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The reduction of 4-nitrobenzene diazonium electrografted layer: An electrochemical study coupled to in situ sum-frequency generation spectroscopy

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A B S T R A C T

This work describes an electrochemical study of 4-nitrobenzene diazonium (4-NBD) reduction onto glassy carbon (GC) electrode coupled to in situ sum-frequency generation (SFG) spectroscopy. After 4-NBD grafting at 0.3 V vs. saturated calomel electrode (SCE) onto GC, SFG allowed a clear signal assigned to the symmetrical vibration mode of the nitro (NO₂) groups to be observed at 1349 cm⁻¹ or 1353 cm⁻¹ depending on whether the spectrum was recorded in air or inside the solution. This result proved that 4-NBD grafting actually occurs at a potential as high as 0.3 V vs. SCE. The combination of SFG data and cyclic voltammetry (CV) also indicated that at such a potential, NO₂ groups did not experience reduction process into hydroxylamine (NHOH) or amine (NH₂) groups. The electrolysis of grafted NO₂ moieties at -0.1 V was followed by CV and in situ by SFG. The exponential decay of the NO₂ signal located at 1353 cm⁻¹ vs. electrolysis time was in accordance with a charge transfer-limited reaction rate for a species immobilized at the electrode surface, and allowed a first order kinetic rate constant for NO₂ reduction to be estimated $k = 0.006 \text{ s}^{-1}$. The integration of the peaks observed on the corresponding cyclic voltammograms (CVs) which were attributed to the NO/NHOH reversible system showed that the NO₂ reduction produced both hydroxylamine and amine groups and was not quantitative. The fact that SFG spectroscopy was silent for long electrolysis time values suggested the remaining nitro groups to be located far from the electrode surface, as a consequence of an electron tunneling efficiency which decreased throughout the film thickness. Further electrolysis at -0.8 V allowed the remaining nitro groups to be reduced into NH₂ with almost quantitative yields. All these results suggest the existence of a stratified layer during the electrolysis process, in which there is no limitation due to H⁺ diffusion in the organic film.

Keywords:

Nitrobenzene diazonium
Electrografting
Sum frequency generation spectroscopy
Cyclic voltammetry
NO₂ reduction mechanism
Glassy carbon

1. Introduction

Since the first report by Delamar et al. in 1992 [1], diazonium grafting has proved to be one of the most up-and-coming strategies for electroactive surface functionalization. This outstanding interest is mainly due to the easy way it affords to covalently immobilize organic groups onto carbon-based materials [2]. Modification using diazonium was also extended to non-carbonaceous materials such

as metals or semiconductors [3–5]. The wide range of potentialities that diazoniums offer has been recently reviewed [6–8], with a particular focus on the control of the modification [9,10]. Depending on the group borne by the aromatic moiety, diazonium compounds have been exploited in many research fields such as energy conversion and storage [11,12], molecular electronics [13,14], and chemical [15–17] and biochemical [18,19] sensing. They may also be used for further functionalization by means of chemical reactions such as amine/carboxyl condensation [20,21] or the trendy click chemistry [22–24], or by electropolymerization in the case of conjugated monomer-functionalized diazonium [8,17,25,26].

The commonly admitted pattern for diazonium grafting is a two-step mechanism: the diazonium cation is reduced into its

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corresponding radical which further evolves to afford a covalent bond with the electrode surface [3]. Mechanistic studies performed by Andrieux et al. have proved that electron transfer is actually concomitant with nitrogen release [27]. More recent studies have shown that spontaneous grafting may also occur [28–30] and Lehr et al. have proposed several pathways to account for this mechanism [31].

