# Localized In situ Generation of Diazonium Cations by Electrocatalytic Formation of a Diazotization Reagent

Galyna Shul,[†] Robert Parent,[†] Hugo A. Mosqueda,[†,‡] and Daniel Bélanger*,[†]

[†]Département Chimie, Université du Québec à Montréal, CP8888, Succ. Centre-Ville, Montréal, Québec, Canada H3C 3P8
[‡]Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, 66451 San Nicolás de los Garza, Mexico

**S** *Supporting Information*

**ABSTRACT:** A new one-step electrochemical approach for the localized generation of diazonium cations in the diffusion layer of an electrode by taking advantage of the electrocatalytic properties of the electrode for the formation of the diazotization agent (nitrite) is proposed. Once nitrite anions are formed by electrocatalytic reduction of nitrate, they immediately react with an arylamine to produce the corresponding diazonium cations, which can be electrochemically readily reduced at the electrode surface. By this method, spontaneous modification of the electrode surface can be avoided. Furthermore, because the potential of the electrochemical nitrate reduction depends strongly on the nature of the electrode material, we also demonstrate that selective grafting can be achieved on a surface, which consists of two different materials: copper—gold or copper—glassy carbon substrates.

**KEYWORDS:** *electrografting, electrode modification, aryl group, selective functionalization, nitrate reduction, copper, carbon surface, diffusion layer, avoidance of spontaneous diazotization*
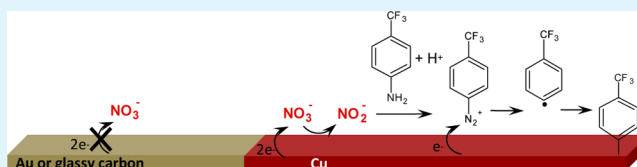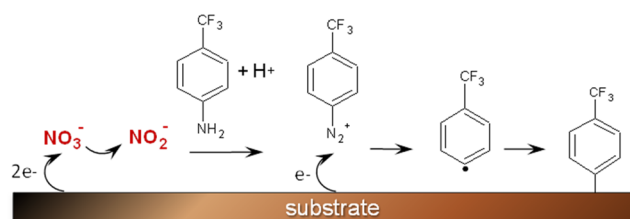
## 1. INTRODUCTION

The ability to selectively modify electrode surfaces is crucial for the development of chemical and biochemical sensors and microelectronics.[1] A widely used procedure for covalent modification of surfaces involves the electrochemical reduction of aryldiazonium salt.[1,2] The high efficiency of this procedure is counterbalanced by a relative instability of some diazonium ions[3] and by the spontaneous reduction of the diazonium ions at the electrode surface, which is subsequently modified.[4,5] Therefore, new methods for the localized functionalization of surfaces are needed. Approaches that allow the selective immobilization of molecules on surface employing diazonium chemistry include the use of scanning electrochemical microscopy,[6−10] microelectrode array,[11] and polystyrene beads,[12,13] as well as electrochemical local generation of diazonium cations.[14−16] Potentially useful methods employ the local generation of diazonium ions and the reactive corresponding radicals by electrochemical reduction of the corresponding nitro derivative to an amine,[8] and from aryltriazenes.[14] In the later case, electrochemical generation of an acid affords the deprotection of the triazene and its conversion to a diazonium ion.[14]

Herein, we propose a new one-step potentiostatic approach for the localized generation of diazonium cations in the diffusion layer of an electrode surface by taking advantage of the electrocatalytic properties of the electrode for the formation of the diazotization agent (nitrite) (Scheme 1). In this approach, the nitrite anions are formed by electrochemical reduction of nitrate in acidic solution.[17] Once nitrite anions are formed in the diffusion layer, they immediately react with an arylamine to produce the corresponding diazonium cations,

**Scheme 1. Mechanism Suggested for Trifluoromethylbenzene Groups Electrografting by Exploiting the Electrochemical Reduction of Nitrate to Nitrite to Initiate Diazotization**



which can be electrochemically readily reduced at the electrode surface provided the nitrate reduction potential is more negative than the potential required for the electrochemical reduction of the diazonium ions (Scheme 1).

In this work, electrode materials characterized by no (gold),[18] medium (carbon), and high (copper),[19,20] activity toward the nitrate reduction were investigated. Furthermore, since the potential of the electrochemical nitrate reduction depends strongly on the nature of the electrode material,[18,19] we also demonstrate that selective grafting can be achieved on a surface that consists of two different materials. For example, with copper—gold and copper—glassy carbon two-component

electrodes, it is shown that electrografting occurs only on copper and not on the gold or glassy carbon surface.

