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Patterning Organic Layers on Carbon Surfaces using Electro-labile Protected Aryl Diazonium Salts.

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ABSTRACT:

The reduction of aryl diazonium salts is nowadays recognized as a powerful technique to functionalize many surfaces included carbon materials. However, efficient and easy-to-perform methods to pattern monolayers on carbon surfaces using aryl diazonium grafting are still missing. Herein, we described the synthesis and the use of a special aryl diazonium salt bearing an electro-labile protecting group. After electrochemical deprotection, it leads to the formation of a reactive benzoic acid layer that can be easily post-functionalized. This approach is successfully implemented in a scanning electrochemical cell microscopy (SECCM) experiment to achieve a facile patterning of an organic layer onto carbon surfaces.

KEYWORDS: Aryl diazonium salts, electro-grafting, lithography, surface functionalization.

1. Introduction.

Aryldiazonium salts (electro-) reduction is a powerful technique that allows the functionalization of various surfaces materials from conductors, semiconductors to insulators.[1, 2] It has been discovered at the beginning of the 1990s by Pinson and coworkers[3] and its use has been growing ever since. This technique has the advantage to be fast (seconds to minutes)[4] and leads to highly robust interfaces (C-C bonds when considering carbon surfaces). Upon reduction, aryl diazonium ions lead to the formation of aryl radicals concomitant with the loose of N_2 . Aryl radicals are highly reactive species that can react with the surfaces of the electrodes where they are produced but also with the already attached aryl moieties. Hence, it generally leads to the grafting of multilayered disordered organic films.[5] Despite this major drawback, this approach has been considered for many applications ranging from sensors and biosensors,[6] antifouling coatings,[7] corrosion protection,[8] supercapacitors[9, 10] active plasmonic devices[11, 12] or molecular electronics.[13, 14] Nevertheless, to unleash the full potential of aryl diazonium grafting, new improvements are needed. As a first step, researchers have proposed few methods allowing the fine control of the reaction in order to only deposit monolayer films, for instance through the formation–degradation approach,[15, 16] steric constraint,[17] protection–deprotection strategies,[18-21] pre-organization strategy[22, 23] or in the presence of radical scavengers.[24] However, fast and easy-to-perform methods to pattern monolayers on carbon surfaces using aryl diazonium grafting are still missing. It is now essential to propose new strategies allowing the patterning of organic layers formed from the reduction of aryl diazonium salts.

Previously, patterning of surfaces using the (electro-) reduction of aryl diazonium salts has been mainly proposed based on methods developed for other modifiers. Inkjet printing,[25]

micro-contact printing (μ CP)[26] or nanosphere lithography[27] are relevant examples of adapted strategies that were successful in patterning surfaces with aryl diazonium salt reduction. Surface probe microscopies (SPM) were also used to locally electro-reduce aryl diazonium salts. For instance, Cougnon *et al.* used scanning electrochemical microscopy (SECM) to locally generate aryl radicals from aryl diazonium salts to pattern carbon surfaces.[28] Palacin *et al.* used similar methodologies to localize electrografting on conducting or insulating substrates using SECM,[29, 30] or a combination of atomic force microscopy (AFM) and SECM.[31, 32] However, such a patterning involves the local reduction of aryl diazonium salts and not the patterning of the electro-grafted layer as it is the case in more common lithographic and photolithographic techniques. Only few examples were described in the literature using the direct patterning of grafted organic layers produced from the diazonium chemistry. First, Downard *et al.* used the tip of an AFM to intentionally damage an organic layer electro-grafted by the reduction of aryl diazonium salts.[33] Patterning can be thus obtained and the part of the organic layer that has been damaged leaves uncovered carbon substrates that can be easily functionalized by a second modifier.[33] Schuhmann and coworkers took advantage of the use of SPM as SECM or scanning droplet cell to locally post-functionalized *p*-nitrobenzene organic films via electrochemical reduction[34] or locally deprotect monolayer quinone films.[35] Finally, local post-functionalization allowing patterning of organic films deposited by electroreduction of aryl diazonium salts was also undertaken using click chemistry under the tip in a SECM experiment.[36, 37]

Contrarily to organic films generated by the reduction of aryl diazonium salts, many strategies have been developed to pattern self-assembled monolayers (SAMs).[38] Particularly, specific design of thiolated compounds bearing electro-labile and photo-labile protecting groups enabled

the use of lithographic and photolithographic techniques to obtain patterned SAMs. Electrochemical patterning of SAMs generally involves the use of protected oxygenated compounds as catechol,[39] quinone[40, 41] or carboxylic groups[42, 43] and finds applications in immobilization of biomolecules[42-44] or cell patterning.[40, 41] Such strategies have also been applied to pattern other surfaces as In_2O_3 ,[45] silicon[46] or TiO_2 . [47] However, there is no reports in the literature of such strategies applied to organic film deposition by the reduction of aryl diazonium salts.

Herein, we present the synthesis and use of a special designed aryl diazonium salt bearing an electrolabile protecting group. This allow us to electrochemically deprotect the electrografted organic film onto carbon substrates, leaving a reactive benzoic acid layer that can be easily post-functionalized by carbodiimide coupling with any amine terminated molecules. Finally, scanning electrochemical cell microscopy (SECCM) is used to pattern such organic films as a proof of concept.

2. Experimental section.

2.1. Chemicals and reagents.

Commercially available reagents were used as received. All aqueous solutions were made employing ultrapure water (18.2 M Ω cm). N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide, N-hydroxysuccinimide, ferrocenecarboxaldehyde, hydroxylamine hydrochloride, 4-nitrobenzoyl chloride, hydroquinone, sodium hydroxide, tetrachloroethane and tetrafluoroboric acid (HBF₄) solution were purchased from Merck.

4-hydroxyphenyl 4-aminobenzoate hydrochloride[48] (0.85 g, 3.2 mM, 1 eq) is dissolved in 48% HBF₄ (17.5 mL) and water (17.5 ml). The solution is then cooled to 0°C with an ice bath and NaNO₂ is added (0.265 g, 1.2 eq). The solution is stirred 30 minutes at this temperature and the formed precipitate is filtered and thoroughly washed with water. After drying under vacuum, it yields 4-((4-hydroxyphenoxy)carbonyl)benzenediazonium tetrafluoroborate **1** (0.57 g, 55 %). ¹H NMR (300 MHz, CD₃CN) δ 8.64 (d, 2H), 8.57 (d, 2H), 7.12 (d, 2H), 6.91 (d, 2H).

