Electrografting via Diazonium Chemistry: From Multilayer to Monolayer Using Radical Scavenger

DATASET · JULY 2013

3 AUTHORS, INCLUDING:

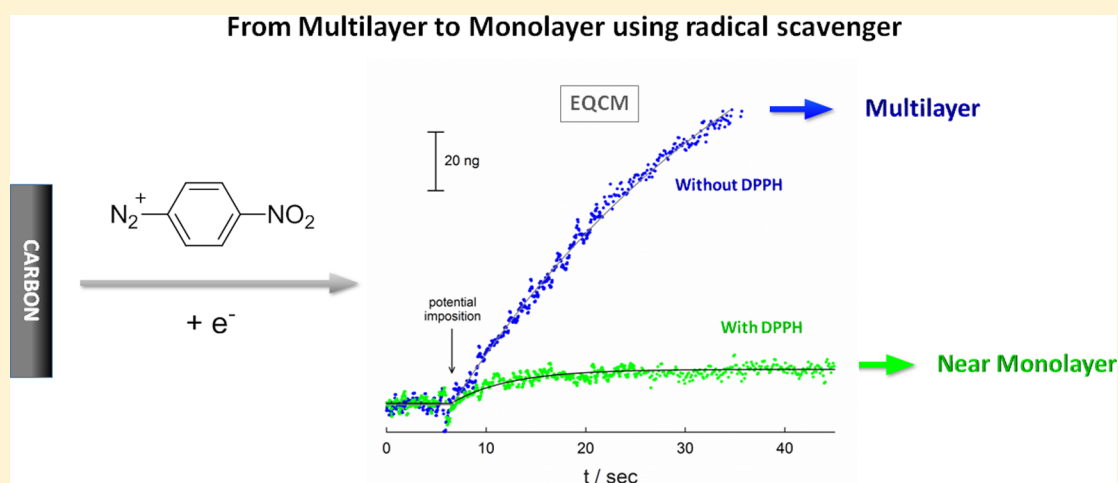Tony Breton
University of Angers
32 PUBLICATIONS **321** CITATIONS

Electrografting via Diazonium Chemistry: From Multilayer to Monolayer Using Radical Scavenger

Thibaud Menanteau, Eric Levillain, and Tony Breton*

MOLTECH-Anjou, Université d'Angers, UMR CNRS 6200, 2 Boulevard Lavoisier, 49045 Angers, France

Ⓢ *Supporting Information*

ABSTRACT: A simple strategy to avoid the formation of polyaryl layer during the functionalization of carbon surface by diazonium electroreduction is presented. The approach proposes to directly act on the polymerization mechanism by the use of a radical scavenger. The kinetic gap between the surface coupling and the multilayer formation is exploited to prevent the growth of the layer without interfering with the grafting. The well-known 4-nitrobenzenediazonium electrografting was used to demonstrate the possibility of reaching a monolayer surface coverage with an excess of DPPH (2,2-diphenyl-1-picrylhydrazyl). Experimental conditions were varied to validate the efficiency of the grafting limitation and the radical capture was confirmed by isolation of the aryl radical/DPPH coupling product.

KEYWORDS: *Surface functionalization, DPPH, diazonium reduction, radical capture*

■ INTRODUCTION

Electrografting of organic structures using diazonium chemistry is a recognized method for obtaining functionalized surfaces.[1] Various conducting materials such as metals[2] and carbon[3] can be modified in aprotic or aqueous media, and provide covalently tethered layers.[4] The efficiency of this grafting process rests upon the high reactivity of the aryl radicals produced at the electrode−solution interface.[5] This reactivity leads to the generation of polyaryl layers via the radicalar attack of already grafted aryl species on the surface.[6] Consequently, the method routinely provides disordered organic films having a thickness varying from 1 to 50 nm.[2,7] The lack of control, in terms of thickness and organization, represents the major drawback of this elegant and versatile technique. However, examples of monolayer grafting were reported by careful control of the consumed charge[8a,b] or by using viqueous ionic liquid to minimize the diffusion during the electroreduction.[8c,d] Since the past few years, the main approach developed to avoid the formation of multilayers and obtain controlled organic films is based on the use of sterically hindered aryldiazonium cations.

In this way, the blocking of aryl-reactive positions by bulky substituents[9] and the use of protected diazonium[10a−d] were reported to generate very thin films and demonstrate the validity of such structural approach to act on the grafting process.