## 2. EXPERIMENTAL SECTION

4-aminobenzotrifluoride, sodium nitrite, sodium nitrate, acetic acid were used as received from Aldrich. All solutions were prepared with Nanopure water and were deaerated with extra dry nitrogen during 15 min before each experiment. Electrochemical measurements were performed in a three-electrode cell where the working electrode was glassy carbon (SPI Supplies/Structure Probe, Inc.), copper foil (Goodfellow, 99.95%, 0.5 mm), polycrystalline gold plate (Arrandee), or glassy carbon and gold plates covered with a 200 nm copper film by resistive evaporation, the counter electrode was a platinum gauze, and the reference electrode was Ag/AgCl (3 M NaCl). The glassy carbon surface was cleaned by polishing with 1 $\mu$m alumina, rinsed and sonicated during 5 min in Nanopure water. The copper foil was polished with 1 $\mu$m alumina followed by a 10 min ultrasonic cleaning in Nanopure water. Then, it was immersed into glacial acetic acid for 30 s and rinsed with Nanopure water prior to modification. The polycrystalline gold plate was cleaned by the following multisteps procedure: annealing by flaming in air; immersion into a 1:1 $H_2SO_4$/$H_2O_2$ mixture at room temperature for about 2 s; 5 min ultrasonic cleaning in Nanopure water; 50 cycles at 50 mV/s in 0.1 M $H_2SO_4$ and 5 min ultrasonic cleaning in Nanopure water. After electrochemical modification the electrode was rinsed abundantly and sonicated in Nanopure water again for 1 min to remove all physically adsorbed species. A Solartron Instruments (SI1287) potentiostat interfaced with a PC, and the electrochemical setups were controlled with DC Corrware (Scribner Associates, version 2.8d) software.

X-ray photoelectron spectroscopy (XPS) measurements were performed with an XPS PHI 5600-ci (Physical Electronics, Eden Prairie, MN, USA) equipped with a monochromatic Al anode (K$\alpha$ = 1486.6 eV) at 300 W for survey spectra (resolution 0.8 eV) and a Mg K$\alpha$ (1253.6 eV) anode at 300 W for high-resolution spectra (resolution 0.05 eV). The survey spectra do not require the compensation of charge (neutralizer). The data were obtained at room temperature and typically the operating pressure in the analysis chamber was below $1 \times 10^{-9}$ Torr. Analysis was carried out at an angle of 45° between the sample and the analyzer. The samples were analyzed without any sputtering of their surface prior to the measurements.

Core level spectra were used to evaluate the atomic concentrations of the species present at the glassy carbon electrode and copper electrode surfaces. The atomic concentration (at %) of each individual element was determined from the relative peak areas of the spectra and the corresponding sensitivity factors according to

$$\text{at \%} = \frac{A_i/s_i}{\sum_i A_i/s_i} \qquad (1)$$

where $A_i$ is the peak area of the element $i$ and $s_i$ is the sensitivity factor for this element. The values 1, 1.8, 2.93, 4.43, and 25.39 were used for C 1s, N 1s, O1s, F 1s, and Cu 2p, respectively.[21]

## 3. RESULTS AND DISCUSSION

**3.1. Electrografting of Electrodes by In situ Generated Diazonium Ions in Presence of Added Nitrite.** Before studying the mechanism of the electrode reaction described in Scheme 1 the electrografting of gold, glassy carbon, and copper electrodes by diazonium ions in situ formed by adding directly nitrite anions to the electrolyte was performed. Figure 1 (gray curves) shows that in presence of nitrite, the in situ generated 4-trifluoromethylbenzene diazonium ions are reduced at about −0.1 V, for the three substrates, in agreement with our previous reports.[5,22]

The one-peak shape of cyclic voltammogram recorded for the glassy carbon electrode (Figure 1, glassy carbon electrode) represents typical voltammetric response for the reduction of in
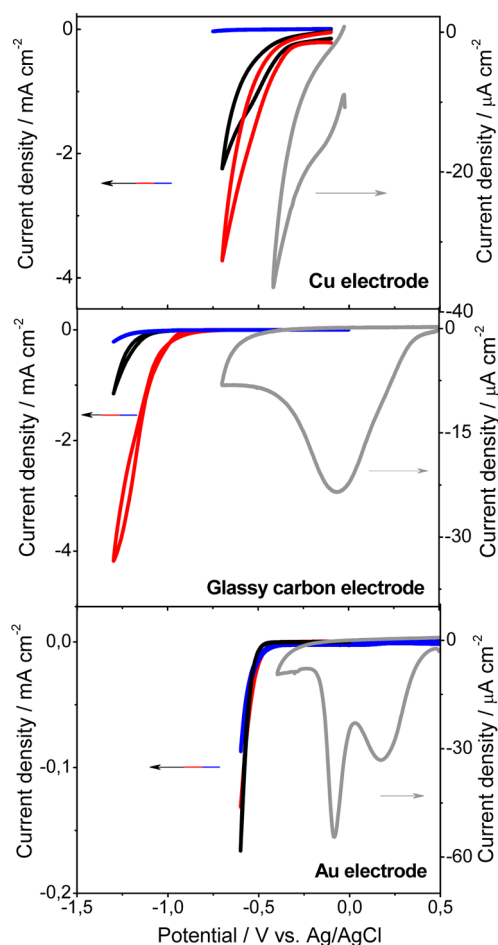


