

PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Evidence of monolayer formation from diazonium grafting with radical scavenger: electrochemical, AFM and XPS monitoring

Cite this: DOI: 10.1039/x0xx00000x

T. Menanteau,^a E. Levillain,^a A. J. Downard^b and T. Breton^{*a}Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

This paper analyzes the impact of the use of a radical scavenger on organic films generated by aryldiazonium electrografting in terms of thickness, morphology and chemical composition. Glassy carbon (GC) and pyrolyzed photoresist film (PPF) were modified by electrochemical reduction of 4-nitrobenzenediazonium salt in the presence of various amounts of 2,2-diphenyl-1-picrylhydrazyl (DPPH). The thicknesses of organic films have been measured by atomic force microscopy (AFM) and the lower threshold value confirms that it is possible to reach a monolayer by radical trapping. X-ray photoelectron spectroscopy (XPS) highlights a decrease in the proportion of nitrophenyl groups grafted via azo bridges as the DPPH concentration is decreased and the film thickness increases. A correlation of electrochemical, XPS and AFM data confirms that not all nitrophenyl groups are electroactive in films greater than 2 nm thick.

1. Introduction

Aryldiazonium salt chemistry is now well exploited to modify the surface of various substrates including metals, carbon, semiconductors and non-conductive materials.¹⁻³ The key step of the process rests on the production, by reduction of the diazonium cation, of highly reactive radical moieties at the substrate/solution interface.⁴ The subsequent anchoring of the radical leads to the formation of robust organic nano-films that can be of interest in the field of nanoelectronics,⁵ energy storage,⁶⁻⁷ spin labelled surfaces,⁸⁻⁹ and sensors.¹⁰⁻¹¹ The high reactivity of radical intermediates generated during the process is a strength of the method, but also its weakness. Hence, depending on the substituent borne by the benzenediazonium ion, the grafting usually leads to the disordered polymerization of aromatics,^{2,12} incompatible with the development of the controlled and well defined nanostructures needed for applications in nanochemistry and nanotechnologies. With an efficient limitation of the layer growth by careful control of the consumed charge remaining complex,¹³⁻¹⁴ several strategies have been developed to avoid radical attacks on already grafted aryl species. The use of ionic liquid to minimize the diffusion of the diazonium salt and control the production of radicals is a promising and versatile strategy.¹⁵⁻¹⁷ One of the most efficient approaches to ensure a strict control of the layer growth consists in the use of diazonium cations bearing a bulky

substituent.¹⁸⁻²⁰ This method has been demonstrated using sterically hindered protecting groups to generate monolayer or near monolayer platforms dedicated to post-functionalization.^{18,20-21} Our group has recently reported a different approach using a radical scavenger to trap reactive species produced in excess, thereby preventing the formation of polyaryl structures.²²⁻²³ It was shown that the electrochemically-determined surface coverage of grafted aryl species depends on the scavenger amount and reaches, at high concentration, a minimum and steady state value. This minimum surface coverage was consistent with a monolayer of grafted groups. In this work, organic films generated on carbon surfaces from 4-nitrobenzenediazonium ion (NBD) in the presence of 2,2-diphenyl-1-picrylhydrazyl (DPPH) were analysed by AFM and XPS. We go further in the analysis of the mode of action of the radical trap by focusing the study on the composition of the grafted layer. In addition we directly measure the thickness of the grafted layers to confirm the formation of monolayers, and compare film thickness data with electrochemically-determined surface coverages.

2. Experimental section

2.1. Material and reagents

4-Nitrobenzenediazonium tetrafluoroborate (Aldrich), 2,2-diphenyl-1-picrylhydrazyl (Aldrich), tetrabutylammonium hexafluorophosphate (Aldrich) and acetonitrile (HPLC grade, Carlo Erba) were used as received. GC electrodes were obtained from Bioanalytical Systems Inc. (Model MF-2012; diameter 3 mm).