In the present paper, we propose to directly intervene on the grafting mechanism using a radical scavenger to control, or prevent, the polymerization of the electrogenerated aryl radicals on a carbon electrode. Previous works reported the use of radical scavengers to evidence mechanistic aspects of the grafting, and they noted the surface modification cannot be completely suppressed.[11a,b] We speculated that it should be possible to exploit the difference of kinetics between the radical/surface (grafting) and radical/aryl (polymerization) reactions. Because the reactive radical species are produced at the electrode−solution interface, the kinetics of the coupling
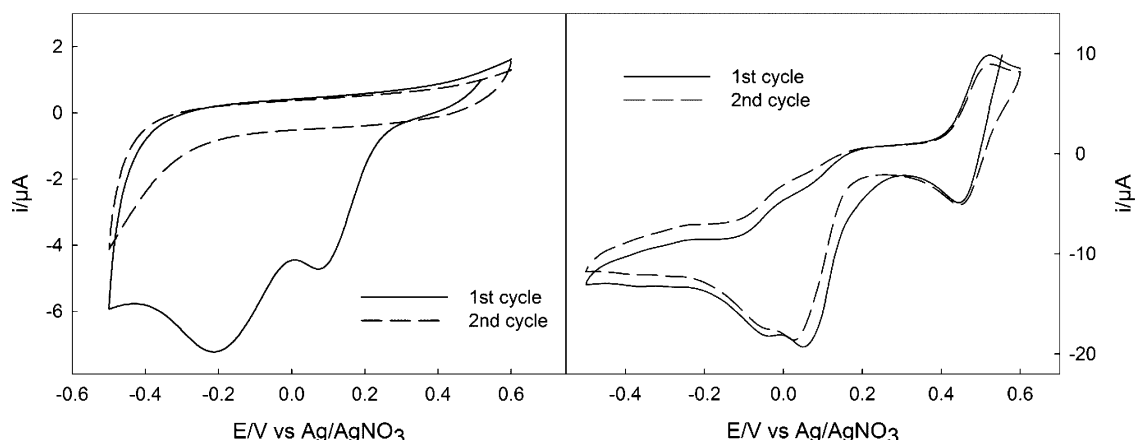
Figure 1. First and second CV cycle recorded in CH_3CN 0.1 nBu_4NPF_6 containing 1 mM of 4-nitrobenzenediazonium on a glassy carbon (GC) electrode at 50 mV/s without DPPH (left) and with 1 mM of DPPH (right).

should be greatly favored compared to the polymerization mechanism, which involves reactions further from the surface. The introduction of an appropriate amount of radical scavenger is expected to prevent the attack of grafted species by electrogenerated aryl radicals, without interfering with the direct grafting process.

■ EXPERIMENTAL SECTION

4-Nitrobenzenediazonium tetrafluoroborate, 2,2-diphenyl-1-picrylhydrazyl, and 4-bromobenzenediazonium tetrafluoroborate were used as received from Aldrich. Glassy carbon electrodes were obtained from Bioanalytical Systems Inc. (Model MF-2012; diameter 3 mm). All potentials were reported versus a Ag/AgCl (sat. KCl) reference electrode in aqueous medium and $Ag/AgNO_3$ (10 mM) in organic medium. The glassy carbon electrode surface was cleaned by polishing with Buehler 1 and 0.05 μm alumina slurry. After each polishing step the electrode was washed with Nanopure water (18.2 MΩ·cm) by sonication. Prior to and after each electrochemical derivatization, the electrode was sonicated in acetonitrile for 1 min. Modification of electrodes was as follows: modified glassy carbon electrodes were prepared at fixed potential or by recording cyclic voltammetry (CV) at 50 mV/s in deaerated acetonitrile containing 0.1 M nBu_4NPF_6 and 1 mM diazonium salt (20 mL cell). A potentiostat/galvanostat model VSP (from Bio-Logic) monitored by ECLab software was used for the electrochemical experiments. Electrochemical impedance spectroscopy (EIS) measurements were performed at open circuit potential in 5 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, 0.1 M KCl. The frequency range was 1 MHz to 2 Hz, using a 20 mV sine wave amplitude. Electrochemical quartz crystal microbalance (EQCM) measurements were performed with a QCA922 (Seiko-EG&G, Princeton Applied Research) associated to carbon-coated quartz crystal (Biologic).