**Figure 1.** Right axis (gray): Cyclic voltammograms (1st cycle) obtained with copper, glassy carbon, and gold electrodes in a 5 mM 4-trifluoromethylaniline and 10 mM $NaNO_2$ in 0.1 M $CH_3COOH$ solution at scan rate of 50 mV s$^{-1}$. Left axis: cyclic voltammograms (1st cycle) obtained with copper, glassy carbon, and gold electrodes in 0.1 M $CH_3COOH$ (blue); 0.1 M $NaNO_3$ in 0.1 M $CH_3COOH$ (red) and 5 mM 4-trifluoromethylaniline and 0.1 M $NaNO_3$ in 0.1 M $CH_3COOH$ (black), solutions at a scan rate of 5 mV s$^{-1}$.

situ generated diazonium ions in acidic solution.[3] The reduction peak is attributed to the formation of highly reactive 4-trifluoromethylbenzene radicals, which subsequently form a bond with the electrode surface. The splitting of the reduction peak in two distinct peaks (Figure 1, Au electrode) is often observed in literature[22] and is explained by the reduction of diazonium cations on distinct crystallographic sites of the electrode substrate.[23] In the case of copper electrode (Figure 1, Cu electrode), the shape of cyclic voltammogram can be affected by the overlap with the reduction of copper oxides.[24] However, before each experiment, the copper electrode was immersed in glacial acetic acid for 30 s and then washed with Nanopure water. Despite these differences in the shape of the cyclic voltammograms (Figure 1, gray lines), all electrodes exhibit a reduction peak potential at around −0.1 V vs Ag/AgCl.

**3.2. Electrografting of Electrodes by In situ Generated Diazonium Ions Following the Electrocatalytic Nitrite Formation.** The potential required for the reduction of nitrate was estimated by comparing the cyclic voltammograms for each electrode in an acetic acid solution in the absence (Figure 1, blue lines) and presence of $NaNO_3$ (Figure 1, red lines). The

1469

dx.doi.org/10.1021/am302971q | ACS Appl. Mater. Interfaces 2013, 5, 1468−1473

copper and glassy carbon electrodes display some electro-catalytic activity for the nitrate reduction, whereas the gold electrode is almost completely inactive.[18] For the latter, the onset of the cathodic current is due to the hydrogen evolution reaction.[25] Cyclic voltammograms for copper and glassy carbon electrodes show an onset of the cathodic current at −0.3 and −0.9 V, respectively, which is attributed to the reduction of nitrate to nitrite. Despite the thermodynamic feasibility of the electrochemical reduction of nitrate anions in acid media[26] (eq 2), the kinetics of the charge transfer is slow and is characterized by a high overpotential.[27]

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O, \; E^0 = 0.625$$
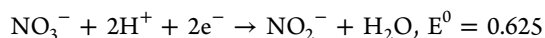
$$V \; vs. \; Ag/AgCl \tag{2}$$

As expected, copper displays a lower overpotential for the nitrate reduction than the glassy carbon electrode.[19] The subsequent addition of 4-trifluoromethylaniline to the nitrate solution led to a decrease in the current that is more noticeable for the glassy carbon electrode (Figure 1, black lines). The decrease in the current is due to the fact that the electrode surface becomes blocked by formation of an organic layer of 4-trifluoromethylbenzene groups (Scheme 1).

Figure 2 provides additional evidence of formation of a blocking layer, which inhibits further electron transfer, as clearly demonstrated by the continuous decrease of the current during
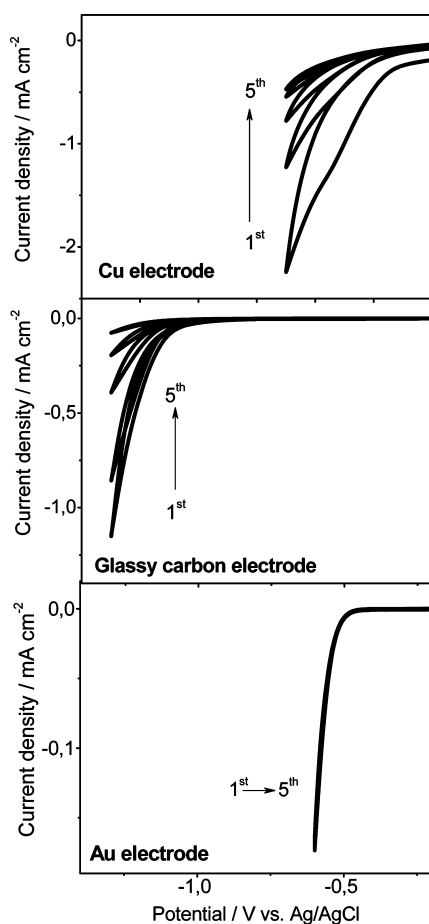