2.2. Electrochemistry and surface modification

A potentiostat/galvanostat model SP150 (from Bio-Logic) monitored by ECLab software was used for the electrochemical experiments on GC. All potentials were reported versus the Ag/AgCl (sat. KCl) reference electrode in aqueous medium and Ag/AgNO₃ (10 mM) in organic medium. The GC 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 each derivatisation, the electrode was sonicated in acetonitrile for 1 minute. Pyrolyzed photoresist film (PPF) preparation and the electrochemical cell used with PPF have been described previously.¹² All electrochemical measurements on PPF were performed using an Eco Chemie Autolab PGSTAT302 potentiostat/galvanostat. The reference electrode was a saturated calomel electrode (SCE) for measurements in aqueous solutions and a calomel electrode with 1 M LiCl for non-aqueous solutions. All electrolytic solutions were deaerated by nitrogen bubbling for 15 min before cyclic voltammetry (CV) experiments. Modification of GC and PPF was achieved by CV at 50 mV/s for two cycles between 0.5 and -0.6 V in deaerated acetonitrile containing 0.1 M nBu₄NBF₄ and 1 mM diazonium salt. After each derivatisation, the electrode was sonicated in acetonitrile for 1 minute.

The surface coverage of electroactive nitrophenyl groups was measured by transferring the modified electrode to a deaerated aqueous solution of 0.1 M KOH and recording CVs between 0 and -1.2 V at a scan rate of 50 mV/s. The charge associated with the hydroxyaminophenyl/nitrosophenyl redox couple was used to estimate the surface coverage of nitrophenyl groups.²⁴

2.3 XPS

XPS data were collected using a Kratos Axis Ultra spectrometer. The X-ray source was monochromated Al K α working at 1486.6 eV. Spectra were accumulated at a take off angle of 90°, using a spot size of 0.7×0.3 mm² at a pressure of less than 10⁻⁸ mbar. High resolution scans (N1s, C1s and O1s) were carried out with 0.1 eV step size and pass energy 20 eV. All spectra were calibrated taking C1s as a reference binding energy of 284.5 eV (graphitic carbon component of the vitreous carbon substrates), without internal standard. XPS spectra were analyzed with the curve fitting program CASA XPS and involved background subtraction using Shirley and a subsequent pseudo-Voigt function mixing Gaussian-Lorentzian functions. Atomic ratios of the surfaces were calculated by normal area divided by number of scans and the element sensitivity factor. For the elements considered, the sensitivity factors are O1s 2.93, N1s 1.78 and C1s 1.00.

2.4. AFM

Film thickness measurements were made on modified PPF working electrodes by depth profiling using an AFM instrument and technique as described previously.¹² A section of film was removed by scratching with the AFM tip (silicon cantilever, NSC 12 model, Ultrasharp) and the scratch was imaged using non-contact tapping mode (silicon cantilever NSC 14 model, Ultrasharp).

3. Results and discussion

Glassy carbon electrodes were modified by CV in the presence of a millimolar solution of 4-nitrobenzenediazonium tetrafluoroborate (NBD) in acetonitrile/nBu₄PF₆ (0.1 M) with increasing DPPH concentrations (Figure 1). A characteristic reduction behaviour (two peaks at 0.42 and 0.14 V) was observed in the absence of DPPH. The electrode passivation recorded for the second cycle is consistent with the grafting process.

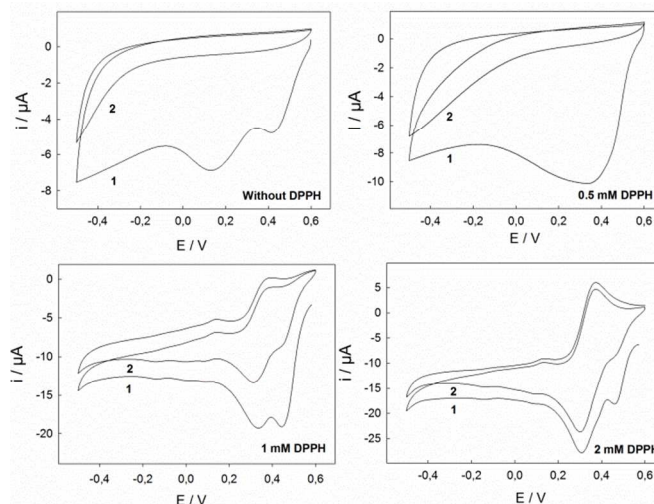


Figure 1. First and second CV cycle recorded in acetonitrile-0.1 nBu₄NPF₆ containing 1 mM NBD on a GC electrode at 50 mV/s without and with increasing DPPH concentrations. Reference was Ag/AgNO₃.