2.2. Preparation of modified substrates.

All surface modifications were performed using a standard three-electrode setup using a potentiostat Autolab PGSTAT 302N (Metrohm). The set of electrodes consisted of glassy carbon (GC) disk electrodes (IJ Cambria, surface area 0.03 cm²) or small squares (15x15 mm²) of PPFs as working electrodes, a platinum mesh as the auxiliary electrode, and a saturated calomel electrode (SCE) as reference. All carbon electrodes were modified by cyclic voltammetry between 0.6 V and – 0.8 V vs SCE in a degassed acetonitrile solution containing 10 mM of aryl diazonium cations and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting salt. Prior to modification, commercially available GC electrodes were polished with 4000

silicon carbide abrasive discs (Struers) and ultrapure water and thoroughly rinsed with ultrapure water and acetone. PPF samples were synthesized as previously described.[49] They typically consist of squares of 15 x 15 mm². For modifying PPFs, no pre-polishing stage is necessary.

2.3. Post-functionalization protocol using carbodiimide coupling.

First, the modified carbon electrodes are immersed in a 40 mM aqueous solution of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide (10 mL) under stirring for one hour. Thereafter, they are thoroughly rinsed with pure water and then put for another hour in a 80 mM aqueous solution of N-hydroxysuccinimide (10 mL). After a thorough rinsing with pure water, the carbon electrodes were soaked overnight in a THF solution(10 mL) containing 5 mM of aminomethylferrocene.[50] The electrodes were finally rinsed with copious amount of THF and dried under a stream of Argon before any analysis. All experiments were repeated on three different electrodes each time and average surface coverage was determined.

2.4. Atomic Force Microscopy (AFM).

Atomic force microscopy (AFM) experiments were performed on modified PPF substrates using a NT-MDT Ntegra microscope. Topographic images were obtained in semi-contact mode using ACTA tips (AppNano Inc.) for which the resonance frequency is around 300 kHz. The images were treated using Gwyddion open-source software.[51] The roughness of the organic films deposited on PPF substrates was estimated, according to the standard ISO 4287/1-1997, as the average of the measured height deviations taken within the image (Root Mean Square (RMS) roughness).

2.5. Scanning Electrochemical Microscopy (SECM) and Scanning Electrochemical Cell Microscopy (SECCM).

Micropipettes were made from borosilicate glass capillaries (BF-100-58-10, Sutter Instrument) by using a CO₂ laser puller (model P-2000, Sutter Instrument). After pulling, micropipettes were soaked into polydimethylsiloxane (PDMS) with argon flowing through the micropipettes (prevented PDMS from entering the tip). This process was repeated several times to form a thin silicone rubber gasket at micropipette nozzle that enables the confinement of the meniscus cell during SECCM experiment. Micropipettes were then filled with the electrolyte solution (0.1 M nBu₄NPF₆ in MeCN) by a MicroFil (World Precision Instrument). The quasi-reference counter electrodes (QRCE) (Ag/AgCl) was placed inside the micropipette. Micropipettes were mounted on a three-axis positioner and moved toward the substrate (serving as the working electrode) at a speed of 100 nm/s until with the contact with the substrate. The voltammetry measurement was then conducted in the confined area defined by the meniscus cell between the micropipette and substrate.

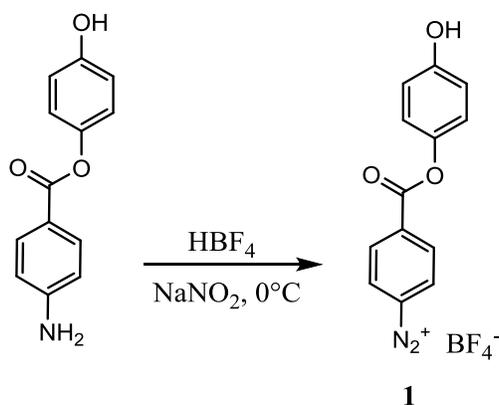
For electrochemical imaging experiments on modified PPF surfaces, SECM measurements were performed using a commercially available CH Instruments model 920C SECM. A typical three-electrode system was used, with a platinum counter electrode and an Ag/AgCl reference electrode. The microelectrode was a homemade 7- μ m-radius platinum disk with a RG value around 3, and was characterized by cyclic voltammetry using the oxidation of dopamine. The applied potential at the tip was chosen at the steady-state diffusion-controlled regime, and the substrate was not electrically connected. The approach curves were recorded on modified surfaces to characterize the local electrochemical deprotection, where the normalized current $I = i/i_{\text{inf}}$ is plotted versus the normalized distance $L = d/a$, in which i is the current at the tip electrode

localized at a distance d from the substrate, i_{inf} is the steady-state current where the tip is at an infinite distance from the substrate. For SECM imaging, the tip was maintained at a constant distance from the substrate and moved in the x,y directions.

3. Results and Discussion.

3.1. Electroreduction and organic film deposition of aryl diazonium salts bearing electro-labile protecting group.

Hydroquinone group has been identified in the literature as a good electro-labile protecting group, especially used in self-assembled monolayers, to protect carboxylic acid.[42] Currently, in order to apply a similar strategy to aryl diazonium salt electroreduction, we protected *p*-aminobenzoic acid by hydroquinone, following literature procedure.[48] In a second step, the diazotation of the corresponding aniline is performed in aqueous conditions to yield 4-((4-hydroxyphenoxy)carbonyl)benzenediazonium tetrafluoroborate **1** (**Scheme 1**).



Scheme 1. Diazotation of the hydroquinone-protected aniline

Figure 1a shows the cyclic voltammograms of the electroreduction of aryl diazonium **1** in 0.1 M TBAPF₆ acetonitrile solution onto glassy carbon electrode. During the first scan, two irreversible reduction peaks are clearly observed at 0.29 V and 0.07 V vs SCE with no oxidation peaks associated to the reduction ones. Whereas the observation of two distinct reduction peaks in aryl diazonium electroreduction has been associated to the reduction of the aryl diazonium ion on different crystal facets when considering gold electrodes, [52] in the case of carbon electrodes, the first peak has been associated to a surface-catalyzed reduction step followed by an