**Figure 2.** Cyclic voltammograms (from 1st to 5th cycles) obtained with copper, glassy carbon, and gold electrodes in a 5 mM 4-trifluoromethylaniline and 0.1 M NaNO$_3$ in 0.1 M CH$_3$COOH solution at a scan rate of 5 mV s$^{-1}$.

the first five cyclic voltammograms for copper and glassy carbon electrodes, whereas the cyclic voltammogram for the gold electrode remained unchanged.

This electrochemical behavior is consistent with the chemical modification of glassy carbon and copper electrode by a formation of a blocking layer, which inhibits further electrode transfer, as typically found for electrode modified by the diazonium chemistry,[26] according to the mechanism shown in Scheme 1. Additionally, the blocking effect of the grafted layer was illustrated through the cyclic voltammetric response of the Fe(CN)$_6^{3−/4−}$ redox system (Supporting Information). Interestingly, the onset of the reduction wave for the copper and glassy carbon electrode is occurring at −0.4 and −1.1 V, respectively. Indeed, the cyclic voltammograms shown in Figures 1 and 2 suggest that nitrate anions are reduced to nitrite anions, which react with the arylamine to form the corresponding diazonium ions. The latter are reduced at these negative potential values that are more negative than the potential required for their reduction (see Figure 1, black lines). The grafting reaction (Scheme 1) occurs by a electrochemical−chemical−electrochemical (E$_i$C$_i$E$_i$) mechanism,[27] where every step of the reaction is irreversible and the product of the chemical reaction (4-trifluoromethylbenzene diazonium cations) is easier to reduce than nitrate anions. It should be noted that the overall process is most likely more complex as it involves an additional step which consists in the reduction of the 4-trifluoromethylbenzene radical to the corresponding carbanion instead of its grafting.[28] However, the further reduction of aryl radical to aryl anion is negligible, especially in our experimental conditions, e.g., aqueous acid solution, where hydrogen abstraction takes place and not affecting the film being formed.[28]

The water contact angle characterization of the modified electrodes can provide additional evidence of the surface modification.[29] The contact angle of a water droplet increased from 30° (unmodified) to 60° (modified) for the copper and glassy carbon surface after functionalization by hydrophobic 4-trifluoromethylbenzene groups (Figure 3).
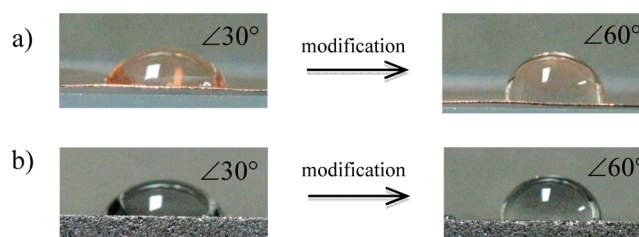


**Figure 3.** Optical images of 30 μL water droplet on the surface of (a) copper and (b) glassy carbon before and after modification with 4-trifluoromethylbenzene groups. The values of the contact angles are shown inside the images.

X-ray photoelectron spectroscopy was also used to confirm electrografting. Figures 4a and 5a show survey spectra for copper and glassy carbon electrodes, respectively, modified with 4-trifluoromethylbenzene groups. The presence of the latter at the electrode surfaces is demonstrated by the F 1s peak, which appear on both the survey spectra (Figures 4a and 5a) and the core level spectra (Figures 4b and 5b) at 687 eV.