When DPPH is added, its reduction into DPPH⁻ is observed at 0.2 V (superimposed on the diazonium ion reduction) and a weaker passivation is visible on the second cycle. As previously reported for nitrophenyl tethered carbon, the surface coverage of electroactive nitrophenyl groups can be extracted from the charge associated with the hydroxyaminophenyl/nitrosophenyl redox couple after transfer of the modified electrode to 0.1 M KOH solution.²⁴ Table 1 summarizes the surface coverages, Γ_{NP} , associated with modified GC.

Concentration of DPPH	0 mM	0.5 mM	1 mM	2 mM
Γ_{NP} ($\times 10^{-10}$ mol/cm ²)	17.0 ± 2.0	8.8 ± 1.5	6.7 ± 1.5	6.4 ± 1.0

Table 1. Calculated surface coverage from the voltammetric response of nitrophenyl groups for GC modified surfaces with increasing DPPH concentrations.

As recently reported by our group, the use of DPPH has a drastic effect on the functionalisation with NBD.²²⁻²³ The surface coverage of nitrophenyl groups is lowered for increasing DPPH concentration and reaches a minimum and steady state value of approximately 6.5×10^{-10} mol/cm². This surface coverage can be compared to values of around 2.5×10^{-10} and 3.2×10^{-10} mol/cm² reported for films of monolayer thickness prepared on PPF, a much smoother substrate.^{12,25} Considering the larger roughness of GC (*vide infra*), these values agree well. Indeed a comparable difference has

previously been reported for a monolayer of porphyrin grafted on both substrates.²⁶

3.1 XPS monitoring

XPS monitoring of GC functionalized surfaces was achieved to determine the composition of the film and investigate the impact of the use of radical scavenger on the polymerization mode. C1s, O1s and N1s signals were closely examined and the relative concentration of each element was determined by integration of the components of the signals (see the supporting information for survey spectra and atomic concentrations, Figure S1, Table S1). No change of the shape of C1s and O1s signals was observed regardless of the DPPH concentration used during the deposition. In contrast, the nitrogen signal can provide valuable information since it allows unambiguous identification of the +5 oxidation state of the nitrogen atom in nitrophenyl groups. Figure 2 shows N1s core level spectra for a bare GC surface and functionalised surfaces in the presence of increasing DPPH amounts.

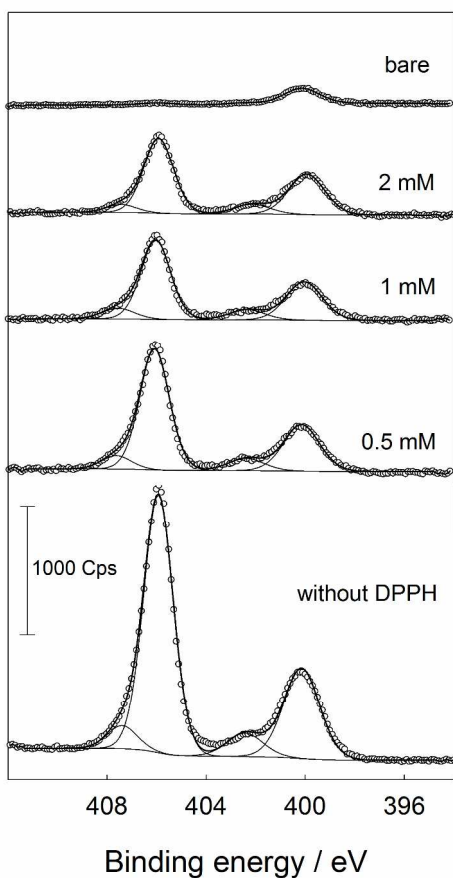


Figure 2. XPS N1s core-level spectra of unmodified GC (bare), and modified GC with 1 mM NBD in the presence of increasing concentrations of DPPH.

The spectral profile of the modified surfaces is similar to those reported in the literature for nitrophenyl modified substrates,^{24,27-28} showing two principal peaks around 406 and 400 eV, respectively attributed to nitro groups and reduced N species.²⁶ The peak located at 402.4 eV is classically assigned to the nitrosophenyl²⁹ or hydroxylamine³⁰ functionality coming from the partial reduction of the nitro group during the grafting.