uncatalyzed reduction one at a more negative potential.[53] Reduction of aryl diazonium is mainly associated to the formation of aryl radicals and cleavage of N₂ groups.[1] No faradaic electrochemical activity are further observed on the second scan which is indicative of a blocked electrode by an insulating organic film. Dopamine (**Figure 1b**), ferrocene (**Figure 1c**) and potassium ferrocyanide (**Figure 1d**) were used as redox probes to characterize the blocking properties of the glassy carbon electrode before and after functionalization. On bare glassy carbon, all redox probes display classical reversible electrochemical signals centered at 0.49 V, 0.40 V and 0.26 V vs SCE for dopamine, ferrocene and potassium ferrocyanide, respectively. After electroreduction of aryl diazonium **1**, no electrochemical signal were observed with the three redox probes, indicating the presence of a dense and compact insulating organic film grafted at the surface of the carbon electrode, with no pinholes or defects. Atomic force microscopy (AFM) was used to image and estimate the thickness of the deposited organic film (see supporting information Figure S1). AFM images confirm the presence of a compact and dense organic film with a rough mean square (RMS) roughness below 1 nm which is close to the bare PPF substrate.[54] The film thickness was found to be 2.8 ± 0.3 nm, in accordance with the formation of a multilayer, as generally observed for organic films formed by aryl diazonium reduction.[1]

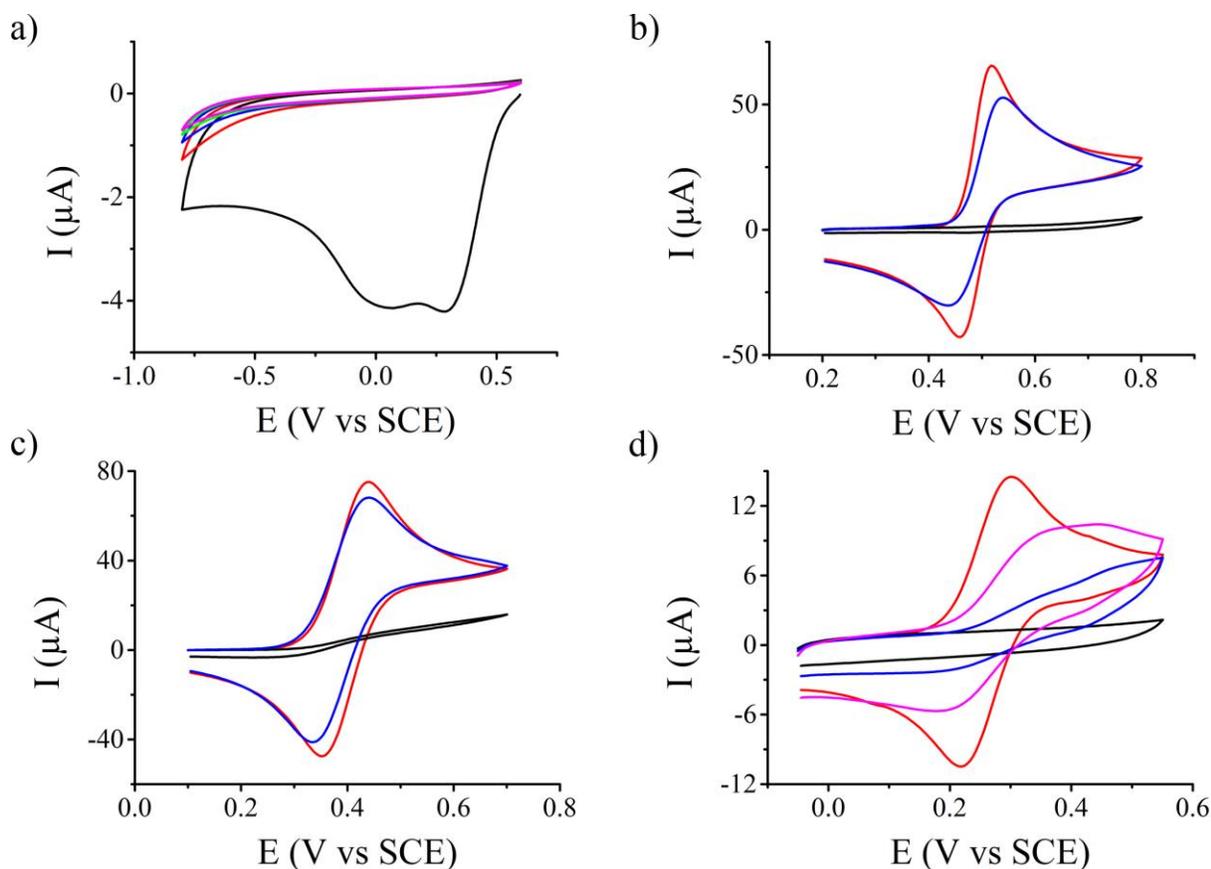


Figure 1. (a) Cyclic voltammograms of a 10^{-2} mol.L $^{-1}$ acetonitrile solution of aryl diazonium **1** containing 0.1 mol.L $^{-1}$ tetrabutylammonium hexafluorophosphate (TBAPF $_6$) as supporting electrolyte, at 50 mV.s $^{-1}$. Cyclic voltammograms of (b) dopamine, (c) ferrocene and (d) potassium ferrocyanide on bare glassy carbon (red curves), glassy carbon modified by the reduction of aryl diazonium **1** before (black curves) and after electrochemical deprotection (blue curves). Cyclic voltammogram of potassium ferrocyanide after electrochemical deprotection at pH = 1 (magenta curve).

3.2. Electrochemical deprotection of electrografted organic films.

The electrochemical deprotection of the grafted organic films was performed in a 0.1 mol.L $^{-1}$ TBAPF $_6$ acetonitrile solution. **Figure 2a** shows the electrochemical behavior of the

functionalized carbon electrode showing an irreversible oxidation peak at 1.48 V vs SCE, with no associated reduction one (**Figure 2a**, blue curve) during the first scan while no electrochemical signal can be observed on the second scan (**Figure 2a**, black dot curve). Similar experiments were performed on bare glassy carbon (**Figure 2b**, blue curve) and glassy carbon modified by the electroreduction of aryl diazonium salt bearing different functional group, namely *p*-nitrophenyl diazonium (**Figure 2b**, red curve) and 4-carboxybenzene diazonium (**Figure 2b**, green curve). No oxidation peak is observed at 1.48 V vs SCE on these different electrodes, confirming that this oxidation peak can only be associated to the electrochemical deprotection of hydroquinone groups protecting the benzoic acid moieties of the grafted organic film. The electrochemical deprotection is efficient since we cannot observed any oxidation peak during the second scan. After this electrochemical deprotection step, leaving only benzoic acid multilayer organic film onto the carbon electrode, the thickness of the organic layer was determined to be 2.2 ± 0.2 nm by AFM experiments (see supporting information Figure S2). Moreover, AFM images still show a dense and compact organic film with RMS roughness comparable (~ 0.5 nm) to the bare PPF substrate.[54]