The electrografting of 4-trifluoromethylbenzene groups at the surface of the copper electrode led to a decrease of Cu 2p peaks (spectrum for the unmodified copper electrode not
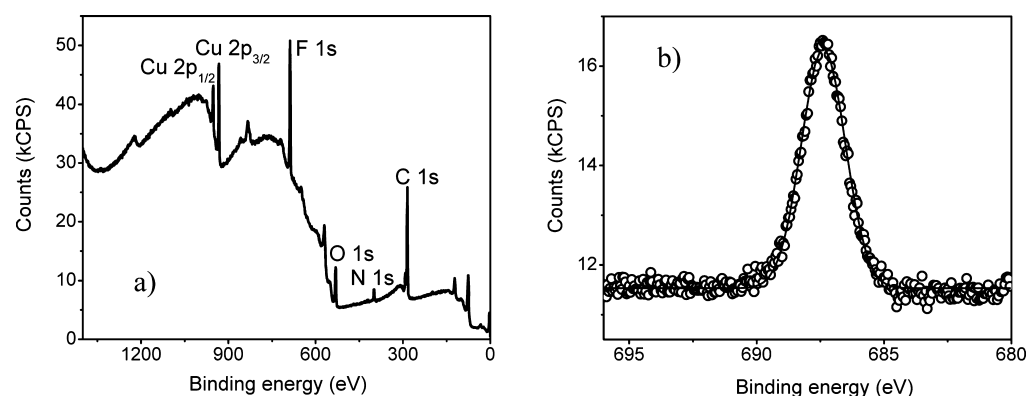
**Figure 4.** (a) XPS survey spectrum and (b) F 1s core level spectrum of copper modified with 4-trifluoromethylbenzene by cyclic voltammetry between 0 and −0.4 V vs Ag/AgCl for 5 cycles in a 5 mM 4-trifluoromethylaniline and 0.1 M NaNO$_3$ in 0.1 M CH$_3$COOH solution.
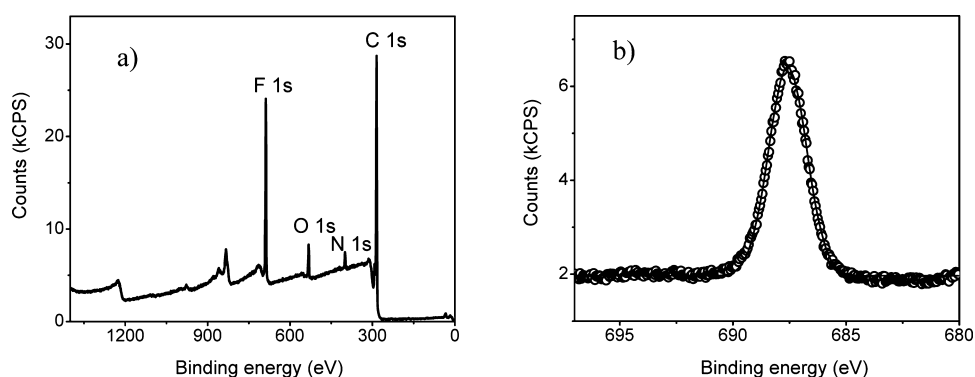


**Figure 5.** (a) XPS survey spectrum and (b) F 1s core level spectrum of a glassy carbon electrode modified with 4-trifluoromethylbenzene groups by cyclic voltammetry between 0 and −1.3 V vs Ag/AgCl for 5 cycles in a 5 mM 4-trifluoromethylaniline and 0.1 M NaNO$_3$ in 0.1 M CH$_3$COOH solution.

shown here), in agreement with previous studies.[30] Another characteristic features of electrografting by electrochemical reduction of diazonium is given by the observation of a N 1s peak that is attributed to the presence of azo bond.[22] The data extracted from XPS core level spectra give the atomic composition of the electrografted films on the electrode substrates (Table 1). The estimated values of the surface concentration $1.8 \times 10^{-9}$ and $5.0 \times 10^{-10}$ mol cm$^{-2}$ for copper and glassy carbon, respectively, suggests close to monolayer and submonolayer coverage of the electrodes in our experimental conditions.[31] It can be observed that the F:C ratios for copper

**Table 1. Atomic Composition of the Glassy Carbon and Copper Electrodes Modified with 4-Trifluoromethylbenzene Groups by Cyclic Voltammetry between 0 and −1.3 V (glassy carbon) and 0 and −0.4 V (copper) vs. Ag/AgCl for 5 Cycles in a 5 mM 4-Trifluoromethylaniline and 0.1 M NaNO$_3$ in 0.1 M CH$_3$COOH Solution**

| | atomic concentration (%)[a] | | | | | |
|---|---|---|---|---|---|---|
| electrode | C 1s | O 1s | N 1s | F 1s | Cu 2p | Γ (mol cm$^{-2}$)[b] |
| copper | 59.9 | 9.8 | 3.9 | 19.9 | 6.1 | $1.8 \times 10^{-9}$ |
| glassy carbon | 77.0 | 4.4 | 2.7 | 15.8 | | $5.0 \times 10^{-10}$ |

[a]For highly sensitive elements (C, O, N, F), the error is around 0.1%, whereas for the less sensitive element (Cu), the error is between 0.5 and 1.0%. [b]The surface coverage, Γ, of the copper electrode by the grafted layer was estimated from Γ = F (%)/3 × 1/Cu (%) × 1.7 × 10$^{-9}$.[30] The surface coverage of the glassy carbon electrode was estimated from Γ = F (%)/3 × 1/C (%) × 7.3 × 10$^{-9}$.[32]

and glassy carbon electrodes are smaller than predicted for a trifluoromethylbenzene film. This could be due to a carbon contamination and, for the case of glassy carbon electrode, to the contribution from the underlying glassy carbon surface to the C 1s peak.