Because available from common chemicals suppliers and bearing an electroactive nitro group, 4-nitrobenzene diazonium (4-NBD) is often used as a model compound to interrogate or modify surface properties. As a redox probe, it has been used for instance to evidence the effect of a radical scavenger on the organic layer formation [32], to highlight the difference of reactivity between graphene single and multilayers [33] or to illustrate the combination of electrografting and scanning probe lithography for nanoscale patterning of carbon surface [34]. It has also been used to modify the electrical properties of graphene field-effect transistors [35] or to prepare optical fiber-based sensors for ammonium [36] or reverse osmosis membrane [37]. As a model compound, the reactivity of 4-NBD has been extensively studied both in organic and aqueous media [38–43]. However, we recently showed [44] that the first step of its reduction mechanism (Scheme 1 reaction 1) remained still unclear since it gave rise to contradictory reports. We also proved that the diazonium grafting actually occurs at less cathodic potentials than usually reported, ca. 0.3 V vs. saturated calomel electrode (SCE) [44]. Thus, this latter process is totally distinct from nitro groups reduction (Scheme 1 reaction 2), hence allowing well-defined functionalization of the surface to be obtained. Nitro reduction is known to proceed according to a complex mechanism which involves an intermediary hydroxylamino (NHOH) species to finally afford amino (NH_2) groups (Scheme 1 reactions 2, 3). However, NHOH may also be reoxidized to give nitroso (NO) groups via a reversible process (Scheme 1 reaction 4). Brooksby and Downard have reported incomplete conversion of NO_2 into NH_2 and the formation of NHOH intermediates even after cathodic polarization of the modified electrode at -0.8 V/SCE during 5 min [45], which has been later confirmed by Yu et al. [46]. Ortiz et al. have also observed the reversible NO/NHOH system while performing NO_2 reduction by cyclic voltammetry from 0.6 to -0.6 V vs. Ag/AgCl [42]. However, in both cases 4-NBD grafting onto the electrode surface was performed in conditions such as NO_2 reduction occurred simultaneously to diazonium grafting, i.e. the resulting organic layer after surface functionalization was already a mixed NO_2 /NHOH film.

In this paper, we take advantage of our previous results to further investigate the reduction of NO_2 moieties immobilized onto GC electrode. Starting from an organic layer which does not bear any NO or NHOH groups, we describe the results obtained by performing several potentiostatic electrolyses in order to verify whereas it is possible or not to selectively tune surface functional groups and get successively NHOH and NH_2 layers. The resulting modified electrodes were characterized using electrochemical techniques. We also report the first time application of sum frequency generation (SFG) spectroscopy to diazonium compounds grafted onto GC. This latter is an intrinsic surface vibrational spectroscopy which exhibits extreme sensitivity towards the electrochemical interface and allows information to be obtained upon various systems such as supported catalysts [47], nanoparticles [48] or thin films adsorbed onto electrode surface [49]. Until now, only the group of Somorjai has studied phenylalanine adsorption and orientation on a GC electrode as a function of the applied potential in the CH stretching IR spectral range [50,51]. Here, the signal corresponding to the symmetric stretch of the NO_2 groups was observed and its decay was followed in situ during the electrolysis process.

2. Experimental

2.1. Reagents and apparatus

All products were used as received. 4-nitrobenzene diazonium (4-NBD) tetrafluoroborate ($\text{C}_6\text{H}_4\text{N}_3\text{O}_2\text{BF}_4$, 97%), ferricyanide(III) potassium ($\text{K}_3\text{Fe}(\text{CN})_6$, 99% powder) and acetonitrile (HPLC grade, $\geq 99.9\%$) were purchased from Aldrich. Deuterium oxide (99.8%), potassium dihydrogenophosphate (KH_2PO_4), dipotassium hydrogenophosphate (K_2HPO_4) were supplied by Acros Organics. Tetra-butylammonium hexafluorophosphate ($\geq 98.0\%$) was from Fluka. Acid solutions were prepared by dilution of concentrated hydrochloric acid (37% HCl) from VWR using Milli-Q water (18 M Ω cm). All solutions were deaerated by bubbling Nitrogen during 10 min. A gas stream was maintained over the solutions during experiments.

All the electrochemical experiments were performed at room temperature using a Metrohm μ -Autolab II potentiostat interfaced to a personal computer and controlled with NOVA 1.10 software package. A classical three-electrode glass cell was used with a Metrohm platinum rod and a Radiometer saturated calomel electrode (SCE) connected to the cell by a capillary as counter and reference electrode, respectively. All the potentials are given with respect to SCE. Working electrode was a 3 mm diameter ($A = 7.07 \text{ mm}^2$) glassy carbon (GC) rotating disk electrode from Radiometer. The geometrical surface area A was used for all the surface concentration calculations. For SFG in situ experiments, working electrode was a GC plate (5.5 mm diameter) from Mersen. For atomic force microscopy (AFM) a pyrolyzed photoresist film (PPF) plate (6 mm diameter) prepared at the Institut des Sciences Chimiques de Rennes according to published procedure [52,53] was used as the working electrode. PPF was used for diazonium layer thickness measurements, as it is known to react like GC while being as flat as highly oriented pyrolytic graphite (HOPG) [45].