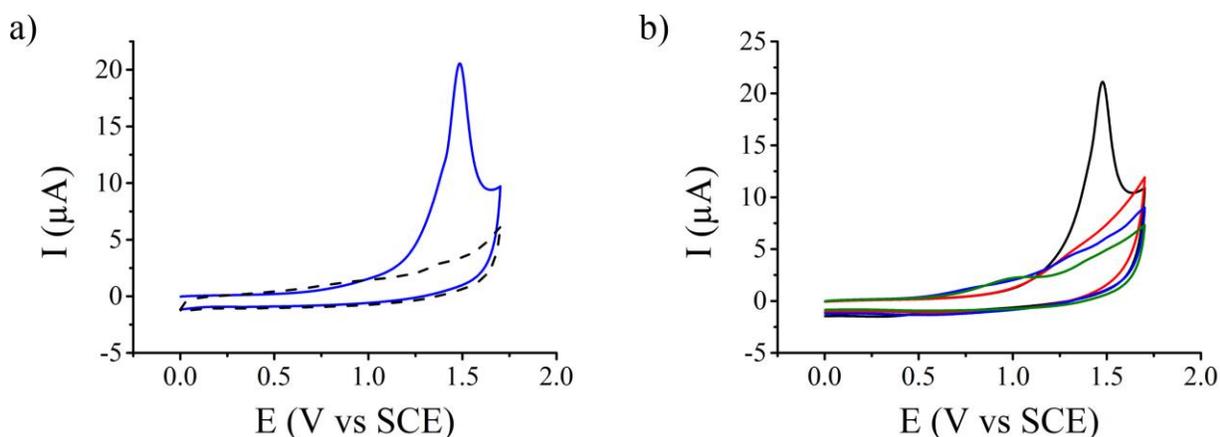


Figure 2. (a) First scan (blue line) and second scan (black dotted line) of electrochemical deprotection of a glassy carbon electrode modified by the reduction of aryl diazonium **1** in

acetonitrile solution containing 0.1 mol.L^{-1} tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting salts, at 100 mV.s^{-1} . (b) Electrochemical behavior of bare glassy carbon (blue line) and glassy carbon electrodes modified by the reduction of aryl diazonium **1** (black line), *p*-nitrophenyl diazonium (red line) and 4-carboxybenzene diazonium (green line) in an acetonitrile solution containing 0.1 mol.L^{-1} TBAPF₆ as supporting salts, at 100 mV.s^{-1} .

The blocking properties of the functionalized carbon electrodes after deprotection were examined with the same three redox probes. The electrochemical oxidation signals of dopamine and ferrocene can be partially recovered on the deprotected functionalized carbon electrode (**Figure 1b** and **1c**, blue curves). Ferrocene, an outer-sphere redox probe, can transfer charges indirectly, by tunneling through the organic layer,[55] meaning in this particular case that the partial recovery of ferrocene oxidation signal is due to decrease of the organic film thickness obtained after electrochemical deprotection. Contrary, dopamine, as an inner-sphere redox probe, needs to be adsorbed onto the electrode carbon surface to efficiently transfer its charge, by direct electron transfer. [55, 56] More precisely, dopamine electron transfer is catalyzed by oxygenated groups at the surface of carbon electrodes. Here, the electrochemical deprotection of the organic layer leads to benzoic acid terminal groups. The presence of these specific oxygenated functional groups allows dopamine to efficiently transfer its charge and is at the origin of the partial recovery of dopamine electrochemical signal. For potassium ferrocyanide, even if a small current increase can be recorded, no clear oxidation peak can be observed (**Figure 1d**, blue curve). Here, the pH of the ferrocyanide solution is not buffered but is close to 7. Once the ferrocyanide pH solution is tuned to 1 (**Figure 1d**, magenta curve), partial reappearance of ferrocyanide oxidation electrochemical signal is observed. This behavior has already been observed in the literature[21]

and is due to the expected acid-base properties of the deprotected organic layer, where electrostatic repulsion at pH 7 leads to a high blocking properties of the organic film toward ferrocyanide anion.

3.3. Post-functionalization with standard carbodiimide coupling.

Deprotection of the deposited organic film leads to benzoic acid functional groups available for post-functionalization. Carbodiimide coupling using ferrocenemethylamine has been tested as post-functionalization route. **Figure 3a** shows the cyclic voltammograms obtained at different scan rates of carbon electrode post-functionalized in these conditions. A clear reversible oxidation peak is observed at half-wave potential $E_{1/2} = 0.39$ V vs SCE with a peak-to-peak separation $\Delta E_p = 0.14$ V. The anodic and cathodic peak currents scale however linearly with the scan rate (**Figure 3b**) underlining the surface confined character of the ferrocene moieties. The surface coverage of ferrocenyl moieties immobilized onto the functionalized carbon surface, Γ , was estimated using the following equation:

$$\Gamma = 4aRT/F^2S \quad (1)$$

with a the slope of the linear variation of the peak current versus the scan rate (**Figure 3b**), R the universal gas constant, T the temperature, F the Faraday constant and S the surface area of the sample. Considering a temperature of 298 K, a ferrocene surface coverage of $\Gamma = (2.1 \pm 0.1) \times 10^{-10}$ mol.cm⁻² is estimated. This is close to the maximum theoretical surface coverage of ferrocene moieties that can be immobilized in a close packing lattice ($\Gamma_{\max} = 4.5 \times 10^{-10}$ mol.cm⁻²).^[57] For comparison, similar post-functionalization was performed on carbon electrodes modified by the electroreduction of 4-carboxybenzene diazonium (see supporting information Figure S3). A ferrocene surface coverage of $\Gamma = (6.6 \pm 0.9) \times 10^{-11}$ mol.cm⁻² is estimated. This

lower surface coverage can be easily explained by the high reactivity of aryl radicals formed during the electrografting process. They could attack the grafted carboxylic functions that can no longer be available for carbodiimide coupling, whereas the carboxylic functions are protected when using aryl diazonium ion **1**.

