Functionalization of Glassy Carbon Electrodes with Metal-Based Species

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Received December 7, 2004. Revised Manuscript Received February 23, 2005

Substituted phenyl-modified glassy carbon electrodes were functionalized with metal/metal oxide/metal hydroxide and inorganic compounds. More specifically, the glassy carbon electrodes were first functionalized with 4-sulfonate phenyl and *N*,*N*-diethylaniline groups by electrochemical reduction of the corresponding diazonium salt in nonaqueous media. Second, the functionalized electrodes were soaked in a solution containing the metallic ions and treated with a reductant ($NaBH_4$) in the case of the formation of the Ru- and Cu-based species or with redox species (Fe(II) or $Fe(CN)_6^{3-}$) in the case of Prussian Blue. The resulting $Cu/Cu(OH)_2$ and $RuO_2/Ru(OH)_2$-modified glassy carbon electrodes displayed electrochemical activity for selected reaction such as nitrate reduction and hydrogen peroxide oxidation, respectively. X-ray photoelectron spectroscopy was also used to confirm the presence of the metallic species and Prussian Blue at the electrode surfaces. The curve-fitting of the appropriate core level spectra was useful to distinguish between the oxide/hydroxide species and the metallic state. The atomic concentration of the metal-based species at the surface of the modified glassy carbon electrodes, estimated from the XPS data, ranged between 0.2 and 1 at. %, which corresponds to surface concentration of 0.55×10^{-10}, 0.87×10^{-10}, and 0.21×10^{-10} mol/cm^2 for Cu, Ru, and Prussian Blue, respectively. These relatively low surface concentrations and the scanning electron micrographs of copper- or ruthenium-modified glassy carbon electrode suggest that very small particles are present at the electrode surface. On the other hand, the presence of submicrometric particles was found to be evident for Prussian Blue formed on the modified surface. In the case of the copper-modified electrode, stripping voltammetry was used to estimate the amount of metallic copper, which was found to be in reasonably good agreement with the XPS data.

Introduction

The formation of metallic particles or aggregates at carbon and electrode surfaces has been recently studied because the resulting assemblies could be potentially used as catalysts and/or electrocatalysts.[1−14] Several studies have dealt with the use of templates to control the formation of these technologically important metallic particles. By carefully selecting the terminal functional group of the template, it was shown that it is possible to load metallic ions or adsorb metallic colloidal particles at the surface or in this template. Thereafter, the use of a suitable reducing agent afforded the reduction of the metal ions and the formation of the metallic species.

A wide variety of templates has been investigated and consisted of self-assembled monolayers (SAMs), dendrimers, multilayered polyelectrolyte films, and polymers bearing terminal groups such as carboxylic acid, amine, thiol, and

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10.1021/cm047871i CCC: $30.25
Published on Web 04/08/2005

hydroxyl.[5−14] As a representative example, the SAMs were formed on a metallic surface such as gold by immersion in an amine-terminated thiol solution.[6] Immersion of the latter in a solution of carboxylic acid derivatized silver colloidal particles afforded the assembly of metallic particles on the SAM surface by electrostatic interaction. On the other hand, transition metal ions such as Cu^{2+}, Ag^{+}, Pt^{2+}, Pd^{2+}, Ru^{3+}, and Ni^{2+} were loaded into the interior of polyamidoamine dendrimers and reduced in situ to yield metal particles encapsulated in the dendrimers.[9,10] The resulting materials were then cast onto an electrode for further investigation. In addition, SAMs were also used as template for the formation of nonmetallic materials (e.g., oxides, etc.).[13]

On the other hand, the number of similar studies on carbon electrodes is much more limited primarily because the procedures for their derivatization with such templates are rather scarce. A first example involved metal formation at highly oriented pyrolytic graphite (HOPG) or glassy carbon electrodes that usually rely on defects as nucleation sites.[14] Another procedure for the controlled derivatization of carbon surfaces is based on the electrochemical reduction of a substituted diazonium salt according to the following:[15−24]

$$\text{Carbon} + {}^{+}N_2C_6H_4R + e^{-} \rightarrow \text{Carbon}/C_6H_4R$$

where R= COOH, NO_2, H, $N(C_2H_5)_2$, CF_3, etc. This procedure can yield a coverage of the carbon surface which can be close to monolayer coverage in appropriate experimental conditions. In addition, we have recently shown that substituted phenyl functionalized carbon electrodes are useful for the recovery of metallic ions (Cu^{2+}, Pb^{2+}, Cd^{2+}) present in aqueous solutions.[21] The recovery yield of such modified electrodes was much higher than that of unmodified electrodes due to the presence of the surface functional groups.

As a natural extension of these previous studies, in the present work we have used these functionalized carbon electrodes as templates for various metallic and redox active species. Along those lines, we have recently reported our preliminary results on copper-modified carbon electrodes,[22] and in related studies, platinum,[23a] silver,[23b] palladium,[23c] and gold[24] nanoparticles have been electrochemically generated on a 4-aminophenyl[23] and 4-mercaptobenzene[24] modified carbon substrate. In the present work, phenyl groups functionalized glassy carbon electrode loaded with metallic ions were placed in contact with a suitable reductant to form the metal particles, whereas Prussian Blue was generated by reaction of the ferricyanide loaded surface with Fe^{2+}. The presence of the metallic (for Cu) and oxide/hydroxide (for Cu and Ru) species was confirmed by X-ray photoelectron spectroscopy and also, indirectly, by evaluating the electrocatalytic activity for the reduction of nitrate (Cu-modified) and the oxidation of hydrogen peroxide (Ru-modified), whereas the presence of Prussian Blue was evidenced by its characteristic redox waves.