2.2. Electrode preparation and functionalization

Prior to modification, GC electrodes and GC plates were manually polished to a mirror-like finish successively with 9 μm , 3 μm and 1 μm diamond powder from Presi on a cloth polishing pad. After each step, the electrode was thoroughly rinsed with Milli-Q water and sonicated in ethanol for 5 min in order to remove any impurity. Freshly polished electrode was modified in 0.1 M HCl solution containing 2.5 mM 4-NBD, by constant potential electrolysis at 0.3 V during 300 s [44]. These conditions were chosen in order to produce multilayered, self-inhibiting films. After modification, the electrode was carefully rinsed with Milli-Q water before and after sonication in ethanol during 5 min to remove weakly adsorbed moieties.

2.3. Diazonium film characterization

Diazonium film thickness was measured by atomic force microscopy (AFM) at the Institut des Technologies Avancées en sciences du Vivant (ITAV USR 3505, Toulouse) using a JPK NanoWizard II (Life Science Version) running a MSNL-E probe in contact mode.

2.4. Sum frequency generation spectroscopy

SFG spectroscopy is a surface sensitive spectroscopy based on the nonlinear second order optical activity of materials (modelled by $\chi^{(2)}$), the nonlinear second order susceptibility of the probed interface), depending on the Infrared and Raman activities of the molecules constituting the interfaces [54]. It is particularly well-suited for the study of the electrochemical interface [55]. It follows the energy ($\omega_{\text{SFG}} = \omega_{\text{vis}} + \omega_{\text{IR}}$) and momentum ($\hbar k_{\text{SFG}} = \hbar k_{\text{vis}} +$

hk_{IR}) conservation rules. The SFG experimental setup used in the CLIO Free Electron Laser (FEL) European facility is described in detail elsewhere [49,54]. Briefly, it is made of two optical parametric oscillators (OPO) tunable in the Infrared (IR) [2.5–8 μm, 2 μJ per pulse, 2 cm⁻¹ spectral resolution] and Visible (Vis) [420–710 nm, 8 μJ per pulse, 6 cm⁻¹ spectral resolution] spectral ranges. The OPOs are pumped by a laser beam (1064 μm wavelength) amplified by a double-pass in flash-pumped Nd:YAG amplifiers (Quantel, 25 Hz repetition rate), delivering 2 μs long trains of pulses. The laser source comes from a diode-pumped picosecond (6.8 ps) Nd:YVO₄ oscillator (High Q Laser, 62.5 MHz repetition rate) after acousto-optic modulation generating the final temporal structure. The CLIO FEL [56] ranging from 5 to 150 μm delivers 10 μs long macropulses containing 2 ps micropulses (10 μJ per pulse, 2 cm⁻¹ spectral resolution) and has the same repetition rate as the OPOs. The monitoring of the higher peak power delivered in the IR spectral range (7–8 μm in the present case) by the FEL with respect to the IR OPO allows working with sufficient energy reaching the surface electrode in a spectro-electrochemical cell designed for in situ SFG spectroscopy in aqueous electrolytes [49,55]. It is worth noting that in the present case we worked with deuterated water in order to be free from water absorption in the investigated IR spectral range. The SFG measurements are performed with the IR and Vis (488 nm wavelength) beams mixed at the same point of the electrode having incidence angles of 65° and 55° (ssp polarized for the SFG, Vis, IR beams, respectively) with respect to the surface normal. SFG photons (456–460 nm wavelengths) of the interface are therefore collected through a monochromator after spatial and spectral filtering. The SFG spectra are obtained after experimental normalization with the SFG signal of a ZnS crystal reference acquired simultaneously, taking into account the potential fluctuations and absorption of the IR laser beam during measurements. In this work, we investigated diazonium films first in air after grafting and drying, then inside the spectro-electrochemical cell filled with 0.1 M HCl in deuterated water.

