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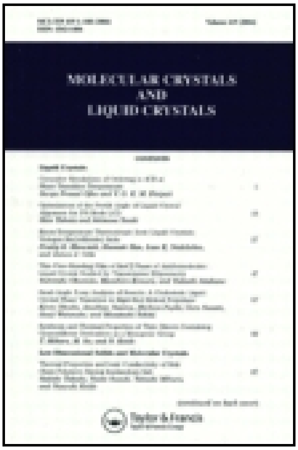

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# Carbon Substrate Functionalization with Diazonium Salts Toward Sensor Applications

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# Carbon Substrate Functionalization with Diazonium Salts Toward Sensor Applications

**Fabien Le Floch[1], Gérard Bidan[2], Luisa Pilan[3], Eleonora-Mihaela Ungureanu[3], and Jean-Pierre Simonato[1]**
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*Grafting of electroactive* p-*phenyldiazonium derivatives was performed on carbon electrodes. Reduction potentials were determined for commercial and new synthesized diazonium salts, in relation to the electronic behaviour of the* para *substituents of the diazophenyl groups. Their covalent attachment on the electrode surface was characterized through electrochemical experiments. The effect of varying several parameters (concentration, substituent, duration…) was investigated for potentiodynamic and potentiostatic grafting reactions. Spontaneous binding was identified by simply deeping the electrodes in diazonium salt solutions, affording low coverage (lower than 3%) and grafting densities of less than* $\Gamma = 3.9 \cdot 10^{-11}\,mol \cdot cm^{-2}$.

**Keywords:** carbon modification; diazonium salt; electrochemistry; electrografting; functionalization

## INTRODUCTION

Single-walled carbon nanotubes (SWNTs) are transducers of choice for the realization of specific electronics as well as optical or biological

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sensors [1]. Low-cost carbon-based transistors can be constructed by employing simple fabrication methods to form thin layers on flexible substrates for lightweight conductive and transparent devices. Both SWNTs and random networks of SWNTs have been investigated as conducting channels in field effect transistors, and their (electro)-chemical functionalization has led to innovative sensing elements. To offer selectivity to the nanotubes, different techniques have been developed to covalently functionalize SWNTs, involving chemical, photochemical and electrochemical processes [2]. In this way, the electrochemical method presents two main advantages in comparison with the others. Firstly, electrochemical process enables selective functionalization of carbon nanotubes incorporated into electrochemical circuits via electrical addressing. Consequently, it is possible to selectively functionalize with a specific compound a device based on carbon nanotubes in a network composed of many transistors. Secondly, the rate of functionalization can be controlled with the density of electrons generated onto the carbon nanotube surfaces. This control is of primary importance to optimize surface sensing properties and to avoid non specific adsorptions.

Here are presented electrochemical experiments concerning the reduction of diazonium ions to radical species, leading to covalent grafting on carbon substrates [3,4]. Phenyl derivatives on the carbon surface were characterized by cyclic voltammetry (CV) and square-wave voltammetry (SWV) after potentiodynamic (using CV) or potentiostatic (using controlled-potential electrolysis CPE) electrografting. To establish suitable grafting conditions, a preliminary study of functionalization was optimized with 4-nitrobenzene group as a model. Experiments were carried out on a glassy carbon electrode taking into account its low porosity and structural similarity with SWNTs. 4-diazo-N,N-diethylaniline tetrafluoroborate (DDEA), a second commercially available salt, was characterized according to the pre-established parameters. Finally, an electroactive diazonium salts 4-diazodiphenylamine tetrafluoroborate was synthesized and characterized by electrochemistry to get complementary results and to define the optimized grafting conditions in order to obtain high-quality monolayers on carbon nanotubes.

## INVESTIGATED SUBSTRATES

4-nitrobenzenediazonium tetrafluoroborate (NBD) (97%, Aldrich 00620BE) and 4-diazo-N,N-diethylaniline tetrafluoroborate DDEA (97%, Aldrich 13012BU) from Aldrich were used as received and kept

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in the freezer. Anhydrous (99.8%) acetonitrile (Aldrich 27,100-4) was used as received. Tetra-n-butylammonium tetrafluoroborate (99%, Aldrich 21,796-4) was dried under vacuum at 60°C for 3 days. Distilled water was obtained from an Elgastat water purification system ($18\,M\Omega \cdot cm$).