Experimental Section

Chemicals. The 4-diazo-*N*,*N*-diethylaniline tetrafluoroborate salt was obtained from Aldrich and was used as received. The 4-sulfonate phenyl diazonium and 4-carboxy phenyl diazonium tetrafluoroborate salts were synthesized from the corresponding amines[15] and characterized by FTIR and NMR. Tetrabutylammonium tetrafluoroborate (NBu_4BF_4) (Aldrich) was heated at 50 °C under vacuum for 8 h. The precursors for the formation of the metallic species at the surface of the modified glassy carbon electrode were CuCl, $RuCl_3$, $K_3Fe(CN)_6$, and $FeSO_4$, and were used as received. All other chemicals were analytical reagent grade (Anachemia or Aldrich).

Procedure. Glassy carbon electrodes (AIMCOR, Pittsburgh, grade GC-10) were prepared from 3-mm diameter rods embodied in epoxy resin (Hysol, 56C) or obtained from Bioanalytical Systems Inc. (model MF-2012; diameter 3 mm) and were used as working electrodes. For the XPS measurements, a glassy carbon plate (GLCP-10; 1 × 2 cm; thickness 2 mm) from The Electrosynthesis Co. was used as working electrode. Platinum gauze and a Ag/AgCl (saturated KCl) electrode were used as counter and reference electrodes, respectively. All potentials were reported versus the Ag/AgCl reference electrode. The glassy carbon electrode surface was cleaned by polishing with 1-μm and 0.05-μm alumina slurries. After polishing, the electrode was washed with water and ultrasonicated for 5 min in acetonitrile.

Electrochemical modification of the glassy carbon electrode was carried out in acetonitrile containing the diazonium salt (5 mM) and 0.1 M NBu_4BF_4. The applied potential was −1 V for the

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deposition of *N*,*N*-diethylaniline and −0.7 V for 4-sulfonate phenyl and 4-carboxy phenyl groups. After a 4-min modification, the electrode was thoroughly washed by rinsing in acetonitrile. The functionalized electrode was then soaked in the metallic ions solution for an appropriate period of time. After rinsing with deionized water, the metal-loaded (Ru and Cu) electrodes were dipped for 1 min in aqueous 0.1 M $NaBH_4$.[8] The amount of copper on the resulting modified electrode was estimated by stripping voltammetry performed between −0.6 and 0.6 V vs Ag/AgCl in 0.1 M CH_3COOH/CH_3COONa (pH = 4) at a scan rate of 20 mV/s. In the case of the ferricyanide-loaded *N*,*N*-diethylaniline/carbon electrode, exposure to a 0.1 M Fe^{2+} (pH 3.5) solution afforded the Prussian Blue/DEA modified electrode.

The adsorption of Cu(I) species was carried out at the surface of a DEA-modified glassy carbon electrode from a 5 mM CuCl pH 3 solution for 30 min. In the case of the Ru system, a 0.5 mM $RuCl_3$ pH 2.9 solution was used and the 4-sulfonate phenyl modified electrode was soaked in this solution for 30 min. A 0.1 M $K_3Fe(CN)_6$ pH 2 solution was used to incorporate ferricyanide anions at the surface of the DEA-modified glassy carbon electrode. It should be noted that, for simplicity, the Cu and Ru loaded electrodes will be designated as DEA-Cu and sulfonate-Ru even though metal oxide and metal hydroxide also can be present at the electrode surface.

Equipment. Electrochemical measurements were performed in a one-compartment cell using the three-electrode configuration. Cyclic voltammetry was performed using either a potentiostat/galvanostat model M263A (EG&G Princeton Applied Research) or an electrochemical interface SI1287 (Solartron Instruments) interfaced with a PC and the electrochemical setups were both controlled with the model DC Corrware (Scribner Associates, version 1.2) software.

X-ray photoelectron spectra (XPS) were obtained for modified glassy carbon plates with an Escalab 220i XL from VG equipped with a hemispherical analyzer and an Al anode (monochromatic Kα X-rays at 1486.6 eV) used at 12−14 kV and 10−20 mA. The data were obtained at room temperature and typically the operating pressure in the analysis chamber was below 1×10^{-9} Torr. XPS survey and core level spectra, as well as Auger spectra, were recorded for the modified electrodes. For the high-resolution spectra, the step size was 50 meV and the analyzer pass energy was fixed at 20 eV in the CAE mode. The conventional method of calibration using the C 1s peak of carbon at 284.5 eV was used. The core level spectra were peak-fitted using the CasaXPS software. The raw data were treated by subtraction of a "Shirley" background and a mixed Gaussian/Lorentzian (30:70) function was used to peak-fit the data.[25]

The core level spectra were used to evaluate the atomic concentration of the species present at the glassy carbon electrode surface. The atomic concentration (at. %) of each individual element was determined, by assuming a homogeneous surface layer, from the relative peak areas of the spectra and the corresponding sensitivity factors according to

$$\text{at. \%} = (A_i/s_i)/\Sigma(A_i/s_i)$$

where A_i is the peak area of the element i and s_i is the sensitivity factor for this element. Sensitivity factor values of 1, 1.8, 2,93, 1.68, 25.4, 9.6, and 16.4 were used for C 1s, N 1s, O 1s, S 2p, Cu 2p, Ru 3p, and Fe 2p, respectively. The surface concentration of the grafted groups was calculated by multiplying the ratio of the total area under the N1s peak and the substituent with respect to the C1s peak by a factor of 7.3×10^{-9} mol/cm^2.[17a] This factor represents the carbon atom surface density of basal plane graphite and was used as a rough approximation of the glassy carbon surface. FTIR measurements were performed with a Michelson Series FTIR spectrometer (Bomem Hartmann & Braun) MB series and NMR measurements were performed with a Gemini 300 MHz spectrometer (Varian Instruments).