**3.3. Selective Functionalization of Two-Component Electrodes.** Because the reduction potential of nitrate anions depends on the nature of the substrate, we hypothesized that it could be possible to selectively modify only one region of a surface consisting of two different materials. To demonstrate the proof-of-concept, glassy carbon and gold electrodes, partially coated with a copper layer, were used as substrates. The electrochemical grafting at copper−gold and copper−glassy carbon electrodes was investigated at a potential of −0.5 V which was chosen for a one-step potentiostatic modification because it is negative enough to generate nitrite anions only on copper electrode and thus only functionalize the copper surface. XPS was used to confirm that selective electrografting can be achieved. Panels a and b in Figure 6 show F 1s core level XPS spectra for copper−gold and copper−glassy carbon electrodes following the one-step functionalization.

The F 1s spectrum for the copper region exhibits an F 1s peak at 687.3 eV that is attributed to the 4-trifluoromethylbenzene groups. A very low intensity F 1s peak is also observed on gold and glassy carbon surface (Figures 6a, b, respectively). Its appearance can be due to either fluorine contamination that presumably originates from cleavage of the C−F bond of the grafted molecules and which could be occurring inside the XPS analysis chamber. The presence of spontaneously grafted aryl
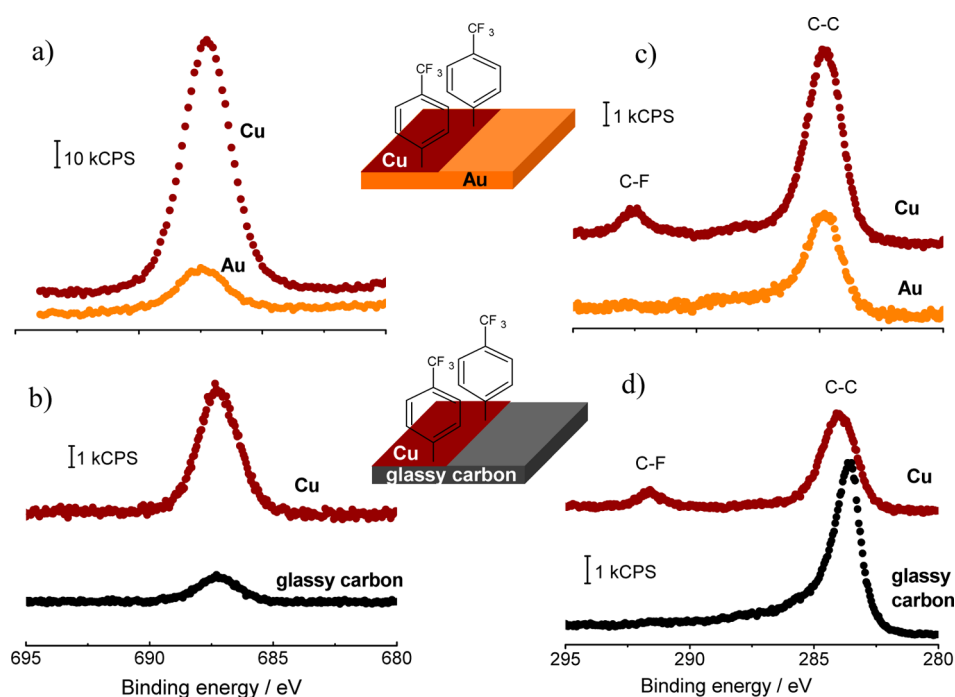
**Figure 6.** XPS (a, b) F 1s and (c, d) C 1s core level spectra for 4-trifluoromethylbenzene modified electrodes: (a, c) copper deposited on gold; (b, d) copper deposited on glassy carbon. The electrodes were modified by one-step potentiostatic deposition at $E = -0.5$ V during 4 min in 5 mM 4-trifluoromethylaniline and 0.1 M NaNO$_3$ in 0.1 M CH$_3$COOH solution.

groups on gold or glassy carbon,[33] can also result from the formation of diazonium ions in the diffusion layer during the nitrate reduction onto copper and which subsequently diffuse to the carbon or gold part of the two-component electrode. The presence of trifluoromethylbenzene groups on copper is also confirmed by the peak associated with C−F bond at 293 eV on the C 1s spectrum (Figure 6c) and which is barely observable for the gold or glassy carbon surface (Figures 6c, d). Another evidence that the 4-trifluoromethylbenzene groups are not grafted on gold is demonstrated by the absence of a peak at about 400 eV that is commonly observed on a N 1s spectrum due to an azo linkage at the surface (vide supra), as a consequence of the grafting through reduction of diazonium cations (Table 2).[22] These observation can indicate either the lack of spontaneous grafting on gold and glassy carbon surface or the very slight spontaneous grafting, so that C−F and N 1s contributions are too low to be observed.