■ RESULTS AND DISCUSSION

4-Nitrobenzenediazonium is undoubtedly the most studied of the functionalized diazoniums.[4,7,12a−i] Its simple structure allows generation of densely packed film under very mild potential conditions and the electroresponsive nitro group can serve as immobilized redox probe to estimate the surface coverage.[7,12h] Cyclic voltammograms on vitreous carbon electrode in the presence of a millimolar solution of 4-nitrobenzenediazonium tetrafluoroborate in acetonitrile/

nBu_4NPF_6 (0.1 M) was recorded without and with 2,2-diphenyl-1-picrylhydrazyl (DPPH), used as radical scavenger (Figure 1). A characteristic reduction behavior (peaks at +0.07 and −0.21 V) was observed in the absence of DPPH. The strong electrode passivation recorded for the second and subsequent cycles is consistent with the grafting process.[5] When one DPPH equivalent is added, the reduction corresponding to the anion formation (DPPH → DPPH⁻) is observed at −0.06 V, superimposed on the diazonium reduction peaks. The reversible oxidation of DPPH into DPPH⁺ is also observed at +0.48 V (the CV of DPPH in solution is presented in the Supporting Information, Figure S1). A weak passivation is visible when repetitive cycles are recorded, consistent with a thin coverage of the surface.

Figure 2 presents frequency−time curves recorded during the modification of a carbon-coated quartz at a fixed potential of
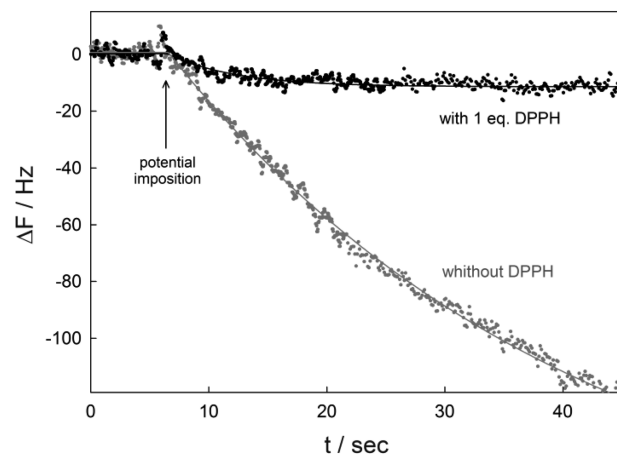

Figure 2. Frequency variation vs time on a carbon quartz measured by EQCM for the electrochemical grafting using 4-nitrobenzenediazonium (1 mM) at a fixed potential of −0.5 V without DPPH (gray plot) and with 1 mM DPPH (black plot). Data are fitted using the Langmuir model (solid lines).

−0.5 V using EQCM. The mass increase obtained without radical scavenger fits with previously reported results on such coated quartz, with a deposition rate of 0.39 mol·s⁻¹·cm⁻² at the initial stage and an absence of stabilization, traducing a continuous grafting.[13] In the presence of one DPPH equivalent, the frequency−time curve drastically differs. First, the grafting

rate is lower (0.16 mol·s^{-1}·cm^{-2} at initial stage), and second, the deposited mass reaches a maximum and steady-state value after 20 s. The calculated surface coverage extracted from this mass plateau is 5.7×10^{-10} mol·cm^{-2}, which corresponds to a monolayer equivalent for an aryl structure.[14]

To further characterize the grafted layer, voltammetric study of modified electrodes was performed in 0.1 M KOH to obtain information from the electroresponsive nitrophenyl group.[12e] Figure 3 shows cyclic voltammograms of a carbon electrode
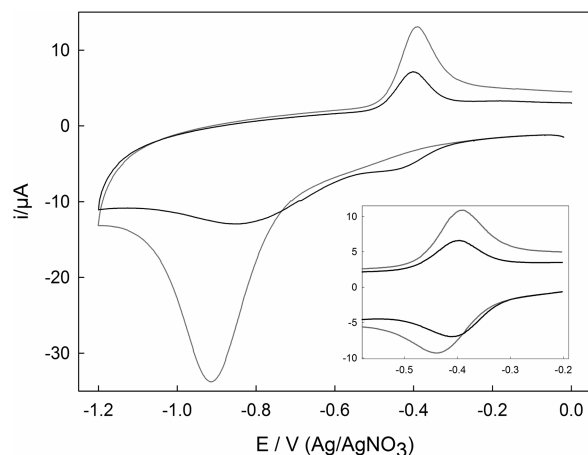