3. Results and discussion

3.1. Electrochemical and AFM characterization of the functionalized electrodes

Two consecutive cyclic voltammograms (CVs) of 4-nitrobenzenediazonium (4-NBD) in 0.1 M HCl were recorded on a

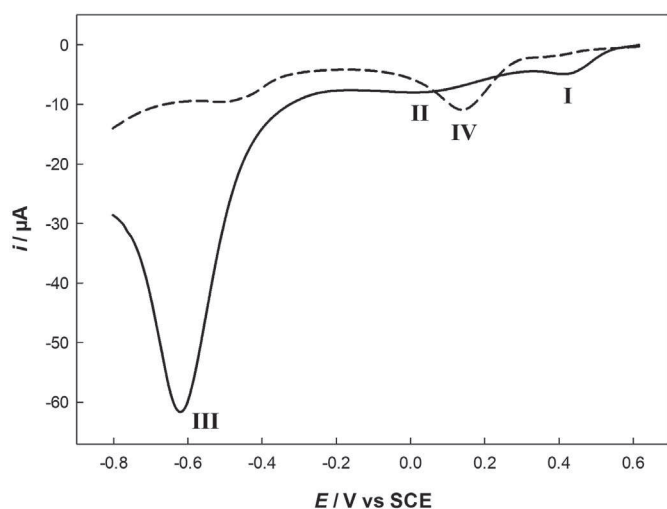


Fig. 1. CVs recorded on a bare GC electrode in a 0.1 M HCl solution containing 2.5 mM 4-NBD. First (solid line) and second (dashed line) forward scans. Scan rate: 100 mV s⁻¹.

freshly polished glassy carbon (GC) electrode (Fig. 1). For the sake of clarity, only the forward scans are depicted. On the first scan (solid line), 3 reduction peaks were observed at 0.4 V (I), 0.05 V (II) and -0.6 V (III), respectively. On the second scan (dashed line), peaks I and II disappeared and peak III strongly decreased, whereas a new peak located at 0.15 V (IV) arose. These voltammograms are typical of 4-NBD grafting and reduction as recently described by our group (Scheme 1) [44]. In particular, we proved by electrochemical and spectroscopic evidences that peak I actually corresponds to diazonium electrografting and that this latter reaction is totally distinct from the reduction of 4-NBD nitro groups, which is rather related to peak II. Peaks I and II were not observed on the second scan as a consequence of low electron transfer kinetics due to self-inhibiting film formation and irreversible reduction process, respectively. Peak IV was attributed to the reversible nitroso/hydroxylamine (NO/NHOH) system [42,44,45]. It has to be noticed that the absence of peak IV on the first forward scan ensures NO₂ groups to remain unaffected by 4-NBD electrografting. Several authors proposed peak III to correspond to the reduction of NO₂ groups into NH₂ via the NO and NHOH intermediary functions [42,45]. It has to be noticed that, except reaction (4) which is known for years, only the first step of the reduction mechanism may be undoubtedly assigned to a single electrochemical process.

In order to get a GC electrode bearing only NO₂ moieties (GC-NO₂) [44], the functionalization was achieved by grafting 4-NBD using constant potential electrolysis at 0.3 V for 300 s. The amount of charge consumed during 4-NBD grafting process was Q_G = 11 ± 3 μC (average value calculated on the basis of 6 different grafting experiments). Taking into account that grafting faradic yield is close to 80% as claimed by Allongue et al. (the rest of the radicals generated by diazonium reduction reacting in the solution) [57], the corresponding surface concentration of 4-NBD was estimated Γ_{4-NBD} = (13 ± 3) × 10⁻¹⁰ mol cm⁻². However, as the work by Allongue et al. was performed in acetonitrile, this value was most likely overestimated in our case. Another determination was conducted by recording a CV of a grafted GC-NO₂ film in an acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (not shown). The integration of the reversible signal located at -1.1 V, and corresponding to the NO₂/NO₂⁻ couple, led to Γ_{4-NBD} = 8.1 × 10⁻¹⁰ mol cm⁻². This time, the value was probably underestimated since the NO₂ groups may not be all responsive towards electrochemical measurements [39]. These Γ_{4-NBD} values may be considered as the upper and lower limits for the true Γ_{4-NBD} in our films, respectively. They both are close to 12.0 × 10⁻¹⁰ mol cm⁻², corresponding to an ideal close-packed monolayer of aromatic moieties [45]. As the film formed during the electrolysis is not ideally closed-packed, both Γ_{4-NBD} values are therefore rather more in accordance with porous multilayers formed in self-inhibiting film conditions. The experimentally measured surface density Γ_{4-NBD} = 8.1 × 10⁻¹⁰ mol cm⁻² will be used for further discussion and comparison, keeping in mind that it constitutes merely a lower limit. The thickness of the resulting organic film was measured by AFM in contact mode. An average value of 4 nm was found, which is in accordance with literature data including our own studies for the formation of a multilayer film [45,58–60].