## 4. CONCLUSION

In summary, we reported a successful approach for the selective covalent attachment of aryl groups onto surfaces by exploiting the electrocatalytic reduction of nitrate to nitrite and in situ diazonium ions formation. This electrografting process is carried out in a simple one-step process. By this method, spontaneous modification of the surface can be avoided. This is because diazonium ions are locally generated in the diffusion layer at the electrode/electrolyte interface[3] only when nitrate ions are electrochemically reduced to nitrite ions. Depending on the nature of the electrode surface, the nitrate reduction is highly catalyzed (copper), poorly catalyzed (carbon), or noncatalyzed (gold). Hence, copper and glassy carbon electrodes act as electrocatalyst for the generation of nitrite anions and could be functionalized by reduction of in situ generated aryldiazonium ions. Because of the different electrocatalytic activity of the electrodes for nitrate reduction,

**Table 2. Atomic Composition of the Two Component Electrodes: Gold and Glassy Carbon Substrates Partially Covered with Copper and Modified with 4-Trifluoromethylbenzene Groups[a]**

| two-component electrode | atomic concentration (%)[b] | | | | | $\Gamma$ (mol cm$^{-2}$)[c] |
|---|---|---|---|---|---|---|
| | C 1s | O 1s | N 1s | F 1s | Cu 2p | |
| copper part[e] | 61.4 | 13.8 | 2.4 | 16.9 | 5.4 | $1.8 \times 10^{-9}$ |
| gold part[e] | 39.4 | 13.5 | | 3.6 | | |
| copper part[f] | 57.2 | 12.3 | 2.3 | 18.6 | 9.2 | $1.1 \times 10^{-9}$ |
| glassy carbon part[f] | 82.7 | 13.6 | 1.0[d] | 3.7 | | |

[a]The electrodes were modified by one-step potentiostatic deposition at −0.5 V vs. Ag/AgCl during 4 min in a 5 mM 4-trifluoromethylaniline and 0.1 M NaNO$_3$ in 0.1 M CH$_3$COOH solution. [b]For highly sensitive elements (C, O, N, F) the error is around 0.1%, whereas for the less sensitive element (Cu) the error is between 0.5 and 1.0%. [c]The surface coverage, $\Gamma$, of the copper electrode by grafted layer was estimated from: $\Gamma = F (\%)/3 \times 1/Cu (\%) \times 1.7 \times 10^{-9}$.[30] [d]Nitrogen is present on both the bare and modified glassy carbon at trace levels. [e]Copper−gold electrode. [f]Copper−glassy carbon electrode.

copper can be selectively functionalized on copper−gold or copper−glassy carbon substrates. The variety of conducting substrates with their respective activity for the nitrate reduction[20] and similarly the wide range of reduction potential of substituted diazonium ions[1] suggest that the approach describes herein could be a versatile method for the selective surface functionalization and potentially useful for biosensing and microelectronic applications.[1,34] Finally, because the local concentration of in situ generated diazonium ions strongly depends on that of generated nitrite anions, it will be interesting to see if the proposed approach could be useful to control the layer formation. Further experiments along those lines are in progress.

1472

dx.doi.org/10.1021/am302971q | ACS Appl. Mater. Interfaces 2013, 5, 1468−1473

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information**

## ■ AUTHOR INFORMATION

**Corresponding Author**
*E-mail: belanger.daniel@uqam.ca. Tel. +1514 987-3000, ext. 3909. Fax: +1514 987-4054.

**Notes**

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

## ■ REFERENCES

(1) Bélanger, D.; Pinson, J. *Chem. Soc. Rev.* **2011**, *40*, 3995−4048.

(2) Mahouche-Chergui, S.; Gam-Derouich, S.; Mangeney, C.; Chehimi, M. M. *Chem.Soc. Rev.* **2011**, *40*, 4143−4166.

(3) Agullo, J.; Canesi, S.; Schaper, F.; Morin, M.; Bélanger, D. *Langmuir* **2012**, *28*, 4889−4895.