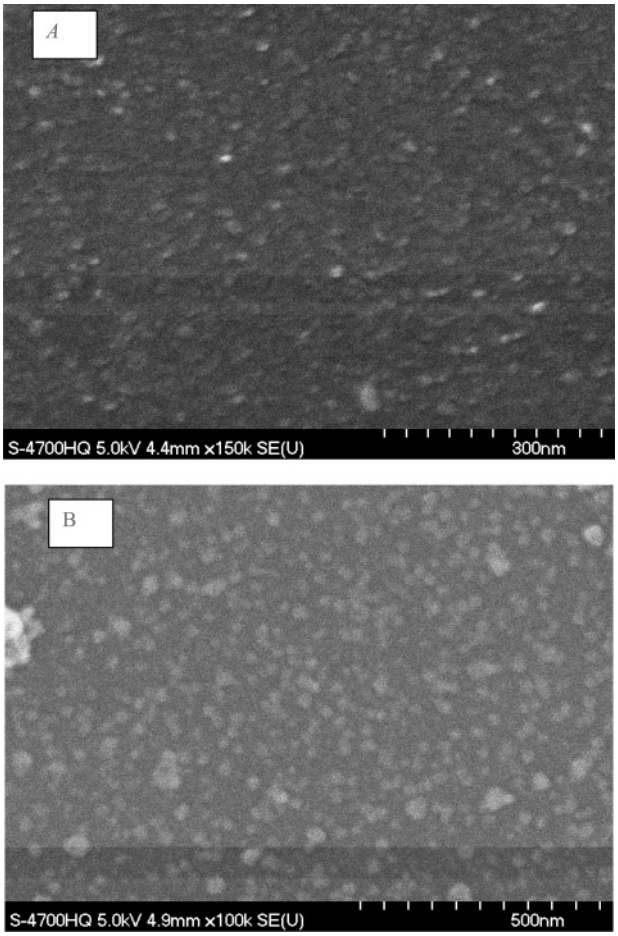

Figure 1. Scanning electron micrographs of (A) Cu/*N*,*N*-diethylaniline-modified glassy carbon electrode, and (B) Prussian Blue/*N*,*N*-diethylaniline-modified glassy carbon electrode.

Results and Discussion

Copper/*N*,*N*-Diethylaniline (DEA-Cu)-Modified Glassy Carbon Electrode. The DEA groups electrochemically grafted at the surface of the glassy carbon electrode are protonated in acidic media and therefore allow for the binding of the negatively charged Cu(I) chloride species ($CuCl_2^-$) that are subsequently chemically reduced. Figure 1A shows the scanning electron micrograph of a DEA-Cu-modified glassy carbon electrode. This micrograph is identical to that obtained for a bare glassy carbon electrode (not shown). However, it will be demonstrated below by X-ray photoelectron spectroscopy and electrochemistry (stripping of Cu and electrocatalytic activity in the presence of nitrate) that Cu is present at the surface of this electrode. Thus, it appears that it is not possible to get the exact information as to whether a copper film or particles are present at the electrode surface. Presumably, the particles are very small as it is the case for Pt particles generated at the surface of a 4-aminophenol modified carbon electrode.[23a] However, the XPS and

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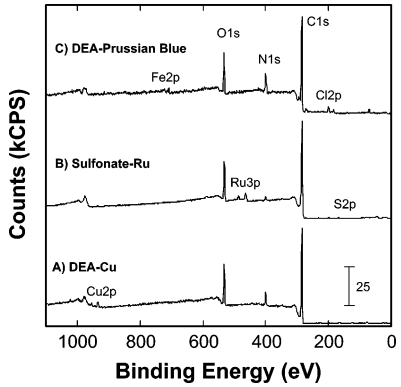

Figure 2. X-ray photoelectron survey spectra for (A) Cu/*N*,*N*-diethylaniline (DEA-Cu)-modified glassy carbon electrode, (B) Ru/4-sulfonate (sulfonate-Ru)-modified glassy carbon electrode, and (C) Prussian Blue/*N*,*N*-diethylaniline (DEA-Prussian Blue)-modified glassy carbon electrode.

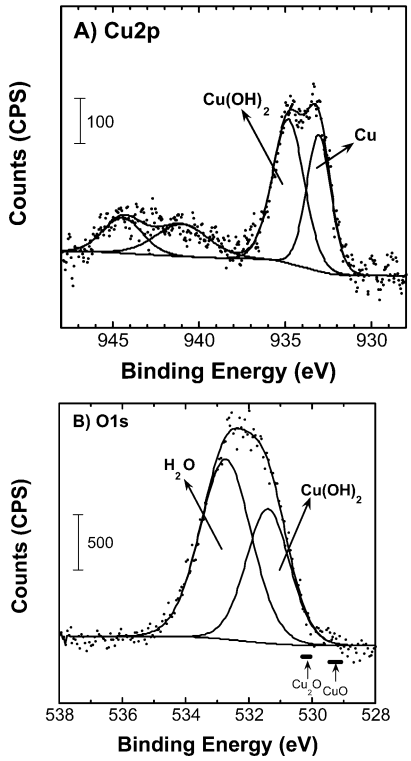

Figure 3. X-ray photoelectron Cu 2p (A) and O 1s (B) core level spectra for a DEA-Cu-modified glassy carbon electrode.

electrochemistry data (vide infra) will suggest that the presence of a continuous metal film is unlikely.

