other two doublets at binding energies of 170.2, 169.0 eV and 165.2, 164.0 eV should be assigned to sulfur species in higher and lower oxidation states, respectively, as compared to the oxidation state of sulfur in sulfonate. These sulfur species might be generated from the X-ray radiation-induced disproportionation of the sulfonate to sulfate (SO_4^{2-}) and sulfoxide ($-\text{SO}-$).⁴²

The mesylate group on 4-GC, as a good leaving group, can undergo various S_N2 reactions. For example, a reaction with sodium azide introduced azide groups onto the surface to furnish 5-GC (Scheme 3). With this transformation, the

intensities of the S 2s and S 2p signals shown in the XPS spectrum of 4-GC decrease significantly in that of 5-GC (Supporting Information Figure S3). Moreover, the N 1s XPS spectrum of 5-GC exhibits a N 1s signal at a binding energy of 404.1 eV (Figure 2c), characteristic of the central electron-deficient nitrogen atom in the azide group.⁵ The signal for the two terminal nitrogen atoms of the azide group overlaps with signals from nitrogen in the electrode and the azo linkages, as a broad peak at a binding energy of 400.0 eV. After a copper-catalyzed [3 + 2] cycloaddition with ethynylferrocene, the characteristic N 1s peak at a binding energy of 404.1 eV is absent (Supporting Information Figure S4), demonstrating conversion of the azide groups on 5-GC in this cycloaddition reaction (Scheme 3). Introduction of ferrocene molecules onto 6-GC was supported by the XPS spectrum containing a Fe 2p signal at binding energies of 720.8 (2p_{1/2}) and 707.9 (2p_{3/2}) eV (Figure 2d). The yield of the overall heterogeneous surface transformation from 2-GC to 6-GC, estimated by comparing the Si/C ratio in 2-GC to the Fe/C ratio in 6-GC, is ca. 20%.

Electrochemical behavior of the surface-attached, redox-active ferrocenyl groups on 6-GC was also investigated. As shown in Figure 4a, the cyclic voltammogram of the 6-GC electrode, in a MeCN solution containing only the electrolyte Bu_4NPF_6 , exhibits a reversible, symmetrical oxidative wave, with a small peak-to-peak separation (for example, $\Delta E_p = E_{p,a} - E_{p,c} = 14$ mV at 100 mV/s). Both the anodic ($i_{p,a}$) and cathodic ($i_{p,c}$) peak currents are linearly dependent on the scan rates (Figure 4b). These observations are characteristic of the electrochemical behavior of surface-bound species. Note that the ΔE_p values remain essentially constant at the different scan rates indicated in Figure 4a, which implies an electron transfer rate at least faster than the scan rate of 500 mV/s.⁴³ Calculated from the area of the electrochemical wave, the coverage of ferrocenyl groups on 6-GC is ca. 8.0×10^{-11} mol/cm²,

approximately 25% of that of the phenyl units on 2-GC (3×10^{-10} mol/cm², *vide supra*), which suggests a ~25% yield of the overall conversion from 2-GC to 6-GC. This value is in good agreement with the yield (20%, *vide supra*) determined from the XPS spectra of 2-GC and 6-GC.

To test the electrochemical stability of 6-GC under aqueous conditions, a repetitive cycling of the 6-GC electrode within a 0–0.70 V (vs Ag/AgCl) was conducted in an aqueous solution of H₂SO₄ (1.0 M). As shown in Figure 4c, the cyclic voltammogram of 6-GC in the acidic solution exhibits 0.42 V (vs Ag/AgCl). This potential is similar to those reported for other ferrocene-modified electrodes.^{5,43} The fairly large capacitive current is presumably due to the disorder of the molecular layer on 6-GC.⁴⁴ Notably, negligible changes in the peak current density and potential of the electrochemical wave were found during 200 scans, which demonstrates good stability for 6-GC in an acidic aqueous environment.

CONCLUSIONS

The results described above highlight the potentially great influence of the structure of diazonium molecules on the structure, thickness, and molecular packing of surface-confined layers, deposited by electroreduction of these diazonium molecules. As shown here, the bulky, freely rotating $-\text{Si}^i\text{Pr}_3$ substituent on 2 effectively suppresses the uncontrolled growth of polyphenylene multilayers, and also separates phenyl units on the surface of 2-GC. The modified electrodes 3-GC, 4-GC, and 5-GC possess the phenyl group organization derived from their precursor 2-GC, and feature reactive hydroxyl, mesylate, and azide groups, respectively, for attachment of a wide range of molecules. The ample space about individual phenyl units on these electrodes, created by removal of the $-\text{Si}^i\text{Pr}_3$ groups, should be advantageous for anchoring sizable molecular species on the surface. A low coverage of molecules on the surface is anticipated, but these methods should be transferable to different forms of carbon with a larger surface area, *e.g.*, carbon nanotubes.

ASSOCIATED CONTENT

Supporting Information

Synthetic scheme, ¹H NMR and FT-IR spectra of the diazonium molecule 2, cyclic voltammograms of 1 and 2, survey and high-resolution XPS spectra of the bare and modified glassy carbon electrodes, a table of the atomic ratios of the modified electrodes determined from their XPS spectra, and a table of xyz coordinates for the optimized geometry of C₆H₅CH₂OSiⁱPr₃. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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