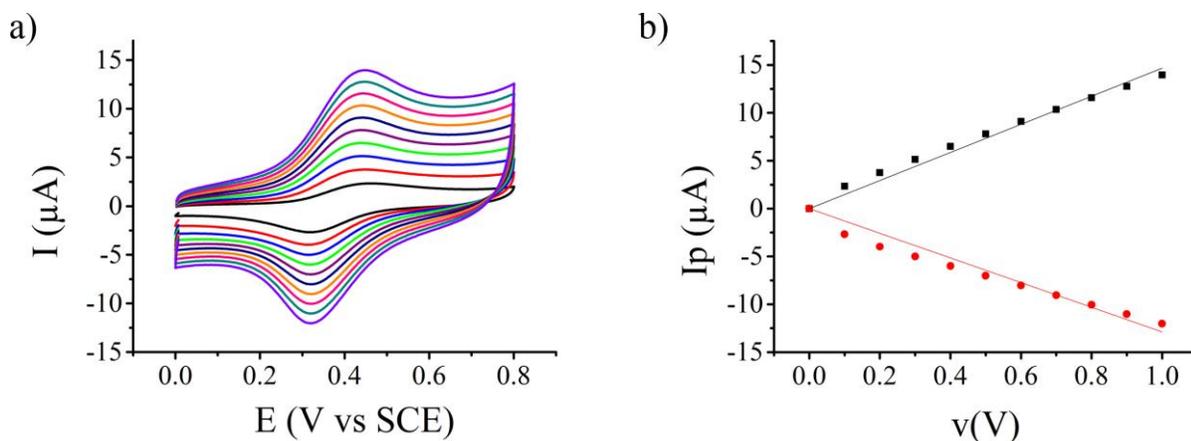


Figure 3. (a) Cyclic voltammograms of a glassy carbon electrode post-functionalized by carbodiimide coupling using ferrocenemethylamine in an ethanol solution containing $0.1 \text{ mol}\cdot\text{L}^{-1}$ LiClO_4 as supporting electrolyte. (b) Variation of the anodic and cathodic peak currents with scan rate recorded at the post-functionalized glassy carbon electrode. Red lines are linear fitting curves.

3.4. Patterning of the organic film.

Scanning electrochemical cell microscopy (SECCM) was used to locally deprotect and pattern the electrolabile organic film. Briefly, in SECCM, the electrochemical cell is determined by the meniscus or droplet at the end of a micropipette in contact with the substrate that serves as working electrode while the counter and reference electrodes are located in the micropipette.[58]

In SECCM, the size of the electrochemical cell is thus directly proportional to the size of the micropipette radius tip. In the present study, the electrochemical deprotection of the electrolabile organic film was confined to the micrometer scale using SECCM by cyclic voltammetry as determined above. The patterning of the substrate was achieved by successive electrochemical deprotection while moving the SECCM tip at different locations onto the substrate.[59] **Figure 4a** shows an example of the local electrochemical deprotection performed by SECCM on an electrolabile organic film deposited on carbon substrate. The electrochemical response is similar to what was observed previously at the macroscopic scale (**Figure 2a**) with a clear irreversible oxidation peak observed at ~ 1.55 V vs Ag during the first scan and no electrochemical signal during the second scan.

To demonstrate the local modification of the substrate, we used scanning electrochemical microscopy (SECM). First, we used SECM in feedback mode to probe the local electrochemical deprotection. In SECM, the active form of a redox species (redox mediator) is produced at the tip electrode of the SECM maintained at the vicinity of the surface under analysis. After diffusion to the sample, the interactions of the mediator with the surface are read from the variations of the tip current when the tip approaches the sample. We have used dopamine as redox mediator in these experiments as we show above that this redox species is especially sensitive to the surface functionalization and deprotection developed in this study (**Figure 1b**). Also, we have previously shown that dopamine is a highly sensitive redox probe in SECM able to probe ultrathin organic films.[60] **Figure 4b** shows the SECM approach curves in feedback mode performed on carbon substrate functionalized by the reduction of electrolabile aryl diazonium salts **1** before and after electrochemical deprotection by SECCM. Negative feedback is clearly observed once the carbon surface is functionalized by the reduction of aryl diazonium salt **1** whereas positive feedback is

recorded on the same surface after electrochemical deprotection. These behaviors are in fair agreement with the ones observed using cyclic voltammetry (**Figure 1b**) and allow us to use dopamine as a sensitive redox probe for SECM imaging of the organic film.

We patterned the organic film using SECCM with a “XMU” motif. The pattern was made by (i) first approaching the SECCM tip that the meniscus is in contact with the surface, (ii) performing local electrochemical deprotection by cyclic voltammetry, then (iii) lift up the SECCM tip and finally (iv) moving it to another location. This multistep process was preferred to avoid any damage due to surface tilt. Hence, the “XMU” motif is composed of multiple dots. SECM imaging with dopamine (**Figure 4c**) clearly highlights the efficient SECCM electrochemical patterning of the electrolabile organic film.