The XPS survey spectrum of a DEA-Cu-modified glassy carbon electrode following chemical treatment with $NaBH_4$ is depicted in Figure 2 (curve A). The XPS spectrum shows the Cu 2p peaks at about 930 and 950 eV in addition to the C 1s (285 eV), O 1s (532 eV), and N 1s (400 eV) peaks. Figure 3A shows the Cu $2p_{3/2}$ region of the core level Cu 2p spectrum with its major component at about 934 eV together with a satellite peaks envelope centered at 942.5 eV. The main envelope of the Cu 2p core level spectrum can be curve-fitted with two peaks at binding energies of 933.0 and 934.8 eV (see Table SI 1 in the Supporting Information). The latter peak can be attributed to $Cu(OH)_2$.[25−30] The presence of $Cu(OH)_2$ at the DEA-Cu electrode is also indicated by the satellite peaks observed above 938 eV.[25−30] These peaks appear about 10 eV above the main Cu $2p_{3/2}$ peak.[27] The Cu $2p_{3/2}$ component at 933.0 eV could be assigned to either metallic copper (932.6 eV) or Cu_2O (932.7 eV), despite that it is located at slightly higher binding energies than those expected for these species.[25,28−30] Since these binding energies are very close to each other, it is hard to distinguish between metallic copper and Cu_2O on the Cu 2p core level spectrum presented.[25,28,30,31] To clarify this, it is useful to consider the O 1s (Figure 3B) and the $CuL_3M_{4,5}M_{4,5}$ Auger (Figure SI 1 in the Supporting Information) spectra.[30c,d] The curve-fitting of the O 1s spectrum yielded two main peaks at binding energies of 532.7 and 531.4 eV, which can be attributed to adsorbed H_2O and $Cu(OH)_2$, respectively.[25,28,29] The $CuL_3M_{4,5}M_{4,5}$ Auger spectrum (Figure SI 1) shows a peak at 568.2 eV characteristic of metallic Cu and a more prominent component above 570 eV that can be attributed to Cu_2O[28b,30c] or $Cu(OH)_2$[25] species.

By analyzing together the Cu 2p, O 1s, and $CuL_3M_{4,5}M_{4,5}$ spectra, it is possible to conclude with fairly good confidence that the DEA-Cu electrode contains metallic copper and $Cu(OH)_2$. Even if the presence of CuO and Cu_2O cannot be ruled out completely at this stage, the following observations will demonstrate that, at the most, only tiny amounts of these species might be present (vide infra). First, the O 1s spectrum can be fitted very well without a component at 529.0−529.6 eV (see arrow on Figure 3B), which would be required to account for the presence of CuO.[30] Accordingly, the curve-fitting of the Cu 2p spectrum was performed without a CuO component at about 933.8 eV. This information obtained from the O 1s spectrum is extremely valuable because it is impossible to completely exclude the presence of Cu(II) species (CuO) on the basis of only the Cu 2p spectrum. Second, the O 1s spectrum could also be possibly fitted with another component at about 530−530.3 eV (assigned to Cu_2O) that could accountfor about 5%, at the most, of the total copper species (not shown). Therefore, this observation confirms the presence of a significant amount of metallic copper since the fit of the Cu 2p spectrum without a Cu^0 contribution and a Cu(I) component representing only 5% of copper species (the remainder being $Cu(OH)_2$) would not be acceptable. The presence of metallic Cu was also confirmed by the $CuL_3M_{4,5}M_{4,5}$ Auger data. In conclusion, the XPS data are consistent with the presence of Cu and $Cu(OH)_2$ at the DEA/Cu electrode surface but it is not possible to unambiguously identify Cu_2O due to the uncertainties associated with curve fitting. Nonetheless, if Cu_2O were to be present, it would not be formed by the decom-

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Table 1. Atomic Composition of the Surface of the Modified Glassy Carbon Electrode Evaluated from the XPS Data

	atomic concentration (%)									
	C	O	N	Cu	Ru	Fe	Cl	S	M^a/C	Γ^b, mol/cm^2
DEA-Cu	79	14	6.4	0.6					0.0076	0.55×10^{-10} (1.5×10^{-10})[c]
sulfonate-Ru	84	12	2		1		0.5	0.5	0.012	0.87×10^{-10}
DEA-Prussian Blue	77	11.4	9.1			0.32	2.2		0.0042	0.32×10^{-10} (0.3×10^{-10})[c]

[a] *M* represents the atomic concentration of the metal (Cu, Ru, or Fe). [b] The surface concentration, Γ, is calculated from the equation: $\Gamma = R/C \times 7.3 \times 10^{-9}$ where *R* is the relative atomic concentration (%) of either Cu, Ru, or Fe. [c] The surface concentration is evaluated from stripping voltammetry (Cu) and cyclic voltammetry (Prussian Blue).

position of Cu(II) species[30d] because monochromatic (not achromatic) X-radiation was used in the present study. The presence of $Cu(OH)_2$ can be explained by the oxidation of copper upon exposure to air and moisture. The presence of $Cu(OH)_2$ instead of CuO is also confirmed by the shape of the shake-up spectrum and the relative intensities of the two components of the peak envelope.[25]

A semiquantitative analysis of the surface was performed by XPS and the results are gathered in Table 1. The atomic concentration of the surface of the DEA-Cu-modified glassy carbon electrode was found to be 0.6 at. % and the surface concentration was 0.55×10^{-10} mol/cm^2. The atomic concentration of nitrogen (6.4%) is much larger than that of copper (0.6%). The nitrogen content is slightly lower than that recently reported for DEA-modified glassy carbon electrodes.[15c] This suggests that some DEA moieties, present at the electrode surface following the grafting step, were desorbed during the ion-exchange and reduction steps. The relatively small Cu concentration is due to the weak interaction between the monovalent protonated amine groups and the copper (I) complex in chloride media ($CuCl_2^-$).[32] This could also have contributed to the loss of copper species that was observed by XPS (not shown) for an electrode before and following the $NaBH_4$ treatment of the modification procedure. The low content of Cu with respect to N (Cu/N ratio = 1:10) suggests the presence of tiny particles distributed at the electrode surface instead of a continuous metallic film. The surface concentration of Cu on the modified electrode, estimated by stripping voltammetry (1.5×10^{-10} mol/cm^2), was found to be in reasonably good agreement with that evaluated by XPS, considering the uncertainties of both procedures.