Figure 3. First CV recorded in aqueous 0.1 M KOH on a modified GC electrode at 50 mV/s. Grafting was achieved at -0.5 V for 30 s in the presence of 1 mM 4-nitrobenzenediazonium without (gray line) and with 1 mM DPPH (black line). Inset: second voltammetric cycle.

modified at -0.5 V for 30 s without and with 1 mM DPPH. During the first scan, the reduction of the Ar$-$NO$_2$ function can be visualized at -0.92 V (-0.84 V with DPPH). During the positive scan, the two-electron reoxidation of Ar$-$NHOH into Ar$-$NO is observed at 0.4 V. It is well-known that, in acidic conditions, the nitrophenyl group (Ar$-$NO$_2$) is partially electroreduced into aminophenyl (Ar$-$NH$_2$), leading to a variable composition of Ar$-$NH$_2$ (six-electron process) and Ar$-$NHOH (four-electron process).[12a,15] However, under our alkaline conditions, the ratio between the integrated charges of the Ar$-$NO$_2$ reduction peak and Ar$-$NHOH reoxidation peak (two electrons to Ar$-$NO) was close to 1.9 and independent of the DPPH concentration (see the Supporting Information, Figure S2). This feature indicates that the electroreduction stopped at the Ar$-$NHOH stage, allowing a reoxidation of the totality of the grafted species during the positive sweep. Under such conditions, the surface coverage can be calculated from the reversible Ar$-$NHOH/Ar$-$NO electrochemical system identified on the second cycle (Figure 3, inset).

Without radical scavenger, a value of 17.5×10^{-10} mol·cm^{-2} is calculated. This surface coverage corresponds to a multilayer deposition, in accordance with EQCM measurements. Note that a higher coverage can be calculated from the gravimetric data (29×10^{-10} mol·cm^{-2} for a 30 s deposition time), what could be interpreted as an incomplete electroactivity of the nitro species inside the layer, as previously reported.[16] With a millimolar concentration of DPPH in solution, a surface coverage of 6.7×10^{-10} mol·cm^{-2} is found. This value is consistent with a near monolayer and in fair agreement with EQCM data. The slight difference observed with data obtained by Downard and co-worker[7] on flat pyrolytic photoresist film (i.e., $2.5 \pm 0.5 \times 10^{-10}$ mol·cm^{-2}) could be assigned to the

roughness of our polished carbon. Furthermore, the peak to peak separation between oxidation and reduction peaks varies from 47 mV without DPPH to only 9 mV when DPPH is used. This evolution, significant of a change in the electron-transfer rate constant, could be interpreted as a decrease of the electroactive layer thickness and/or a more favorable organization of the nitrophenyl group when the modification is achieved in the presence of DPPH.

A better understanding of the radical scavenger role in the grafting process can be undertaken by varying the concentration of DPPH in the deposition solution. Voltametric data presented in Figure 4 show the electrode response for
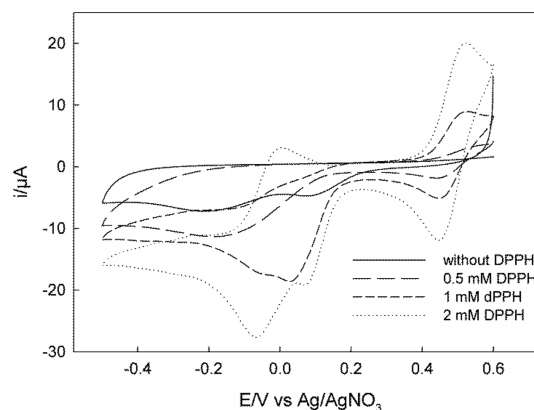

Figure 4. First CV cycle recorded in CH$_3$CN 0.1 nBu$_4$PF$_6$ containing 1 mM 4-nitrobenzenediazonium on a GC electrode at 50 mV/s without DPPH and with various DPPH concentrations.

increasing DPPH concentrations. The two DPPH reversible redox systems superimposed to the diazonium reduction signal are clearly observed. In Figure 5 (left), the surface coverage, determined via the Ar$-$NHOH/Ar$-$NO redox system, is plotted as a function of the DPPH concentration. The evolution can be divided in two parts. For low concentrations (<0.5 mM), a rapid decrease of the surface coverage is observed, from 17 to 7×10^{-10} mol·cm^{-2}. For higher DPPH concentrations, the coverage reaches a quasi-stable value of 6.5×10^{-10} mol·cm^{-2}. This behavior demonstrates the strong effect of the radical scavenger on the grafting process but the most interesting feature is that this effect cannot prevent the coupling between the surface and the radicalar reactive species, even for high DPPH concentration. The surface coverage reached is close to a nitrophenyl monolayer equivalent.