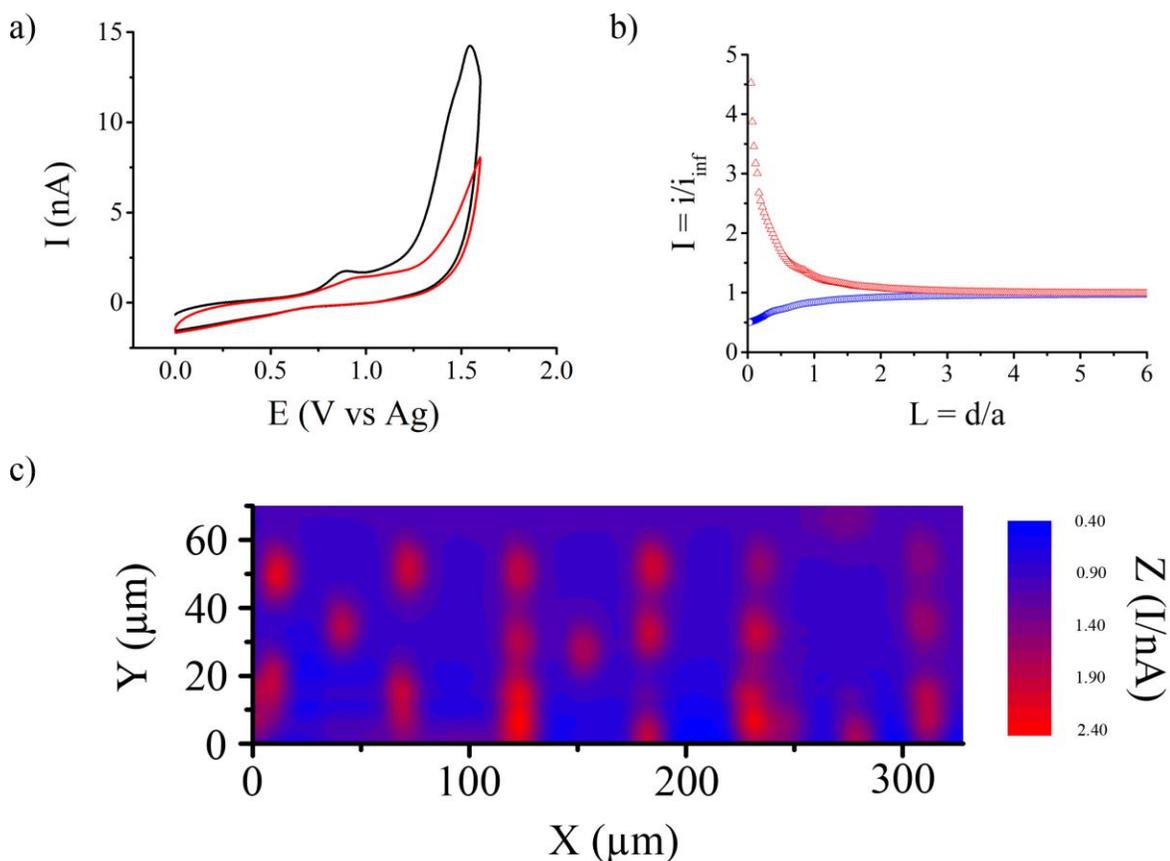


Figure 4. (a) First scan (black line) and second scan (red line) of local electrochemical deprotection using SECCM set up of a carbon electrode modified by the reduction of aryl diazonium **1** in acetonitrile solution containing 0.1 mol.L^{-1} tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte, with a $15 \text{ }\mu\text{m}$ pipette tip radius at 100 mV.s^{-1} . (b) SECM approach curves on carbon substrate modified by the reduction of aryl diazonium **1** before (\circ) and after deprotection (Δ) using dopamine (1 mM) as redox probe in a 0.1 mol.L^{-1} H₂SO₄ solution. (c) SECM image recorded with dopamine (1 mM) in 0.1 mol.L^{-1} H₂SO₄ solution after patterning with SECCM a “XMU” motif. Scale bar represents the normalized current $I = i/i_{\text{inf}}$.

4. Conclusion.

We present in this study the synthesis and electrochemical properties of a specially designed aryl diazonium salt bearing an electrolabile protecting group. Its electroreduction leads to the deposition of a multilayer organic film that is efficiently deprotected by electrochemically applying an oxidative potential in organic solution. Post-functionalization of the obtained benzoic acid film is demonstrated with a ferrocenyl derivative as a proof-of-concept showing a high surface coverage of the modifier. Finally, the patterning of the deposited organic layer is demonstrated using scanning electrochemical cell microscopy (SECCM). Image of the patterned layer is obtained via scanning electrochemical microscopy (SECM) using dopamine as redox probe highlighting the efficiency and versatility of the present strategy to obtain patterned ultrathin organic layer onto carbon materials.

ASSOCIATED CONTENT

Supporting Information. Atomic force microscopy (AFM) and electrochemical data are available free of charge.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

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REFERENCES

- [1] J. Pinson, F. Podvorica, Attachment of organic layers to conductive or semiconductive surfaces by reduction of diazonium salts, *Chemical Society Reviews*, 34 (2005) 429-439.
- [2] D. Bélanger, J. Pinson, Electrografting: a powerful method for surface modification, *Chemical Society Reviews*, 40 (2011) 3995-4048.
- [3] M. Delamar, R. Hitmi, J. Pinson, J.M. Saveant, Covalent modification of carbon surfaces by grafting of functionalized aryl radicals produced from electrochemical reduction of diazonium salts, *Journal of the American Chemical Society*, 114 (1992) 5883-5884.
- [4] J.M. Hicks, Z.Y. Wong, D.J. Scurr, N. Silman, S.K. Jackson, P.M. Mendes, J.W. Aylott, F.J. Rawson, Tailoring the Electrochemical Properties of Carbon Nanotube Modified Indium Tin Oxide via in Situ Grafting of Aryl Diazonium, *Langmuir*, 33 (2017) 4924-4933.
- [5] J.K. Kariuki, M.T. McDermott, Formation of Multilayers on Glassy Carbon Electrodes via the Reduction of Diazonium Salts, *Langmuir*, 17 (2001) 5947-5951.
- [6] C. Cao, Y. Zhang, C. Jiang, M. Qi, G. Liu, Advances on Aryldiazonium Salt Chemistry Based Interfacial Fabrication for Sensing Applications, *ACS Applied Materials & Interfaces*, 9 (2017) 5031-5049.
- [7] C. Fairman, J.Z. Ginges, S.B. Lowe, J.J. Gooding, Protein Resistance of Surfaces Modified with Oligo(Ethylene Glycol) Aryl Diazonium Derivatives, *ChemPhysChem*, 14 (2013) 2183-2189.