The electrocatalytic activity of copper electrode toward the electrochemical reduction of nitrate has been demonstrated in our laboratory for bulk copper electrode.[26] This property was used to indirectly show that copper is indeed present at the DEA-modified electrode. The cyclic voltammogram of a DEA-Cu-modified glassy carbon electrode in aqueous 2 M NaCl displays little electroactivity between −0.6 and −1.5 V vs Ag/AgCl (Figure 4, curve —). The slight increase of the cathodic current with an onset at about −1.3 V is attributed to the hydrogen evolution reaction at the copper surface. This is confirmed by the smaller current between −1.3 and −1.5 V for the DEA-modified glassy carbon electrode relative to the DEA-Cu-modified electrode.

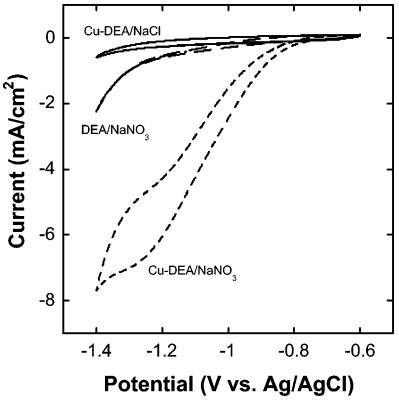

Figure 4. Cyclic voltammetry for a DEA-Cu-modified glassy carbon electrode in 2 M NaCl (—), a DEA-modified glassy carbon electrode in 2 M $NaNO_3$ (— —), and a DEA-Cu-modified glassy carbon electrode in 2 M $NaNO_3$ (- - -). Scan rate = 50 mV/s.

In the presence of 2 M $NaNO_3$, a significant modification of the cyclic voltammogram is observed for the DEA-Cu-modified glassy carbon electrode (Figure 4, curve - - -). Indeed, a cathodic wave with an onset potential of about −0.8 V is clearly detected and is related to the presence of copper at the electrode surface and the reduction of nitrate. In the absence of copper, this cathodic wave decreased substantially and only a modest increase of the current is observed for potential more negative than −1.2 V (Figure 4, curve — —).

The reduction of the Cu(I) species is required to get some significant electrocatalytic activity. The cyclic voltammogram recorded following adsorption of Cu(I) species at the DEA-modified electrode, but without the chemical reduction step, displays some electrocatalytic activity but only at more negative potential values (not shown). The increased electrocatalytic activity for the latter in comparison with that of the DEA-modified electrode can be explained by the presence of some metallic copper that is being generated during the cyclic voltammetry experiment. This phenomenon can also occur for the DEA-Cu electrode if the chemical reduction of all Cu(I) species with $NaBH_4$ is incomplete.

Several other copper loaded electrodes or surfaces[8,9a,10,31,33] have been prepared but only few of them have been tested for some catalytic or electrocatalytic processes. One of these studies dealt with copper microparticles dispersed into functionalized polypyrrole which has been shown to be active for the electrochemical reduction of nitrobenzene to aniline.[33] Thus, the latter and other electrocatalytic reactions such as

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the reduction of carbon dioxide[34] can be envisioned for the DEA-Cu-modified glassy carbon electrode. Finally, the short-term stability of the electrode was also evaluated and no variation of the electrochemical response was observed after 10 voltammetric cycles. The modified electrode was also left exposed to air for 4 days without any significant decrease of activity.

The adsorption of Cu(II) at the surface of 4-carboxy phenyl modified carbon electrodes has been recently demonstrated in our laboratory.[21] In these instances, cationic metal complexes are required. It is interesting to note that the change from DEA to 4-carboxy phenyl to initially modify the glassy carbon electrodes did not affect the electroactivity of copper toward nitrate.

Ruthenium/4-Sulfonate Phenyl Modified Glassy Carbon Electrode. In a 0.5 mM $RuCl_3$ pH 2.9 solution, ruthenium exists as an oxo-hydrated species,[35] $[RuO(H_2O)_4]^{2+}$, and therefore cannot be ion-exchanged at the surface of a 4-carboxy phenyl modified carbon electrode because at this pH the 4-carboxy groups are protonated.[15a] Instead, a 4-sulfonate phenyl ($pK_a = -7$)[36] modified electrode was used to adsorb ruthenium species. It should be noted that a solution of higher pH, which would be required to deprotonate the 4-carboxy phenyl groups and have a negatively charged surface to adsorb $[RuO(H_2O)_4]^{2+}$, could not be used with Ru due to the formation of a black RuO_2 precipitate.

The XPS survey spectrum of the Ru-loaded 4-sulfonate phenyl modified electrode shows the characteristic C 1s, O 1s, N 1s, and S 2p peaks at 285, 532, 400, and 167 eV, respectively (Figure 2B). The latter is attributed to the sulfonate groups as evidenced by the S $2p_{1/2}$ and S $2p_{3/2}$ doublet at 168.6 and 167.5 eV for the S 2p core level spectrum (not shown).[21b] The presence of Ru species is confirmed by the survey spectrum by the 3p components around 463 and 485 eV and the Ru 3d core level spectrum presented in Figure 5A. It should be noted that some chloride is detected by XPS on the survey spectrum (Figure 2B). This might be due to the presence of adsorbed $RuCl_3$ at the modified electrode surface.