It can be excluded that this peak comes from traces of DPPH since the signal corresponding to reduced nitrogen atoms of DPPH is located at 401 eV³¹ and the component at 402.4 eV is present even for modification carried out without DPPH. With respect to the peak at 407 eV, although several studies mention its presence in nitro-modified surfaces, no clear explanation has been proposed.^{30,32}

The intensity of the N 1s signal corresponding to nitro groups (N 1s406) is DPPH concentration dependent. Evolution of this component is represented in Figure 3, through the plotting of the [N1s406/C1s] ratio as function of the DPPH concentration. Following DPPH addition to the deposition solution, a drastic decrease is observed, from 7.4% in the absence of DPPH to a constant value of 2 % at ≥ 1 mM of radical trap. As expected from the electrochemical surface coverage measurements at GC, XPS shows that the layers grown in the presence of 1 and 2 mM radical trap are the same. The factor of 3.7 decrease in the XPS [N1s406/C1s] ratio as the DPPH concentration increases from 0 to 1 or 2 mM can be compared with the factor of 2.7 decrease in the concentration of electroactive nitrophenyl groups as the DPPH concentration is similarly varied (Table 1). There is a similar discrepancy, but less marked, when comparing the ratio of electrochemical surface concentrations in the presence of 0.5 mM and 1 mM DPPH (a factor of 1.4) with the XPS [N1s406/C1s] ratios for films prepared with the same concentration of scavenger (a factor of 1.6). The most reasonable explanation for this difference is that the voltammetric technique underestimates the nitrophenyl coverage in thick films prepared with ≤ 0.5 mM DPPH (*vide infra*). This phenomenon has been noted previously and was attributed to the presence of non-electroactive groups due to limited ion and/or solvent diffusion within the film.^{33,34}

The peak located at 400 eV is assigned to the presence of azo bridges in the film, coming from the attack of non-reduced aryldiazonium ions on the surface (direct grafting) or on already attached nitrophenyl moieties (polyaryl layer growth). Evolution of this component with increasing DPPH concentration (Figure 3) follows the same trend as the N1s406 one but is characterized by a smaller amplitude. When a 1 or 2 mM DPPH concentration is used giving the minimum film coverage, the [N1s406/N1s400] ratio is 2:1. Assuming there is just a monolayer of nitrophenyl groups on the surface, the azo groups must link the groups to the GC surface. In that case, a [N1s406/N1s400] ratio of 2:1 corresponds to 1 in 4 groups attached through an azo link. For increasingly thick films, the ratio decreases, indicating that there are relatively fewer azo links in the bulk of the film although the precise ratio of nitrophenyl groups attached via azo groups to those attached through C-C bonds cannot be calculated as it depends on how many links are at the surface (connected to one nitrophenyl group and how many are within the film (connected to two nitrophenyl groups)). The XPS data can be compared with that previously reported by our group on the controlled spontaneous modification of GC with NBD.²³ For modified surfaces without radical trap, [N1s406/N1s400] ratios are very similar for both modification methods (i.e. 17% and 20% of azo groups in the layer for electrochemical and spontaneous grafting respectively). In contrast, as radical scavenger was added, the increase in azo group concentration for decreasingly thick films was more pronounced for spontaneous modification than for electrochemical modification. Indeed, for monolayers prepared by spontaneous grafting, it was found that 50% of the nitrophenyl groups were attached to the surface via azo bridges. The lower proportion found in the current work (i.e. 25%) is

attributed to the electrochemical induction mode which promotes a sustainable production of aryl radicals and consequently favors direct radical coupling.

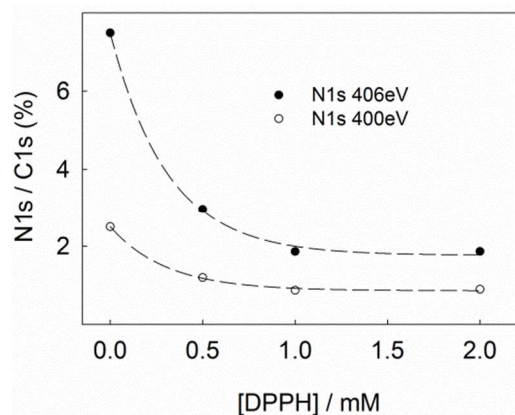


Figure 3. N1s/C1s atomic ratios of GC modified with 1 mM NBD calculated from XPS as a function of the DPPH concentration in the deposition solution. The dashed lines are a guide for the eye.