- [8] C. Combellas, M. Delamar, F. Kanoufi, J. Pinson, F.I. Podvorica, Spontaneous Grafting of Iron Surfaces by Reduction of Aryldiazonium Salts in Acidic or Neutral Aqueous Solution. Application to the Protection of Iron against Corrosion, *Chemistry of Materials*, 17 (2005) 3968-3975.
- [9] T. Menanteau, C. Benoît, T. Breton, C. Cougnon, Enhancing the performance of a diazonium-modified carbon supercapacitor by controlling the grafting process, *Electrochemistry Communications*, 63 (2016) 70-73.
- [10] Y. Aceta, Y.R. Leroux, P. Hapiot, Evaluation of Alkyl-Ferrocene Monolayers on Carbons for Charge Storage Applications, a Voltammetry and Impedance Spectroscopy Investigation, *ChemElectroChem*, 6 (2019) 1704-1710.
- [11] D. Schaming, V.-Q. Nguyen, P. Martin, J.-C. Lacroix, Tunable Plasmon Resonance of Gold Nanoparticles Functionalized by Electroactive Bisthienylbenzene Oligomers or Polythiophene, *The Journal of Physical Chemistry C*, 118 (2014) 25158-25166.
- [12] V. Stockhausen, P. Martin, J. Ghilane, Y. Leroux, H. Randriamahazaka, J. Grand, N. Felidj, J.C. Lacroix, Giant Plasmon Resonance Shift Using Poly(3,4-ethylenedioxythiophene) Electrochemical Switching, *Journal of the American Chemical Society*, 132 (2010) 10224-10226.
- [13] H. Yan, A.J. Bergren, R.L. McCreery, All-Carbon Molecular Tunnel Junctions, *Journal of the American Chemical Society*, 133 (2011) 19168-19177.
- [14] S.Y. Sayed, A. Bayat, M. Kondratenko, Y. Leroux, P. Hapiot, R.L. McCreery, Bilayer Molecular Electronics: All-Carbon Electronic Junctions Containing Molecular Bilayers Made with “Click” Chemistry, *Journal of the American Chemical Society*, 135 (2013) 12972-12975.
- [15] L.T. Nielsen, K.H. Vase, M. Dong, F. Besenbacher, S.U. Pedersen, K. Daasbjerg, Electrochemical Approach for Constructing a Monolayer of Thiophenolates from Grafted Multilayers of Diaryl Disulfides, *Journal of the American Chemical Society*, 129 (2007) 1888-1889.
- [16] K. Malmos, M. Dong, S. Pillai, P. Kingshott, F. Besenbacher, S.U. Pedersen, K. Daasbjerg, Using a Hydrazone-Protected Benzenediazonium Salt to Introduce a Near-Monolayer of Benzaldehyde on Glassy Carbon Surfaces, *Journal of the American Chemical Society*, 131 (2009) 4928-4936.
- [17] C. Combellas, F. Kanoufi, J. Pinson, F.I. Podvorica, Sterically Hindered Diazonium Salts for the Grafting of a Monolayer on Metals, *Journal of the American Chemical Society*, 130 (2008) 8576-8577.
- [18] C. Lagrost, Y. Leroux, P. Hapiot, Localized Electrochemistry for Studying Functional Carbon Surfaces, *Electroanalysis*, 28 (2016) 2680-2687.
- [19] P. Hapiot, C. Lagrost, Y.R. Leroux, Molecular nano-structuration of carbon surfaces through reductive diazonium salts grafting, *Current Opinion in Electrochemistry*, 7 (2018) 103-108.
- [20] L. Lee, Y.R. Leroux, P. Hapiot, A.J. Downard, Amine-Terminated Monolayers on Carbon: Preparation, Characterization, and Coupling Reactions, *Langmuir*, 31 (2015) 5071-5077.
- [21] L. Lee, H. Ma, P.A. Brooksby, S.A. Brown, Y.R. Leroux, P. Hapiot, A.J. Downard, Covalently Anchored Carboxyphenyl Monolayer via Aryldiazonium Ion Grafting: A Well-Defined Reactive Tether Layer for On-Surface Chemistry, *Langmuir*, 30 (2014) 7104-7111.
- [22] V.Q. Nguyen, X. Sun, F. Lafolet, J.-F. Audibert, F. Miomandre, G. Lemerrier, F. Loiseau, J.-C. Lacroix, Unprecedented Self-Organized Monolayer of a Ru(II) Complex by Diazonium Electroreduction, *Journal of the American Chemical Society*, 138 (2016) 9381-9384.

- [23] A. Mattiuzzi, I. Jabin, C. Mangeney, C. Roux, O. Reinaud, L. Santos, J.-F. Bergamini, P. Hapiot, C. Lagrost, Electrografting of calix[4]arene diazonium salts to form versatile robust platforms for spatially controlled surface functionalization, *Nature Communications*, 3 (2012) 1130.
- [24] T. Menanteau, E. Levillain, T. Breton, Electrografting via Diazonium Chemistry: From Multilayer to Monolayer Using Radical Scavenger, *Chemistry of Materials*, 25 (2013) 2905-2909.
- [25] A. Garcia, N. Hanifi, B. Jousselme, P. Jégou, S. Palacin, P. Viel, T. Berthelot, Polymer Grafting by Inkjet Printing: A Direct Chemical Writing Toolset, *Advanced Functional Materials*, 23 (2013) 3668-3674.
- [26] D.J. Garrett, J. Lehr, G.M. Miskelly, A.J. Downard, Microcontact Printing Using the Spontaneous Reduction of Aryldiazonium Salts, *Journal of the American Chemical Society*, 129 (2007) 15456-15457.
- [27] V.-Q. Nguyen, D. Schaming, D.L. Tran, J.-C. Lacroix, Ordered Nanoporous Thin Films by Nanosphere Lithography and Diazonium Electroreduction: Simple Elaboration of Ultra-Micro-Electrode Arrays, *ChemElectroChem*, 3 (2016) 2264-2269.
- [28] C. Cougnon, F. Gohier, D. Bélanger, J. Mauzeroll, In Situ Formation of Diazonium Salts from Nitro Precursors for Scanning Electrochemical Microscopy Patterning of Surfaces, *Angewandte Chemie International Edition*, 48 (2009) 4006-4008.
- [29] F.G. Julienne Charlier, Achraf Ghorbal, Cédric Goyer, Serge Palacin, Localized Electrografting of Diazonium Salts in the SECM Environment, *Materials Science Forum*, 730-732 (2013) 221.226.
- [30] F. Grisotto, A. Ghorbal, C. Goyer, J. Charlier, S. Palacin, Direct SECM Localized Electrografting of Vinyllic Monomers on a Conducting Substrate, *Chemistry of Materials*, 23 (2011) 1396-1405.
- [31] A. Ghorbal, F. Grisotto, J. Charlier, S. Palacin, C. Goyer, C. Demaille, Localized Electrografting of Vinyllic Monomers on a Conducting Substrate by Means of an Integrated Electrochemical AFM Probe, *ChemPhysChem*, 10 (2009) 1053-1057.
- [32] A. Ghorbal, F. Grisotto, J. Charlier, S. Palacin, C. Goyer, C. Demaille, A.B. Brahim, Nano-Electrochemistry and Nano-Electrografting with an Original Combined AFM-SECM, *Nanomaterials*, 2013, pp. 303-316.
- [33] P.A. Brooksby, A.J. Downard, Nanoscale Patterning of Flat Carbon Surfaces by Scanning Probe Lithography and Electrochemistry, *Langmuir*, 21 (2005) 1672-1675.
- [34] L. Stratmann, J. Clausmeyer, W. Schuhmann, Non-destructive Patterning of Carbon Electrodes by Using the Direct Mode of Scanning Electrochemical Microscopy, *ChemPhysChem*, 16 (2015) 3477-3482.
- [35] J. Clausmeyer, J. Henig, W. Schuhmann, N. Plumeré, Scanning Droplet Cell for Chemoselective Patterning through Local Electroactivation of Protected Quinone Monolayers, *ChemPhysChem*, 15 (2014) 151-156.
- [36] D. Quinton, A. Maringa, S. Griveau, T. Nyokong, F. Bedioui, Surface patterning using scanning electrochemical microscopy to locally trigger a “click” chemistry reaction, *Electrochemistry Communications*, 31 (2013) 112-115.
- [37] S. Lhenry, Y.R. Leroux, C. Orain, F. Conan, N. Cosquer, N.L. Poul, O. Reinaud, Y.L. Mest, P. Hapiot, Locally Induced and Self-Induced “Electroclick” onto a Self-Assembled Monolayer: Writing and Reading with SECM under Unbiased Conditions, *Langmuir*, 30 (2014) 4501-4508.