Impedance spectroscopy measurements were achieved in the presence of Fe(CN)$_6^{3-/4-}$ to obtain information on the charge-transfer resistance (R_{CT}) of the deposited layers. Figure 5 (right) shows the variation of the R_{CT} for increasing concentration of DPPH in the diazonium solution. The curve looks very similar to the surface coverage one. For electrodes modified in the presence of low DPPH concentration, the electronic transfer is completely blocked (see the corresponding voltammetric data in Supporting Information, Figure S3) and then a rapid decrease of the R_{CT} (from 10^4 to 10^3 Ω is observed. At higher concentration, the RCT tends to reach a stable value around 420 Ω (150 Ω for a bare electrode). The passivation behavior observed for modification achieved without radical scavenger is consistent with reported data for electrografting of diazonium derivatives in similar conditions.[12h] The decrease of the layer resistivity recorded for increasing
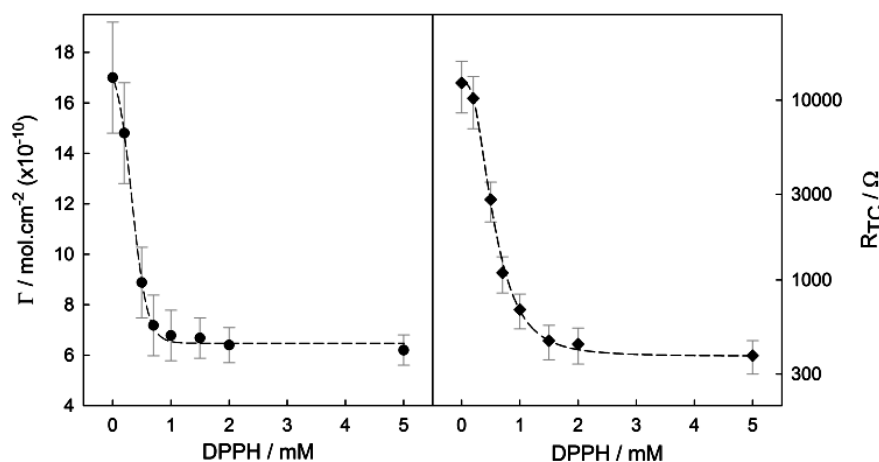
Figure 5. (Left): Nitrophenyl surface coverage on a modified carbon electrode as a function of the DPPH concentration. (Right): Charge-transfer resistance calculated from EIS measurement in 5 mM $Fe(CN)_6^{3-/4-}$, 0.1 M KCl. (Nyquist representations are shown in Supporting Information, Figure S4).

DPPH concentrations confirms the effect of the radical scavenger on the organic layer growth. The stabilization at a very low R_{CT} value (lower than values reported in the literature[12h,i]) traduces the presence of a very thin layer when more than one DPPH equivalent is used. The combination of this result with the surface coverage variation prove that the polymerization can be controlled and stopped independently of the grafting process.

Grafting conditions were varied to prove the efficiency of the radical scavenger independently of the grafting potential (Table 1). First, functionalizations were carried out at more anodic

Table 1. Surface Coverage of Modified GC Electrode as a Function of the Potential Grafting Conditions and DPPH Concentration[a]

grafting conditions	without DPPH, $\times10^{-10}$ mol/cm^2	1 mM DPPH, $\times10^{-10}$ mol/cm^2	2 mM DPPH, $\times10^{-10}$ mol/cm^2
$E = 0.06$ V[b]	9.2	5.81	5.64
$E = -0.21$ V[b]	12.5	6.03	5.90
one cycle[c]	17	6.78	6.37
two cycles[c]	17	7.40	6.59

[a]4-Nitrobenzenediazonium concentration was 1 mM for modification in CH_3CN, 0.1 M nBu_4NPF_6. [b]Fixed potential was applied for 30 s. [c]Cyclic voltammograms were recorded between 0.6 and −0.5 V at 50 mV/s.