The presence of a higher proportion of azo links at the surface compared with in the bulk can be explained by the reaction of the aryldiazonium ion with the carbon substrate being faster than with already grafted nitrophenyl groups. The nitro substituent increases the electrophilicity of the aryldiazonium ion,³⁵ but the electron withdrawing nitro group on already grafted entities makes attack of the aryldiazonium ion relatively unfavourable compared with attack at GC which is promoted by electron donating O functionalities on the surface, eg -OH groups.²⁷ This phenomenon is probably reinforced when the radical trap is used because the reactive aryl radical concentration at the substrate/solution interface is lowered by the trapping of DPPH.

3.2. AFM monitoring

Although the electrochemically determined surface coverage of nitrophenyl groups in films prepared with high DPPH concentration is consistent with a monolayer, unambiguous confirmation of monolayer formation can be obtained by directly measuring the film thickness by AFM depth profiling. This technique requires a substrate having very low roughness. The roughness of our polished GC was determined using AFM (see the supporting information, Figure S2). In agreement with reported data for GC surfaces,³⁶ a mean value of 3.2 ± 0.5 nm was obtained, confirming that such a surface is not appropriate for accurate topographic measurement of nanometer or sub-nanometer layers with AFM. For that purpose, PPF was prepared and electrochemically modified using identical conditions as for GC. PPF is a glassy carbon-like material having a low surface roughness (< 0.5 nm),³⁷⁻³⁸ well adapted to the characterization of nanoscale films.³⁹ The voltammetric behavior observed during the electrografting of the PPF is identical to that obtained for GC (CVs are presented in the supporting information, Figure S3). Surface coverages calculated from the hydroxyaminophenyl/nitrosophenyl redox couple are summarized in Table 2 (CVs are presented in the supporting information, Figure S4).

Concentration of DPPH	0 mM	0.5 mM	1 mM	2 mM
Γ_{NP} ($\times 10^{-10}$ mol/cm ²)	16.9 ± 2.0	10.7 ± 2.0	8.6 ± 1.5	3.9 ± 1.5

Table 2. Calculated surface coverage from the voltammetric response of nitrophenyl groups for PPF modified surfaces with increasing DPPH concentrations.

Without radical trap, the calculated surface coverage is similar to that calculated on GC, despite the greater roughness of GC. This is not surprising: for sufficiently thick films, with thickness greater than the substrate roughness, the effect of substrate roughness on the measured surface concentration is expected to be insignificant. Additionally, as indicated by the XPS study of films grafted at GC, the electrochemically measured surface coverage of thick films may underestimate the amount of film. Hence the actual surface coverage of nitrophenyl groups on PPF may be higher than that measured. When radical trap is added, PPF substrates behave similarly to GC substrates: the surface coverage of the organic film decreases with increasing DPPH concentration. In contrast to GC, the minimum surface coverage is not obtained with 1 mM DPPH, however additional experiments carried out on PPF with a higher concentration of DPPH (3 mM) confirmed that the minimum surface concentration of nitrophenyl groups on PPF is between 3 and 4×10^{-10} mol/cm². This value is lower than that obtained for GC (6.4×10^{-10} mol/cm²) which is attributed to the lower surface roughness of PPF than GC (*vide supra*). A surface coverage of $3 - 4 \times 10^{-10}$ mol/cm² is consistent with monolayer surface coverage on PPF.^{12,25}