## ELECTROCHEMICAL EQUIPMENT

The electrochemical studies were carried out using a BioLogic model EC-Lab®V9.25 potentiostat/galvanostat with 5 channels. All electrochemical experiments were performed in millimolar organic solutions containing a supporting electrolyte, using conventional three-electrode cells. The working electrodes were glassy carbon (GC) or modified (see below) glassy carbon disks ($\Phi = 3\,mm$); the counter electrodes were platinum wires and a Ag/10 mM $AgNO_3$, 0.1 M tetra-n-butylammonium tetrafluoroborate ($Bu_4NBF_4$) electrode served as reference ($Ag/Ag^+$ electrode, 0.56 V vs. NHE). The grafted species were monitored in transfer solutions containing 0.1 M $Bu_4NBF_4$ in $CH_3CN$. The solutions were degassed with argon for 20 min before each measurement and kept under dry argon during the entire experimental period. All experiments were run at 25°C.

## ELECTROCHEMICAL STUDY OF 4-NITROBENZENEDIAZONIUM TETRAFLUOROBORATE GRAFTING

A preliminary study was realized using the commercially available nitro derivative 4-nitrobenzenediazonium tetrafluoroborate to define the grafting conditions of the diazonium salts, and to infer low coverage grafting conditions transposable to various carbon substrates. Performing electrochemistry on 4-nitrobenzenediazonium tetrafluoroborate [4,5], leads to a cathodic peak ranging from 0 to $-0.5\,V$ (the value is dependent on the electrode nature, the concentration of the preparation solution and on the scan rate) attributed to the diazonium function reduction (Fig. 1a). This voltammetric wave is irreversible and thus indicative of an irreversible reaction, i.e. dinitrogen cleavage associated with electron transfer. As already reported [5], on the second scan the wave disappears completely, due to the blocking effect on the electrode surface by the grafted organic groups (Scheme 1). This general grafting behaviour of diazonium salts is related both to their easy reduction and to the concerted process of the electron transfer/dinitrogen cleavage which ensures that the formation of the radical species actually takes place on the surface.

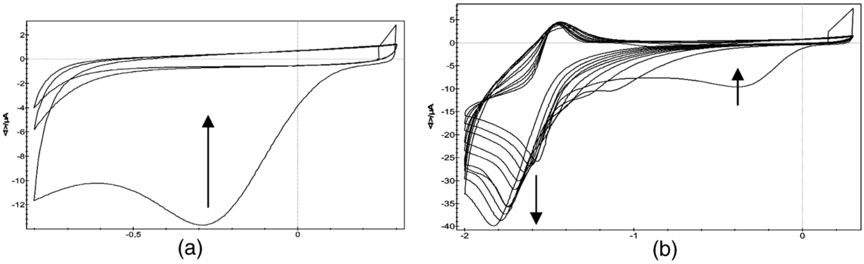

**FIGURE 1** (a) Influence of cycling on the diazonium reduction in 5 mM 4-nitrobenzenediazonium tetrafluoroborate (0.1 V/s, GC). (b) Influence of cycling on the CV in 0.5 mM 4-nitrobenzenediazonium tetrafluoroborate (0.1 V/s, GC).