potentials: −0.21 and 0.06 V, corresponding to the two reduction peaks of the diazonium. Without DPPH, the grafting occurs in both cases, and the surface coverage appears correlated to the fixed potential, as previously reported in the literature for several aryldiazoniums.[4] When DPPH is added, the coverage strongly decreases and reaches a quasi-constant value, around 5.8×10^{-10} mol·cm^{-2}. These experiments confirm the efficiency of the polymerization control by the DPPH, independently of the chosen potential (before and after the DPPH reduction peak). Electrografting was also carried out using cyclic voltammetry (one or two cycles). From a high surface coverage (17×10^{-10} mol·cm^{-2}), similar to the one calculated for the modification at −0.5 V, the nitrophenyl group surface concentration falls to 6.5×10^{-10} mol·cm^{-2} after DPPH addition.

Those results demonstrate that the grafting conditions have almost no influence on the Ar−NO_2 surface concentration

obtained with an excess of scavenger, which corresponds to a monolayer equivalent. This noteworthy result can be explained if we consider the coupling of the electrogenerated aryl radical with the surface much faster than the attack of a grafted phenyl. Considering the aryl radical/DPPH coupling is more efficient than the aryl attack, it becomes possible to avoid polymerization reactions without interfering with the grafting.

Confirmation of the nitrophenyl radical capture was obtained by electrolysis at the grafting potential (−0.5 V) in the presence of 1.9 mM 4-nitrobenzenediazonium and 3.8 mM DPPH using a 8 cm^2 electrode. Three milligrams of the coupling product was isolated and identified as 2-[4-(4-nitro)phenyl]-2-phenyl-1-picrylhydrazine (Scheme 1) (see the Supporting Information,

Scheme 1. Structure of 2-[4-(4-Nitro)phenyl]-2-phenyl-1-picrylhydrazine
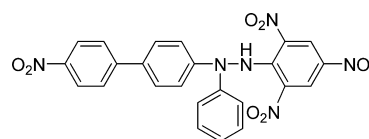
Figures S5−S7 for characterization data). The scavenging mechanism is still under investigation but seems to proceed via a radical attack on one of the positively polarized diphenylamino end of DPPH, as already evidenced for phenol[17] and NO_2[18] radicals.

CONCLUSION

This work proposes a new approach for controlling the growth of a layer electrografted via the diazonium reduction method. We show that it is possible to considerably lower the amount of attached organic species by the use of a radical scavenger in solution. Moreover, it seems to be possible to easily obtain a monolayer when the radical scavenger is introduced in excess. To obtain such control, the electrogenerated aryl radicals are supposed to undergo coupling according to the following order: surface ≫ DPPH > grafted phenyl. The very high reproducibility of electrode modifications (i.e., voltammetric peak shape, surface coverage, and RCT measurements) prepared in the presence of radical scavenger opens the way for the preparation of well-controlled materials via diazonium

chemistry. Furthermore, this approach does not suffer from the synthetic limitations encountered when hindered structures must be built, and thus could be generalized. Preliminary work using 4-bromobenzenediazonium was achieved and confirms the efficiency of radical control independently of the diazonium substitution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CV recorded in KOH on modified electrodes with various DPPH concentrations (Figure S1), CV recorded in the presence of DPPH on GC electrode (Figure S2), CV recorded in $Fe(CN)_6^{3-/4-}$ on modified electrodes (Figure S3), Nyquist representations from modified electrodes (Figure S4), MALDI spectrum of the coupling product (Figure S5), ^1H NMR spectrum of the coupling product (Figure S6), and ^{13}C NMR spectrum of the coupling product (Figure S7). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: tony.breton@univ-angers.fr.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

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

(2) Adenier, A.; Combellas, C.; Kanoufi, F.; Pinson, J.; Podvorica, F. I. *Chem. Mater.* **2006**, *18*, 2021−2029.

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

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

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

(6) Kariuki, J. K.; McDermott, M. T. *Langmuir* **2001**, *17*, 5947−5951.

(7) Brooksby, P. A.; Downard, A. J. *Langmuir* **2004**, *20*, 5038−5045.