The curve-fitting results of the Ru 3p core level spectrum are also shown in Figure 5A. The Ru 3p signal was chosen as the Ru 3d peak strongly overlaps with the C 1s signal of the carbon support. The peak with the binding energy of 462.6 eV is attributed to RuO_2[37−40] while the signal at higher binding energy (464.0 eV) is assigned to hydrous RuO_2 (see Table SI 2).[37] A comparison with literature data for the Ru 3d core level data suggests the presence of hydrated RuO_2 ($RuO_2 \cdot xH_2O$) as indicated by the shift to higher binding

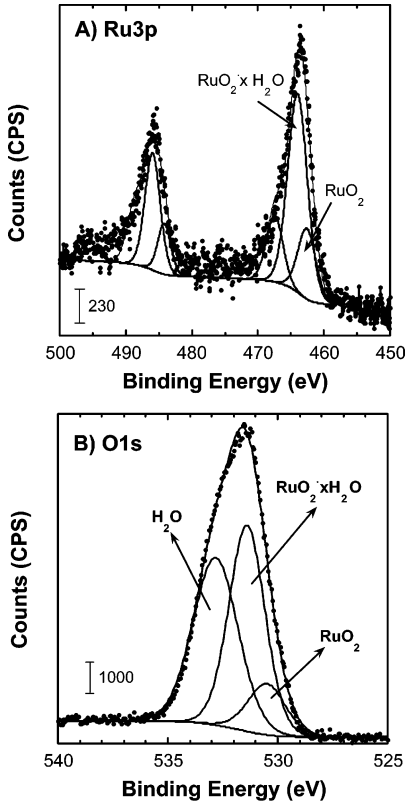

Figure 5. X-ray photoelectron Ru 3p (A) and O 1s (B) core level spectra for a sulfonate-Ru-modified glassy carbon electrode.

energy and the broader peaks expected for a hydrated form in comparison to anhydrous RuO_2.[41] The shift of about 1.4 eV between RuO_2 and $RuO_2 \cdot xH_2O$, even if the metal is in the same oxidation state, was ascribed to the presence of OH functionalities on Ru.[41] A shift is also expected for the components of the Ru 3d core level spectrum. On the other hand, some caution should be taken with this attribution since similar binding energies have been also reported for anhydrous and hydrated RuO_2.[38] The third component of the Ru 3p spectrum at 467.5 eV can be tentatively assigned to the contribution of core−hole coupling.[42] Evidence for the metallic Ru state has not been given by XPS. The O 1s core level spectrum (Figure 5B) shows three peaks at 530.5, 531.4, and 532.8 eV, which can be attributed to RuO_2, hydrous RuO_2, and adsorbed water, respectively.[43]

The curve-fitting of the Ru 3p is not straightforward and may appear arbitrary due to the contribution at higher binding energies. However, the validity of the fit can be confirmed by comparing the results of the curve-fitting of the Ru 3p, Ru 3d, and O 1s spectra. This approach has recently proved to be useful for the analysis of conducting polymer-dopant electrodes.[44] For these three core level spectra (data not shown for the Ru 3d spectrum) the contribution of RuO_2 was found to be 23 ± 2% of the ruthenium species.

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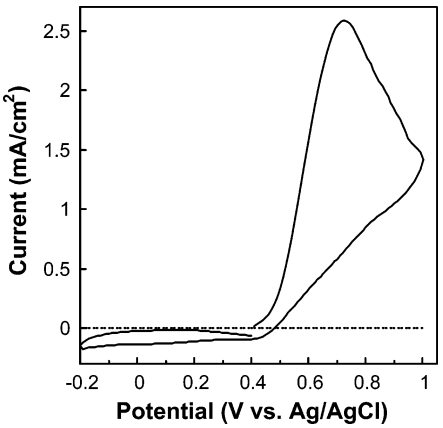

Figure 6. Cyclic voltammetry for a bare (- - -) and a sulfonate-Ru-modified (—) glassy carbon electrode in 0.01 M H_2O_2, phosphate buffer, pH 7. Scan rate = 50 mV/s.

The Ru atomic concentration of the surface of the modified glassy carbon electrode was found to be 1 at. % and the surface concentration was 0.87×10^{-10} mol/cm^2 (Table 1). Surprisingly, the Ru concentration is larger than that of sulfur. This is unexpected on the basis of the charge of the sulfonate and ruthenium moieties. The formation of ruthenium particles was also detected at a bare glassy carbon electrode when this electrode was soaked in the 0.5 mM $RuCl_3$ pH 2.9 solution. However, the amount of ruthenium species being deposited in this case is much smaller than that for the 4-sulfonate phenyl modified electrode as evidenced by XPS. The spontaneous deposition of metal at glassy carbon electrode has been reported and is thought to occur in the presence of incompletely oxidized functionalities.[4c] The spontaneous deposition was not investigated in detail in this study but our results demonstrate clearly that more metallic species can be immobilized in the presence of the 4-sulfonate functionalities. Nonetheless, it seems obvious that the ruthenium species present at the electrode cannot only originate from cationic ruthenium species involved in electrostatic interaction with the surface sulfonate groups. Finally, as was the case for the DEA-Cu electrode, the SEM did not reveal the presence of any particles at the electrode surface (Figure SI 2).

The electrocatalytic activity of Ru electrode toward the electrooxidation of hydrogen peroxide is well-known.[45] This electrochemical reaction is relevant to the biosensing of glucose with enzyme electrode and has been used to characterize the Ru-modified electrode prepared in this study. A set of representative cyclic voltammograms for both an unmodified and a sulfonate-Ru-modified glassy carbon electrode are depicted in Figure 6. The bare glassy carbon electrode does not display any electrochemical activity in the presence of 0.01 M H_2O_2 at pH 7 between −0.2 and 1 V (Figure 6, - - -). On the other hand, the sulfonate-Ru-modified electrode is characterized by a broad anodic wave centered at about 0.75 V corresponding to the oxidation of H_2O_2. This cyclic voltammetry response is in very close agreement with that reported for Ru particles dispersed in a carbon paste electrode.[45] Thus, the sulfonate-Ru-modified electrode could be eventually used for biosensing. Moreover, in the case of glucose sensing the presence of biological interferent such as anionic ascorbate in the solution to analyze is detrimental since ascorbate is electrooxidized at a potential similar to that of hydrogen peroxide.[46] Interestingly, the 4-sulfonate phenyl layer which is present with the Ru particles might play the role of barrier to such anionic interferents. This is confirmed by the cyclic voltammogram (not shown) recorded for bare and 4-sulfonate-modified glassy carbon electrodes in the presence of 10 mM ascorbate at pH 7 which revealed a 50% decrease of the anodic peak current for the modified electrode in comparison to the bare one. Further experiments are required to optimize the conditions to obtain the best barrier properties of the 4-sulfonate layer.