(4) Combellas, C.; Jiang, D.; Kanoufi, F.; Pinson, J.; Podvorica, F. *Langmuir* **2009**, *25*, 286−293.

(5) Lyskawa, J.; Bélanger, D. *Chem. Mater.* **2006**, *18*, 4755−4763.

(6) Valenti, G.; Bardini, L.; Bonazzi, D.; Rapino, S.; Marcaccio, M.; Paolucci, F. *J. Phys. Chem. C* **2010**, *114*, 22165−22170.

(7) Cougnon, C.; Mauzeroll, J.; Bélanger, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 7395−7397.

(8) Cougnon, C.; Gohier, F.; Bélanger, D.; Mauzeroll, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 4006−4008.

(9) Grisotto, F.; Ghorbal, A.; Goyer, C.; Charlier, J.; Palacin, S. *Chem. Mater.* **2011**, *23*, 1396−1405.

(10) Coates, M.; Cabet, E.; Griveau, S.; Nyokong, T.; Bedioui, F. *Electrochem. Commun.* **2011**, *13*, 150−153.

(11) Harper, J. C.; Polsky, R.; Dirk, S. M.; Wheeler, D. R.; Brozik, S. M. *Electroanalysis* **2007**, *19*, 1268−1274.

(12) Corgier, B. P.; Bélanger, D. *Langmuir* **2010**, *26*, 5991−5997.

(13) Santos, L.; Ghilane, J.; Lacroix, J.-C. *Electrochem. Commun.* **2012**, *18*, 20−23.

(14) Kongsfelt, M.; Vinther, J.; Malmos, K.; Ceccato, M.; Torbensen, K.; Knudsen, C. S.; Gothelf, K. V; Pedersen, S. U.; Daasbjerg, K. *J. Am. Chem. Soc.* **2011**, 3788−3791.

(15) Han, S.; Yuan, Y.; Hu, L.; Xu, G. *Electrochem. Commun.* **2010**, *12*, 1746−1748.

(16) Cougnon, C.; Nguyen, N. H.; Dabos-Seignon, S.; Mauzeroll, J.; Bélanger, D. *J. Electroanal. Chem.* **2011**, *661*, 13−19.

(17) Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solutions*; Marcel Dekker: New York, 1985.

(18) Dima, G. E.; De Vooys, A. C. A.; Koper, M. T. M. *J. Electroanal. Chem.* **2003**, *554−555*, 15−23.

(19) Ghodbane, O.; Sarrazin, M.; Roué, L.; Bélanger, D. *J. Electrochem. Soc.* **2008**, *155*, F117−F123.

(20) Milhano, C.; Pletcher, D. *The Electrochemistry and Electrochemical Technology of Nitrate*; White, R. E., Ed.; Springer: New York, 2009; Vol. *45*, pp 1−61.

(21) Wagner, C. D.; Davis, L. E.; Zeller, M. V.; Taylor, J. a.; Raymond, R. H.; Gale, L. H. *Surf. Interface Anal.* **1981**, *3*, 211−225.

(22) Baranton, S.; Bélanger, D. *J. Phys. Chem. B* **2005**, *109*, 24401−24410.

(23) Benedetto, A.; Balog, M.; Viel, P.; Le Derf, F.; Sallé, M.; Palacin, S. *Electrochim. Acta* **2008**, *53*, 7117−7122.

(24) Deutscher, R. L.; Woods, R. *J. Appl. Elechtrochem.* **1986**, *16*, 413−421.

(25) Perez, J.; Gonzalez, E. R.; Villullas, H. M. *J. Phys. Chem. B* **1998**, *102*, 10931−10935.

(26) Saby, C.; Ortiz, B.; Champagne, G. Y.; Bélanger, D. *Langmuir* **1997**, *7463*, 6805−6813.

(27) Bard, A. J.; Faulkner, L. R.; Swain, E.; Robey, C. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons: New York, 2001.

(28) Andrieux, C. P.; Pinson, J. *J. Am. Chem. Soc.* **2003**, *125*, 14801−14806.

(29) Yu, S. S. C.; Tan, E. S. Q.; Jane, R. T.; Downard, A. J. *Langmuir* **2007**, *23*, 11074−11082.

(30) Chamoulaud, G.; Bélanger, D. *J. Phys. Chem. C* **2007**, *111*, 7501−7507.

(31) Pinson, J.; Podvorica, F. *Chem. Soc. Rev.* **2005**, *34*, 429−439.

(32) Liu, Y.-C.; McCreery, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 11254−11259.

(33) Barrière, F.; Downard, A. J. *J.Solid State Electrochem.* **2008**, *12*, 1231−1244.

(34) McCreery, R. L. *Chem. Rec.* **2012**, *12*, 149−163.