(8) (a) Allongue, P.; Henry de Villeneuve, C.; Cherouvrier, G.; Cortes, R. *J. Electroanal. Chem.* **2003**, *550*, 161−174. (b) Uetsuka, H.; Shin, D.; Tokuda, N.; Saeki, K.; Nebel, C. E. *Langmuir* **2007**, *23*, 3466−3472. (c) Ghilane, J.; Martin, P.; Fontaine, O.; Lacroix, J-C; Randriamahazaka, H. *Electrochem. Commun.* **2008**, *10*, 1060−1063. (d) Fontaine, O.; Ghilane, J.; Martin, P.; Randriamahazaka, H.; Lacroix, J.-C. *Langmuir* **2010**, *26*, 18542−18549.

(9) Combellas, C.; Kanoufi, F.; Pinson, J.; Podvorica, F. *J. Am. Chem. Soc.* **2008**, *130*, 8576−8577.

(10) (a) Nielsen, L. T.; Vase, K. H.; Dong, M.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K. *J. Am. Chem. Soc.* **2007**, *129*, 1888. (b) Peng, Z.; Holm, A. H.; Nielsen, L. T.; Pedersen, S. U.; Daasbjerg, K. *Chem. Mater.* **2008**, *20*, 6068. (c) Leroux, Y. R.; Fei, H.; Noël, J.-M.; Roux, C.; Hapiot, P. *J. Am. Chem. Soc.* **2010**, *132*, 14039−14041. (d) Malmos, K.; Dong, M.; Pillai, S.; Kingshott, P.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K. *J. Am. Chem. Soc.* **2009**, *131*, 4928−4936.

(11) (a) Mesnage, A.; Lefèvre, X.; Jégou, P.; Deniau, G.; Palacin, S. *Langmuir* **2012**, *28*, 11767−11778. (b) Cui, B.; Gu, J.-Y.; Chen, T.; Yan, H.-J.; Wang, D.; Wan, L.-J. *Langmuir* **2013**, *29*, 2955−2960.

(12) (a) Ortiz, B.; Saby, C.; Champagne, G. Y.; Bélanger, D. *J. Electroanal. Chem.* **1998**, *455*, 75−81. (b) Adenier, A.; Cabet-Deliry, E.; Chaussé, A.; Griveau, S.; Mercier, F.; Pinson, J.; Vautrin-Ul, C. *Chem. Mater.* **2005**, *17*, 491−501. (c) Baranton, S.; Bélanger, D. *Electrochim. Acta* **2008**, *53*, 6961−6967. (d) Jayasundara, D. R.; Cullen, R. J.; Soldi, L.; Colavita, P. E. *Langmuir* **2011**, *27*, 13029−13036. (e) Kullapere, M.; Marandi, M.; Matisen, L.; Mirkhalaf, F.; Carvalho, A. E.; Maia, G.; Sammelselg, V.; Tammeveski, K. *J. Solid State Electrochem.* **2012**, *16*, 569−578. (f) Delamar, M.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 5883−5884. (g) Richard, W.; Evrard, D.; Gros, P. *J. Electroanal. Chem.* **2012**, *685*, 109−115. (h) Saby, C.; Ortiz, B.; Champagne, G. Y.; Bélanger, D. *Langmuir* **1997**, *13*, 6805−6813. (i) Khoshroo, M.; Rostami, A. A. *J. Electroanal. Chem.* **2010**, *647*, 117−122.

(13) Breton, T.; Bélanger, D. *Langmuir* **2008**, *24*, 8711−8718.

(14) Kuo, T.-C.; McCreery, R. L.; Swain, G. M.. *Electrochem. Solid State Lett.* **1999**, *2*, 288−290.

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

(16) (a) Brooksby, P. A.; Downard, A. J. *J. Phys. Chem. B* **2005**, *109*, 8791−8798. (b) Ceccato, M.; Nielsen, L. T.; Iruthayaraj, J.; Hinge, M.; Pedersen, S. U.; Daasbjerg, K. *Langmuir* **2010**, *26*, 10812−10821.

(17) Weil, J. A.; Sane, K. V.; Kinkade, J. M. *J. Phys. Chem.* **1961**, *65*, 710−712.

(18) Hristea, E. N.; Covaci-Cìmpeanu, I. C.; Ionita, G.; Ionita, P.; Draghici, C.; Caproiu, M. T.; Hillebrand, M.; Constantinescu, T.; Balaban, A. T. *Eur. J. Org. Chem.* **2009**, 626−634.