Prussian Blue/*N*,*N*-Diethylaniline Modified Glassy Carbon Electrode. The formation of Prussian Blue at *N*,*N*-diethylaniline (DEA)-modified carbon electrodes required two steps. The positively charged *N*,*N*-diethylaniline groups bind $Fe(CN)_6^{3-}$ anions in the first step which is followed by their complexation with Fe^{2+}. This procedure is analogous to that described by Guo et al. for the formation of Prussian Blue at sulfonated monolayer surface.[47] The scanning electron micrograph of Figure 1B presents Prussian Blue formed at the DEA-modified glassy carbon electrode surface. It shows the arrangement of submicrometric particles over the whole surface. The morphology of the surface differs significantly from that of a bare glassy carbon electrode (vide supra).

Figure 2C shows the XPS survey spectrum of a DEA-Prussian Blue-modified glassy carbon electrode. In addition to the Fe 2p and N 1s peaks at 710 and 400 eV, respectively, which suggest the presence of Prussian Blue, the spectrum also shows C 1s (285 eV), O 1s (532 eV), and Cl 2p (200 eV) peaks. The latter can be attributed to the presence of chloride anions, which act as charge compensating species for the protonated nitrogen of DEA. The presence of a small amount of potassium is also evidenced on the core level spectrum recorded between 275 and 295 eV by the K 2p peak at 293.5 eV (Figure SI 3). The Fe 2p core level spectrum also provides further evidence for Prussian Blue formation and is shown in Figure 7A. The curve-fitting of the Fe $2p_{3/2}$ envelope yielded three distinct components at 709.0, 710.2, and 713.6 eV. The first two are attributed to Fe(II) and Fe(III) species and the broad satellite at the higher binding energy is characteristic of Fe (II) species[48,49] The ratio for the peaks at 709 and 710.2 eV is about 2:1. This ratio differs somewhat from the value of 3:4 expected for Prussian Blue based on the formula ($Fe_4^{III}[Fe^{II}(CN)_6]_3$). On the other hand, the observed ratio and the presence of the broad satellite at 713.6 eV, associated with Fe (II) suggests that the partial reduction of Prussian Blue to Everitt's salt ($K_4Fe_4^{II}[Fe^{II}(CN)_6]_3$) occurred during the formation of the surface film.[49] The formation of the latter is also in agreement

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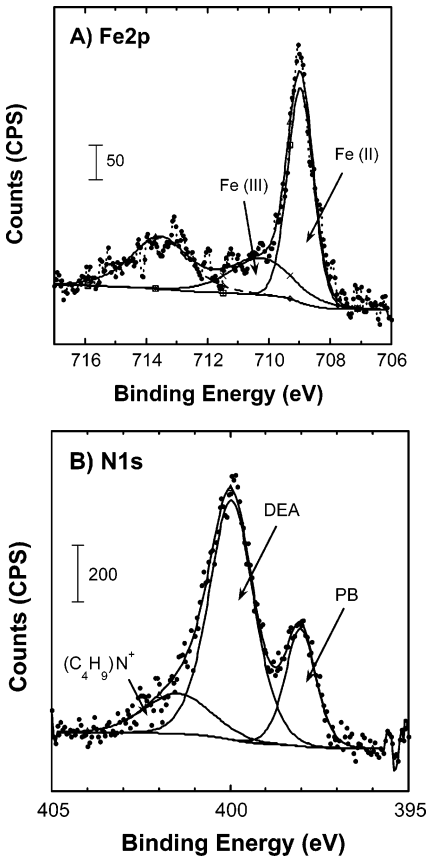

Figure 7. X-ray photoelectron Fe 2p (A) and N 1s (B) core level spectra for a DEA-Prussian Blue-modified glassy carbon electrode.

with the presence of potassium that was confirmed by XPS (vide supra). The N 1s core level spectrum (Figure 7B) can be peak-fitted with three components at 398.0, 400, and 401.5 eV that can be attributed to the presence of Prussian Blue,[48] the grafted DEA,[15c] and excess supporting electrolyte (Bu_4N^+) with a ratio of 1.9:5.8:1.4, respectively. The surface concentration of Prussian Blue was evaluated from the XPS data (Table 1) and was found to be in the submonolayer range as a value of 0.32×10^{-10} mol/cm^2 was determined. This surface coverage corresponds to only about 6% of the coverage of the aryl groups. A lower coverage is expected because only one ferricyanide anion is required to compensate the protonated nitrogens of three diethylaniline groups. The N/Fe ratio of 6, albeit slightly larger than that expected for Prussian Blue (2.6) or Everitt's salt (3.6), can be considered in relatively good agreement with that expected for these compounds.

Figure 8 displays the cyclic voltammograms of a bare glassy carbon electrode (···), a *N*,*N*-diethylaniline-modified electrode after successive immersion in ferricyanide and Fe^{2+} solutions (–) and after three sequential immersions in the two solutions (- - -). The presence of Prussian Blue is confirmed by the sets of reversible redox waves at 0.25 and 0.94 V which correspond to the well-known Prussian Blue/Everitt's salt and Prussian Blue/Berlin Green redox interconversions.[47,50−54] The cyclic voltammograms of Figure 8