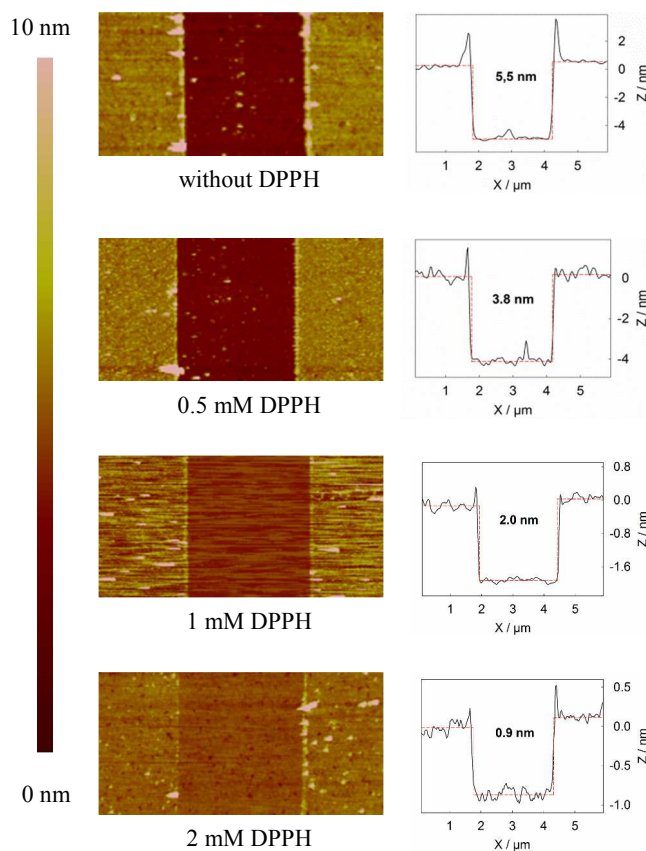


Figure 4. AFM topography images ($6 \mu\text{m} \times 3 \mu\text{m}$) and corresponding depth profiles of nitrophenyl PPF modified with 1 mM NBD and increasing DPPH concentrations. Uncertainty is ± 0.5 nm for depth measurements.

The thickness of films grafted to PPF was measured by removing small sections of attached film by scratching with an AFM tip, followed by profiling perpendicularly to the scratch. Figure 4 shows topographic images of a scratch in nitrophenyl films prepared with increasing DPPH concentrations. Corresponding depth profiles are presented on the right part of Figure 4. When no radical trap is used, an average film thickness of 5.5 ± 0.5 nm can be estimated. Such a value is consistent with those previously reported for various diazonium salts.^{12,33,39} The calculated height of a nitrophenyl group perpendicularly oriented on a flat surface is ~ 0.8 nm (calculated via a CPK model), hence the film is multilayered with a minimum of 6-7 layers. The increasing DPPH concentration in solution progressively decreases the thickness of the organic film from 5.5 to 0.9 nm. For a radical trap concentration of 2 mM, a homogeneous coverage can be observed on the AFM image with a well-defined contrast between the scratch and the top of the film. (Black spots correspond to carbon surface defects.) The measured film thickness (0.9 ± 0.5 nm) is consistent with monolayer formation on PPF.

These results illustrate that when using the same modification conditions as for GC, at the highest scavenger concentration the film growth is restricted to a monolayer, whereas at lower scavenger concentrations the films are clearly multi-layered, confirming the efficiency of the technique in film thickness control and monolayer preparation.

3.3. Correlation between AFM, Electrochemistry and XPS

AFM measurements have been correlated with electrochemical and XPS data in order to further characterise the grafted films. Surface coverage of electroactive species as a function of the thickness is presented in Figure 5. Data can be fitted by different models, however, considering the uncertainties associated with the voltammetric measurements, the best fit to the experimental points is to use a linear relationship for the lower portion of the layer, followed by a curved part. The linear dependency obtained for thickness ≤ 2 nm suggests that all nitrophenyl groups are electroactive in this range. The film density extracted from the slope (i.e. $3 \pm 0.5 \times 10^{-10} \text{ mol.cm}^{-2}.\text{nm}^{-1}$) is 0.38 g.cm^{-3} . The second part of the curve is consistent with either a decrease of the film compactness and/or electroactivity above a thickness of 2 nm. From the comparison of electrochemical and XPS data for films grafted to GC it was deduced that the electrochemical determination of surface coverage of films prepared with ≤ 0.5 mM DPPH underestimates the amount of film. Hence the deviation in linearity of the plot shown in Figure 5 can be best explained by the incomplete electroactivity of films of thickness > 2 nm.

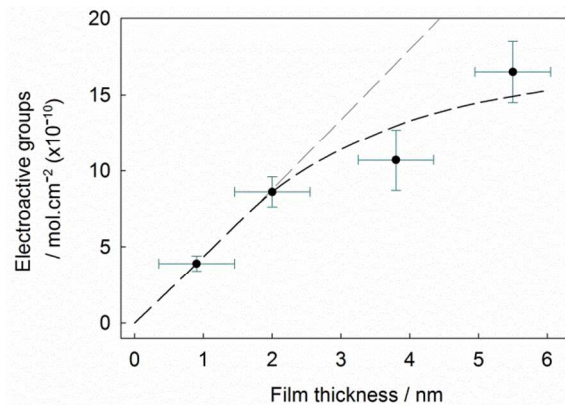


Figure 5. Nitrophenyl surface coverage calculated by integration of the electrochemical response of the nitrophenyl groups for PPF modified with 1 mM NBD as a function of the film thickness measured by AFM depth profiling. The curved part was fitted by a logarithmic model following equation: $f = y_0 + a \cdot \ln(x - x_0)$ with $a = 6,4393 \times 10^{-10}$, $x_0 = -0,5276$ and $y_0 = 3,1316 \times 10^{-10}$.