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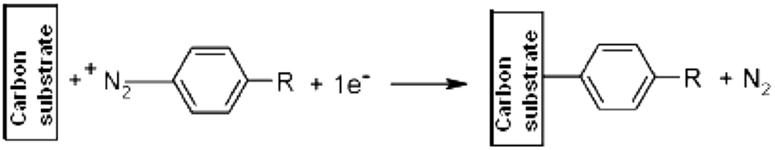
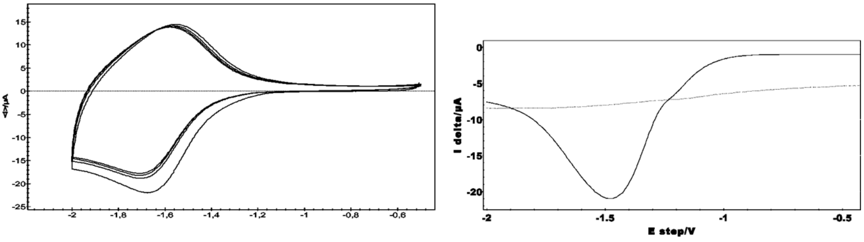
The influence of cycling on the CV in the obtained GC modified electrode is shown in Figure 1b when cycling toward the nitro reduction in 0.5 mM solutions. During the 4-nitrobenzenediazonium tetrafluoroborate electrografting, the voltammetric response, made up of the irreversible process associated with the diazonium salt reduction and of the reversible wave related to the nitrobenzene reduction [6], shows variations following the successive scans. In the first cycles, shifts of the cathodic peaks, especially strong for the diazonium reduction, are observed. The shifts increase progressively and a broadening of the reversibility related to the nitro group reduction to the radical anion appears. After the first scan the electrode presents a blocking effect toward the reduction of diazonium in solution because, in this potential range, no electroactive relay continue to exist for the grafted molecules. At the same time, the signal of the nitro reduction is maintained because electrons may be transferred from the electrode to the nitro groups in solutions, through the grafted nitro groups. In fact, because of the electronic transfer, diazonium reduction is still observed after the first scan but the signal is displaced in the feet wave of the electronic process of nitro reduction as for the commutating effect observed with ultrathin films [7]. Performing several scans leads



**SCHEME 1** Concerted reduction and $N_2$ cleavage leading to grafting of the phenyl moiety.



(a) (b)

**FIGURE 2** (a) CVs ($0.2\,\text{V}\cdot\text{s}^{-1}$, 4 successive cycles) of modified electrode obtained by ten cycles between 0.3 to $-2\,\text{V}$ in 0.5 mM 4-nitrobenzenediazonium tetrafluoroborate ($0.1\,\text{V}\cdot\text{s}^{-1}$, GC, ACN $Bu_4NBF_4$ 0.1 M). Charge measured $Q = 12.7\,\mu\text{C}$. (b) SWV measurements of a modified GC electrode vs. bare electrode.

to a more difficult electron transfer induced by thicker layers formed on the electrode surface. In the range $-1.3\,\text{V}$ to $-2\,\text{V}$, the cathodic response combines a mixture of the $NO_2$ electroactivity in the solution with the one of the immobilized groups.

After the potentiodynamic experiments and after washing the electrode in an ultrasonication bath, the modified electrode responses were examined in new solutions free of diazonium to determine the effectiveness of the grafting. In Figure 2a and 2b are respectively presented the CV and SWV measurements that evidenced the presence of the grafted nitrophenyl group, since a peak appears at the potential of $-1.6\,\text{V}$ ($-1.5\,\text{V}$ in SWV). The observed response (Fig. 2a) presents a broad reversible and stable wave due to the presence of grafted nitro phenyl groups. The measured charged of $12.7\,\mu\text{C}$ of the potentiodynamic grafting in Figure 2 is in accordance with the theoretical charge calculated for a closely dense packed monolayer [8,9]. In SWV a strong wave is obtained (Fig. 2b), in agreement with the reversible and stable character of the grafted molecules.

The choice of the electrolysis potential for covalent potentiostatic electrografting with 4-nitrobenzenediazonium tetrafluoroborate was also examined. It was observed that different electrolysis potentials for electrode modifications led to significant differences in grafting. Particularly, the intensity of the signal of the nitrophenyl group observed in all the cases at $-1.5\,\text{V}$, becomes higher as the electrolysis potential is set to a more negative value. The quantity of charge obtained by the integration of the cathodic peak in CV, as well as the corresponding grafting values are presented in Table 1.