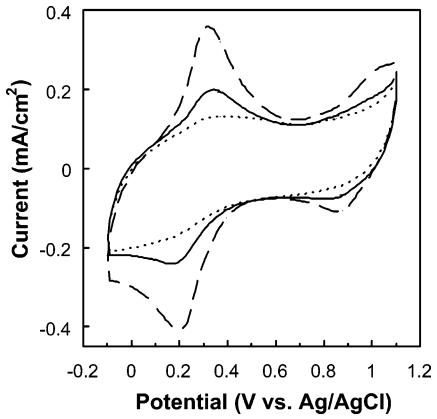

Figure 8. Cyclic voltammetry for a DEA-modified glassy carbon electrode without (···) and with Prussian Blue (—) and three sequential immersions in $Fe(CN)_6^{3-}$ and Fe^{2+} solutions (- - -) in a 1 M KCl pH 3 solution. Scan rate = 50 mV/s.

are in agreement with those reported for bulk layer,[50−52] sol gel composite,[47] and Langmuir−Blodgett Prussian Blue films.[54] The redox waves centered at 0.25 V are well defined compared to those at 0.94 V. The potential peak separation between the anodic and cathodic peaks is larger for the latter indicating slower redox kinetics.[50] The surface coverage, as evaluated by integration of the first voltammetric anodic wave, was found to be 0.3×10^{-10} mol/cm^2 and therefore is in very good agreement with that determined from the XPS data (Table 1). Figure 8 also shows that additional immersions led to an increase of the Prussian Blue surface coverage. The stability of the voltammetric response of the Prussian-Blue-modified electrode was investigated. First, an electrode that was allowed to stand overnight in air displayed an increase of the voltammetric waves. This observation is in agreement with a previous report and can presumably be due to loss of water in the film.[52] Second, the voltammetric response remained unchanged following potential cycling in a pH 3 solution over a potential window ranging from −0.1 to 1.1 V. As a control experiment, the bare glassy carbon electrode was also subsequently soaked in the $Fe(CN)_6^{3-}$ and the Fe^{2+} solutions but in this case the characteristic Prussian Blue redox waves were not observed. Interestingly, a Prussian Blue film can also be generated at a 4-sulfonate phenyl modified electrode. For this experiment, the modified electrode is initially soaked in the Fe^{2+} solution and thereafter in an $Fe(CN)_6^{3-}$ solution. The CV of the resulting electrode is similar to that shown in Figure 8 (curve –).

General Discussion. The XPS data revealed the presence of Cu, Ru, and Prussian Blue on the glassy carbon modified surface. The analysis of the spectra by curve-fitting also demonstrated the presence of metallic species with different oxide states. More specifically, in the Cu 2p, O 1s XPS core level and the $CuL_3M_{4,5}M_{4,5}$ Auger spectra the presence of both metallic copper and $Cu(OH)_2$ was clearly evidenced. On the other hand, it was also shown that the peak for metallic Ru does not appear in the Ru 3p core level spectrum. It is likely that the Cu and Ru metal undergo significant oxidation upon exposure to solution and ambient air to form

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the corresponding metallic oxides and hydroxides. However, the electroactivity of the Cu-, Ru-, and Prussian Blue-modified glassy carbon electrodes was clearly demonstrated by cyclic voltammetric measurements. The fact that these electrodes display electrochemical activity might be surprising in light of the blocking behavior of substituted phenyl modified carbon electrode in some selected experimental conditions.[15a,c] Indeed, the electrochemical response of an anionic redox probe such as $Fe(CN)_6^{3-}$ was substantially suppressed in a pH 7 electrolyte in which the 4-carboxy group of a phenyl-modified electrode was deprotonated and became negatively charged. The results presented here indicate that the blocking effect does not seem to be an important issue, especially for the reduction of anionic nitrate at the 4-carboxy modified electrode. In contrast, the DEA-Cu electrode should favor the preconcentration of nitrate at the electrode surface due to the presence of the protonated amine groups.[18a] The observation of similar electrochemical activity for both the DEA-Cu and the Cu/4-carboxy phenyl modified electrodes seems to suggest that the metallic species are in direct electrical contact with the underlying glassy carbon electrode.

Thus, it seems plausible to assume that the metal-based species are surrounded by substituted aryl groups. Presumably, these organic species might have a beneficial effect on the long-term electrochemical activity of the modified electrode if they can prevent the agglomeration of the metal-based species. The detrimental agglomeration would lead to a decrease of the active surface area of the catalytic or electroactive species.[55] These phenomena are relevant for applications such as fuel cells that require dispersed and high-surface-area catalyst. The nature of the forces that maintain the metallic species at the electrode surface is also of the utmost importance. In addition to the role of the organic groups (vide supra), another possibility lies in the formation of a C−O-metal bond as was recently proposed for the electroless deposition of copper onto 4-mercaptobenzoic acid self-assembled on a gold electrode.[56]

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Conclusion

In this study, we demonstrated that substituted phenyl groups electrochemically grafted at carbon electrode surfaces could be used as template for the formation of catalysts (metal, oxide, and hydroxide of Cu and Ru) and inorganic compounds (Prussian Blue). The substituents were chosen to be positively or negatively charged in a solution of appropriate pH. The resulting ionized interface was then used to adsorb metallic species of opposite charge. Thus, the factors that need to be closely considered for the preparation of such electrodes are the pK_a of the surface groups and the form of the metallic species. For the latter, the nature of the electrolyte (e.g., potential ligands) is very important and will control the resulting charge of the metallic complex. Further chemical treatment (reduction, reaction with other chemical species) allowed the formation of the targeted materials. This procedure is very versatile and could be used to prepare a variety of other metal and metal oxide structures at a carbon surface. Experiments along those lines are currently underway in our laboratory, and, more specifically, we are interested in the preparation of platinum (and other metal) particles at electrochemically modified carbon electrodes[57] and chemically modified carbons.[58]

Acknowledgment. The financial support of the Natural Science and Engineering Research Council of Canada (NSERC) is acknowledged for a Research Grant to D.B. and for an Equipment grant for the XPS spectrometer (to D.B. and 9 others).

Supporting Information Available: XPS data for modified glassy carbon electodes (PDF), auger and X-ray spectra for modified glassy carbon electrodes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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