Conclusions

The correlation between voltammetric, XPS and AFM experiments confirms that the presence of radical scavenger during electrografting of nitrophenyl groups acts on the layer thickness. Direct measurement of film thickness by AFM depth profiling shows the formation of a monolayer at high concentration of radical trap in solution, and XPS measurements reveal that one quarter of the nitrophenyl groups are directly grafted onto carbon via azo coupling. As the film thickness increases, the relative abundance of azo links in the films decreases. Combining results from CV, XPS and AFM experiments, performed on different layer thicknesses, provides clear evidence that film electroactivity decreases for thickness above 2 nm.

From a general point of view, the increase of the azo bond proportion when using DPPH does not represent a drawback as covalent bonds are involved. However, the stability of the layers to further electrochemical and chemical manipulations, especially under reductive conditions, must be investigated. Extension of the strategy presented here to prepare controlled molecular layers bearing chemical groups designed for coupling with various functionalities is currently under investigation and could be of great interest to modulate structure/properties relationships of complex structures. Furthermore, the transposition of the radical control strategy to other carbon, metal and semiconductor materials remains to be studied. A key factor will be the kinetics of the direct grafting compared to the polymerization reactions at those substrates.

Acknowledgements

This work was supported by the "Centre National de la Recherche Scientifique" (CNRS France), the "Agence Nationale de la Recherche" (ANR France), the "Région des Pays de la Loire" (France), and the MacDiarmid Institute for Advanced Materials and Nanotechnology.

Notes and references

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

b MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand

Electronic Supplementary Information (ESI) available: XPS survey spectra of glassy carbon modified by cyclic voltammetry (2 cycles between 0.5 and -0.6 V at 50 mV/s) in the presence of 1 mM NBD and increasing concentrations of DPPH in acetonitrile, 0.1 M Bu₄NPF₆ (Figure S1), AFM image of a bare glassy carbon sheet used for modification (Figure S2), CVs recorded at 50 mV/s on PPF in the presence of 1 mM NBD and increasing concentrations of DPPH in acetonitrile, 0.1 M Bu₄NPF₆ (Figure S3), CVs recorded at 50 mV/s in KOH (0.1M) on modified PPF in the presence of 1 mM NBD and increasing concentrations of DPPH in acetonitrile, 0.1 M Bu₄NPF₆ (Figure S4). See DOI: 10.1039/b000000x/