First of all, for the same potential the obtained responses are moderately dependent on the concentration of the solution for

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**TABLE 1** Results From CV and SWV Measurements for GC Modified Electrodes in 1 mM 4-Nitrobenzenediazonium tetrafluoroborate Solution by CPE at Different Potentials

| E, V | Time, min | $C_4$-nitrobenzenediazonium tetrafluoroborate, mM | $Q_{film}$, μC | Γ, $mol \cdot cm^{-2}$ |
|---|---|---|---|---|
| −0.2 | 10 s | 0.1 | 0.9 | $8.90 \cdot 10^{-11}$ |
| −0.2 | 10 min | 0.1 | 2.1 | $0.21 \cdot 10^{-9}$ |
| −0.4 | 10 min | 0.1 | 2.4 | $0.24 \cdot 10^{-9}$ |
| −0.4 | 10 s | 1 | 2.0 | $0.20 \cdot 10^{-9}$ |
| −0.4 | 10 min | 1 | 3.0 | $0.30 \cdot 10^{-9}$ |
| −0.8 | 10 s | 0.1 | 1.5 | $0.15 \cdot 10^{-9}$ |
| −0.8 | 1 min | 0.1 | 2.4 | $0.24 \cdot 10^{-9}$ |
| −0.8 | 10 min | 0.1 | 4.3 | $0.42 \cdot 10^{-9}$ |
| −0.8 | 10 min | 1 | 4.5 | $0.44 \cdot 10^{-9}$ |
| −1.2 | 10 min | 1 | 24 | $2.37 \cdot 10^{-9}$ |

electrografting period below 15 min. Table 1 shows small differences in grafting rate when the electrolysis takes place in 0.1 M and 1 M 4-nitrobenzenediazonium tetrafluoroborate solutions. From the comparative analysis of the charges obtained by the integration of the *p*-nitrophenyl reduction peak (Table 1), it can be observed that at the same electrolysis potential, the electrolysis time has a stronger influence than the concentration of the substrate in the control of the grafting density.

More significantly, in the case of 4-nitrobenzenediazonium tetrafluoroborate, it is the potential value of electrolysis that has a paramount effect on the grafting quality. The surface concentration obtained in our experimental conditions is less than a close-packed monolayer when the electrolysis is realized at a potential above −1 V. Nevertheless, the surface coverage becomes higher when the potential is fixed to a more negative value. It exceeds the monolayer at the most negative electrolysis potential (−1.2 V). This is attributed to the commutating effect of the ultrathin layer that allows the electron transfer through the nitro reduction and thus leads to an increase of the layer thickness.

## CHEMICAL GRAFTING OF 4-NITROBENZENEDIAZONIUM TETRAFLUOROBORATE

As recently reported [10], during the potentiostatic experiment we also examined that the grafting of aryl groups may take place at the carbon

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electrodes without any electrochemical induction ($E = E_{ocp}$). Indeed, dipping the substrate into an appropriate diazonium salt solution results in its coverage by an organic aryl layer. The presence of arylgroups on the substrate after its immersion in a diazonium salt solution in acetonitrile was demonstrated by electrochemistry thanks to the nitrophenyl groups signature (after thorough rinsing and sonication in $CH_3CN$ of the electrode) both in CV and SWV.

The effect of 4-nitrobenzenediazonium tetrafluoroborate concentration for the spontaneous grafting was investigated. This was performed by varying concentration by three orders of magnitude in a low concentration domain (1 mM to 1 μM) while keeping the immersion time constant (1 h). The purpose of the immersion experiments was to detect the lowest concentration for which the grafted nitrophenyl signal was still detectable. As the 4-nitrobenzenediazonium tetrafluoroborate concentration decreases, so do the surface coverage and the surface of the nitrophenyl group reduction peak. The estimation of the thickness of the layer, deduced from the integration of the reduction peak, gives lower values than those corresponding to an ordered monolayer for 4-nitrobenzenediazonium tetrafluoroborate concentrations going from 1 mM to 0.01 mM. The evaluation of the grafting density obtained by cyclic voltammetry is shown in Table 2.

By decreasing the concentration of the immersion solution below 0.01 mM, it is observed by SWV measurements that grafting occurs even until micromolar values (Fig. 3).

In the low concentration domain, i.e. 1 μM to 0.01 mM, a linear dependence of $I_{delta}$ vs. concentration is found (Fig. 3b). For higher concentrations (>25 μM) the waves become constant, reflecting the formation of the organic layer on the surface and the progressive saturation of the grafting by this way. It has to be noticed that in the saturation range a measured charged of ~1.5 μC is obtained, indicating that a grafting rate of ~10% of the theoretical value is reached.