- [38] R.K. Smith, P.A. Lewis, P.S. Weiss, Patterning self-assembled monolayers, *Progress in Surface Science*, 75 (2004) 1-68.
- [39] C.D. Hodneland, M. Mrksich, Design of Self-Assembled Monolayers That Release Attached Groups Using Applied Electrical Potentials, *Langmuir*, 13 (1997) 6001-6003.
- [40] M.N. Yousaf, B.T. Houseman, M. Mrksich, Turning On Cell Migration with Electroactive Substrates, *Angewandte Chemie International Edition*, 40 (2001) 1093-1096.
- [41] W.-S. Yeo, M. Mrksich, Electroactive Self-Assembled Monolayers that Permit Orthogonal Control over the Adhesion of Cells to Patterned Substrates, *Langmuir*, 22 (2006) 10816-10820.
- [42] K. Kim, H. Yang, E. Kim, Y.B. Han, Y.T. Kim, S.H. Kang, J. Kwak, Electrochemical Deprotection for Site-Selective Immobilization of Biomolecules, *Langmuir*, 18 (2002) 1460-1462.
- [43] K. Kim, M. Jang, H. Yang, E. Kim, Y.T. Kim, J. Kwak, Electrochemically Induced and Controlled One-Step Covalent Coupling Reaction on Self-Assembled Monolayers, *Langmuir*, 20 (2004) 3821-3823.
- [44] W.S. Yeo, M. Mrksich, Electroactive Substrates that Reveal Aldehyde Groups for Bio-Immobilization, *Advanced Materials*, 16 (2004) 1352-1356.
- [45] M. Curreli, C. Li, Y. Sun, B. Lei, M.A. Gundersen, M.E. Thompson, C. Zhou, Selective Functionalization of In₂O₃ Nanowire Mat Devices for Biosensing Applications, *Journal of the American Chemical Society*, 127 (2005) 6922-6923.
- [46] Y.L. Bunimovich, G. Ge, K.C. Beverly, R.S. Ries, L. Hood, J.R. Heath, Electrochemically Programmed, Spatially Selective Biofunctionalization of Silicon Wires, *Langmuir*, 20 (2004) 10630-10638.
- [47] M. Hellstern, M. Gantenbein, L. Le Pleux, G. Puebla-Hellmann, E. Lörtscher, M. Mayor, Electrochemical Multiplexing: Control over Surface Functionalization by Combining a Redox-Sensitive Alkyne Protection Group with “Click”-Chemistry, *Advanced Materials Interfaces*, 6 (2019) 1801917.
- [48] H. Ebadi, S. Mehdipour-Ataei, Heat-resistant, pyridine-based polyamides containing ether and ester units with improved solubility, *Chinese Journal of Polymer Science*, 28 (2009) 29.
- [49] Y. Aceta, P. Hapiot, Y.R. Leroux, Investigation of Protective Properties of Organic Layers toward Reactive Oxygen Species, *Langmuir*, 35 (2019) 16210-16216.
- [50] A. Baramee, A. Coppin, M. Mortuaire, L. Pelinski, S. Tomavo, J. Brocard, Synthesis and in vitro activities of ferrocenic aminohydroxynaphthoquinones against *Toxoplasma gondii* and *Plasmodium falciparum*, *Bioorganic & Medicinal Chemistry*, 14 (2006) 1294-1302.
- [51] Gwyddion Open Source Software.
- [52] A. Benedetto, M. Balog, P. Viel, F. Le Derf, M. Sallé, S. Palacin, Electro-reduction of diazonium salts on gold: Why do we observe multi-peaks?, *Electrochimica Acta*, 53 (2008) 7117-7122.
- [53] L. Lee, P.A. Brooksby, P. Hapiot, A.J. Downard, Electrografting of 4-Nitrobenzenediazonium Ion at Carbon Electrodes: Catalyzed and Uncatalyzed Reduction Processes, *Langmuir*, 32 (2016) 468-476.
- [54] Y.R. Leroux, H. Fei, J.-M. Noël, C. Roux, P. Hapiot, Efficient Covalent Modification of a Carbon Surface: Use of a Silyl Protecting Group To Form an Active Monolayer, *Journal of the American Chemical Society*, 132 (2010) 14039-14041.
- [55] R.L. McCreery, *Advanced Carbon Electrode Materials for Molecular Electrochemistry*, *Chemical Reviews*, 108 (2008) 2646-2687.

- [56] S.H. DuVall, R.L. McCreery, Control of Catechol and Hydroquinone Electron-Transfer Kinetics on Native and Modified Glassy Carbon Electrodes, *Analytical Chemistry*, 71 (1999) 4594-4602.
- [57] K. Seo, I.C. Jeon, D.J. Yoo, Electrochemical Characteristics of Ferrocenecarboxylate-Coupled Aminoundecylthiol Self-Assembled Monolayers, *Langmuir*, 20 (2004) 4147-4154.
- [58] N. Ebejer, A.G. Güell, S.C.S. Lai, K. McKelvey, M.E. Snowden, P.R. Unwin, Scanning Electrochemical Cell Microscopy: A Versatile Technique for Nanoscale Electrochemistry and Functional Imaging, *Annual Review of Analytical Chemistry*, 6 (2013) 329-351.
- [59] P.M. Kirkman, A.G. Güell, A.S. Cuharuc, P.R. Unwin, Spatial and Temporal Control of the Diazonium Modification of sp² Carbon Surfaces, *Journal of the American Chemical Society*, 136 (2014) 36-39.
- [60] S. Lhenry, Y.R. Leroux, P. Hapiot, Use of Catechol As Selective Redox Mediator in Scanning Electrochemical Microscopy Investigations, *Analytical Chemistry*, 84 (2012) 7518-7524.