References

1. D. Belanger and J. Pinson, *Chemical Society Reviews*, 2011, 40, 3995-4048.
2. A. Adenier, C. Combellas, F. Kanoufi, J. Pinson and F. I. Podvorica, *Chemistry of Materials*, 2006, 18, 2021-2029.
3. P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson and J.-M. Savéant, *Journal of the American Chemical Society*, 1997, 119, 201-207.
4. J. Pinson and F. Podvorica, *Chemical Society Reviews*, 2005, 34, 429-439.
5. S. Y. Sayed, A. Bayat, M. Kondratenko, Y. Leroux, P. Hapiot and R. L. McCreery, *J Am Chem Soc*, 2013, 135, 12972-12975.
6. C. Martin, O. Crosnier, R. Retoux, D. Bélanger, D. M. Schleich and T. Brousse, *Advanced Functional Materials*, 2011, 21, 3524-3530.
7. G. Pognon, T. Brousse, L. Demarconnay and D. Bélanger, *Journal of Power Sources*, 2011, 196, 4117-4122.
8. C. Cougnon, S. Boisard, O. Cador, M. Dias, E. Levillain and T. Breton, *Chem Commun (Camb)*, 2013, 49, 4555-4557.
9. J. P. Blinco, B. A. Chalmers, A. Chou, K. E. Fairfull-Smith and S. E. Bottle, *Chem Sci*, 2013, 4, 3411-3415.
10. G. Liu, T. Böcking and J. J. Gooding, *Journal of Electroanalytical Chemistry*, 2007, 600, 335-344.
11. S. Hana, Y. Yuana, L. Hua, G. Xu, *Electrochemistry Communications*, 2010, 12.
12. P. A. Brooksby and A. J. Downard, *Langmuir*, 2004, 20, 5038-5045.
13. P. Allongue, C. Henry de Villeneuve, G. Cherouvrier, R. Cortès and M. C. Bernard, *Journal of Electroanalytical Chemistry*, 2003, 550-551, 161-174.
14. H. Uetsuka, D. Shin, N. Tokuda, K. Saeki and C. E. Nebel, *Langmuir*, 2007, 23, 3466-3472.
15. J. Ghilane, P. Martin, O. Fontaine, J.-C. Lacroix and H. Randriamahazaka, *Electrochemistry Communications*, 2008, 10, 1060-1063.
16. S. Descroix, G. Hallais, C. Lagrost and J. Pinson, *Electrochimica Acta*, 2013, 106, 172-180.
17. G. Shul, C. A. C. Ruiz, D. Rochefort, P. A. Brooksby and D. Bélanger, *Electrochimica Acta*, 2013, 106, 378-385.
18. Y. R. Leroux, H. Fei, J.-M. Noël, C. Roux and P. Hapiot, *Journal of the American Chemical Society*, 2010, 132, 14039-14041.
19. C. Combellas, F. Kanoufi, J. Pinson and F. I. Podvorica, *Journal of the American Chemical Society*, 2008, 130, 8576-8577.
20. L. Lee, H. Ma, P. A. Brooksby, S. A. Brown, Y. R. Leroux, P. Hapiot and A. J. Downard, *Langmuir*, 2014, 30, 7104-7111.
21. L. Lee, P. A. Brooksby, Y. R. Leroux, P. Hapiot and A. J. Downard, *Langmuir*, 2013, 29, 3133-3139.
22. T. Menanteau, E. Levillain and T. Breton, *Chemistry of Materials*, 2013, 25, 2905-2909.
23. T. Menanteau, E. Levillain and T. Breton, *Langmuir*, 2014, 30, 7913-7918.
24. M. Kullapere, M. Marandi, L. Matisen, F. Mirkhalaf, A. Carvalho, G. Maia, V. Sammelselg and K. Tammeveski, *J Solid State Electrochem*, 2012, 16, 569-578.
25. D. J. Garrett, J. Lehr, G. M. Miskelly and A. J. Downard, *Journal of the American Chemical Society*, 2007, 129, 15456-15457.
26. A. J. Gross, C. Bucher, L. Coche-Guerente, P. Labbé, A. J. Downard and J.-C. Moutet, *Electrochemistry Communications*, 2011, 13, 1236-1239.
27. C. Saby, B. Ortiz, G. Y. Champagne and D. Bélanger, *Langmuir*, 1997, 13, 6805-6813.
28. B. Ortiz, C. Saby, G. Y. Champagne and D. Bélanger, *Journal of Electroanalytical Chemistry*, 1998, 455, 75-81.
29. M. D'Amour and D. Bélanger, *The Journal of Physical Chemistry B*, 2003, 107, 4811-4817.
30. S. S. C. Yu, E. S. Q. Tan, R. T. Jane and A. J. Downard, *Langmuir*, 2007, 23, 11074-11082.
31. I. W. Drummond and H. Harper, *Nature Physical Science*, 1971, 232, 71-72.
32. J. H. Moon, J. H. Kim, K.-j. Kim, T.-H. Kang, B. Kim, C.-H. Kim, J. H. Hahn and J. W. Park, *Langmuir*, 1997, 13, 4305-4310.
33. P. A. Brooksby and A. J. Downard, *The Journal of Physical Chemistry B*, 2005, 109, 8791-8798.
34. M. Ceccato, L. T. Nielse, J. Iruthayaraj, M. Hinge, S. U. Pedersen and K. Daasbjerg, *Langmuir*, 2010, 26, 10812-10821.
35. P. Pérez, *The Journal of Organic Chemistry*, 2003, 68, 5886-5889.
36. M. T. McDermott, K. Kneten and R. L. McCreery, *The Journal of Physical Chemistry*, 1992, 96, 3124-3130.
37. S. Ranganathan, R. McCreery, S. M. Majji and M. Madou, *Journal of The Electrochemical Society*, 2000, 147, 277-282.
38. S. Ranganathan and R. L. McCreery, *Analytical chemistry*, 2001, 73, 893-900.

39. F. Anariba, S. H. DuVall and R. L. McCreery, *Analytical chemistry*, 2003, 75, 3837-3844.