**TABLE 2** Charges Obtained from the Integration of the Nitro Reduction Peak for the Grafted Electrodes (Immersion at Various 4-Nitrobenzenediazonium tetrafluoroborate Concentrations for 1 h)

| 4-nitrobenzenediazonium tetrafluoroborate conc (μM) | >100 | 100 | 50 | 25 | 10 | 5 | 2 | 1 |
|---|---|---|---|---|---|---|---|---|
| Q (μC) | 1.4–1.6 | 1.4–1.6 | 1.4–1.6 | 1.3–1.5 | 0.8–0.7 | 0.4–0.1 | 0.05–0.1 | 0–0.05 |

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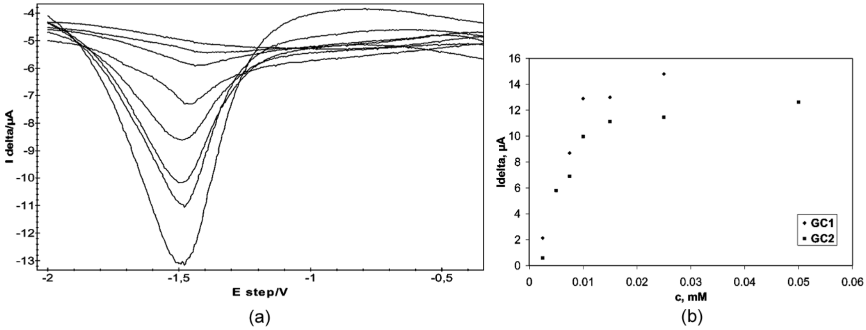

(a) (b)

**FIGURE 3** (a) SWVs responses of the grafted GC electrode obtained by immersion for 1 h in 4-nitrobenzenediazonium tetrafluoroborate solutions with various concentrations: 1, 2, 3, 4, 5, 8, 10 and 25 µM. (b) The dependence $I_{delta}$ (intensity variation between the feet and the peak wave) values obtained in SWV measurements for two GC modified electrodes *vs* concentration of the immersion solution.

## ELECTROCHEMICAL STUDY OF THE GRAFTING OF DIAZO COMPOUNDS WITH ELECTRODONATING SUBSTITUENTS

To establish grafting conditions applicable to all kinds of diazonium derivatives on carbon substrates and more especially on SWNTs, we completed the grafting behavior study with another commercial diazonium salt (4-diazo-N,N-diethylaniline tetrafluoroborate (DDEA)) and with a new electroactive diazonium salts synthesized in our laboratory. These compounds were chosen for the contrasted electronegativity of the *para* substituents compared to 4-nitrobenzenediazonium tetrafluoroborate, in order to enlarge the panel of grafted molecule and measure the relationship that could exist between each diazonium salt and the grafting parameters. For these compounds we observed different diazonium potential reduction values (Table 3).

After studying the strong electroacceptor derivative 4-nitrobenzenediazonium tetrafluoroborate, experiments were carried out with the electrodonating diethylamino group [11] diazonium. In comparison, the potential reduction of this compound is highly shifted toward cathodic values as a consequence of the electronic enrichment of the diazonium group that becomes harder to reduce. Unfortunately, because of the lack of reversibility of the redox reaction of the grafted entities, it is impossible to observe real characterization of the modified surface by electrochemistry for DDEA. Then, an other compound was examined to support the preliminary observation made with 4-nitrobenzenediazonium tetrafluoroborate. Particularly, DPA give

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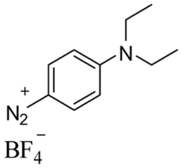
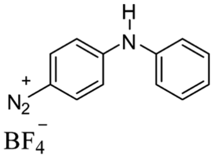
**TABLE 3** Characteristic Electrochemical Potential Values of Diazonium Salts

| |  DDEA |  DPA |
|---|---|---|
| Diazonium reduction (V) | −0.90 | −0.83 |
| Grafted molecule (V) | – | ~0.60 |

stable reversible oxidation systems in CV and strong waves in SWV (Fig. 4 and Table 3) after both potentiostatic or potentiodynamic grafting. A similar trend as observed for 4-nitrobenzenediazonium tetrafluoroborate is evidenced for cathodic potentials before −1 V:

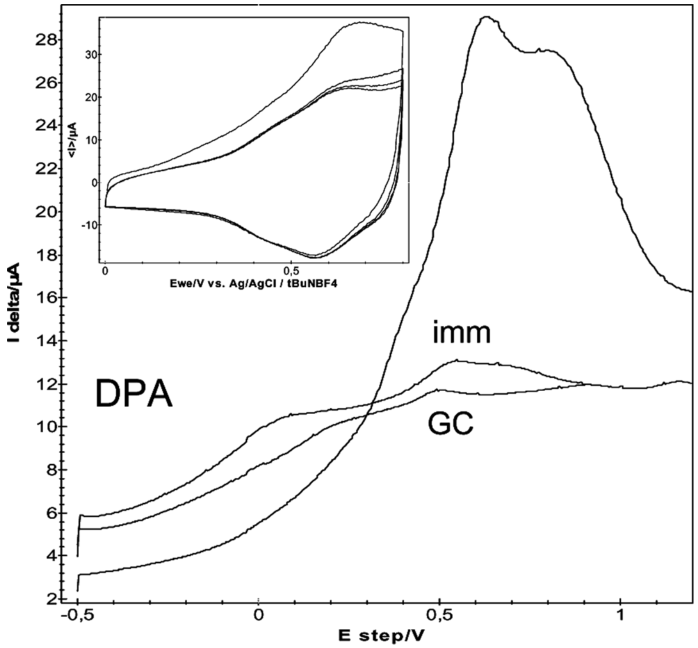


**FIGURE 4** Voltammogram (SWV, inset 4 cycles in CV) of the electrochemically grafted DPA. Comparisons with bare GC electrodes (GC) and grafting by immersion of the electrode for 1 h in 1 mM solutions of the diazonium salt.

electrochemical grafting leads to a maximum coverage of ~30% (Q equals 4 μC by integrating waves in CV) and spontaneous grafting is discriminated with difficulty from the bare electrode signal. Moreover, the spontaneous grafts are very weak compared to those obtained from 4-nitrobenzenediazonium tetrafluoroborate and a saturation layer of less than 3% of the maximum theoretical coverage is obtained for this product. This could be attributed to the electronegativity of the para substituents which induce a modification of the ability to form phenyl radicals. Finally, for grafting potentials under $-1\,V$ (until $-2\,V$), no increasing coverage values were observed. This supports the idea of electron transfer through the $NO_2$ groups, allowing the multilayer formation.

## CONCLUSION

The electrochemical study of 4-nitrobenzenediazonium tetrafluoroborate as a model allowed the identification and optimisation of grafting conditions, notably for low coverage densities. Grafting of three diazonium salts was performed by electrochemical methods (CV and CPE). For electroactive diazonium salts, the presence of molecules on the electrode surface was demonstrated by transfer experiments where the signature of the functional groups could be monitored. It was also found that low coverage can be obtained directly by simple immersion, without any electrochemical induction.

Studies are ongoing to understand further transformations of the grafted species that may occur on the electrode surface. Attempts are also in progress to graft diazonium based molecules on single-walled carbon nanotubes for the fabrication of sensing devices.

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[8] The electrical charge of the grafted layer ($Q_{film}$) is calculated by integration of the voltammetric peak corresponding to the reduction of p-nitrophenyl groups. The surface coverage $\Gamma$ can be calculated as $Q/FA$, where $F$ is the Faraday number and $A$ is the geometric area of the electrode. From molecular models, a monolayer on a perfect plane would correspond to a surface concentration of $1.35 \cdot 10^{-9}$ mol cm$^{-2}$.[6]

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It was reported also that coverage of $1.2 \cdot 10^{-9}$ mol cm$^{-2}$ has been calculated for a close packed layer of *p*-nitrophenyl groups on a flat surface.[9] So the charge expressed in Coulombs that corresponds to a monolayer grafted on the electrode surface (in consideration of one exchanged electron during the redox process and with a geometric area of 0.07 cm$^2$) is $Q = nFN \approx 8$–9 μC. Considering a surface roughness factor of around 1.5 for polished GC, hence a monolayer should correspond to a charge around 13 μC.

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