In order to determine the quality of the films, CVs were recorded before and after the electrolysis at 0.3 V for 300 s in a 0.1 M phosphate buffer saline (PBS) solution (pH 7) containing 5 mM Fe(CN)₆³⁻ as a redox probe (Fig. 2a and b). On bare GC, Fe(CN)₆³⁻ exhibited a quasireversible system with a ΔE_p = 210 mV consistent with literature data [43]. On GC-NO₂, the reversible signal was almost totally suppressed, in accordance with the barrier effect of the organic layer [2], suggesting that the film is continuous enough to prevent access to the electrode surface. Two consecutive constant potential

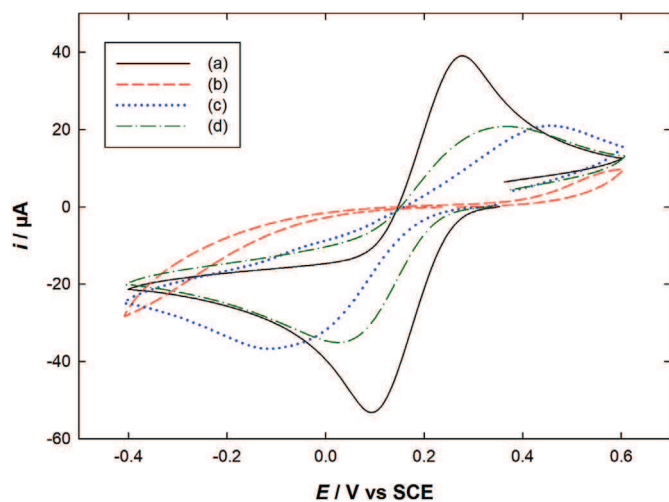
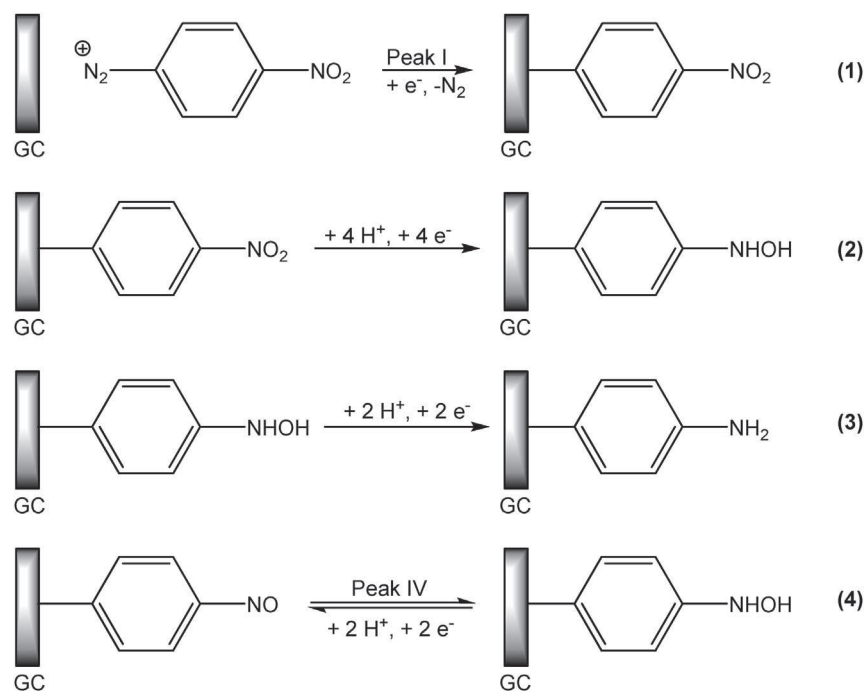


Fig. 2. CVs recorded in a 0.1 M PBS solution (pH 7) containing 5 mM $\text{Fe}(\text{CN})_6^{3-}$ on: (a) unmodified GC; (b) GC- NO_2 without further treatment after 4-NBD grafting; (c) GC- NO_2 which experienced a constant potential electrolysis at -0.1 V for 300 s; (d) GC- NO_2 which successively experienced constant potential electrolyses at -0.1 V for 300 s and at -0.8 V for 300 s. Scan rate: 100 mV s^{-1} .

electrolyses were then performed on GC- NO_2 in a diazonium-free 0.1 M HCl solution. They were operated for 300 s at -0.1 V and -0.8 V, ie for potential values corresponding to Peak II and III, respectively. The behaviors of the resulting films were examined towards $\text{Fe}(\text{CN})_6^{3-}$ (Fig. 2c and d). Contrary to what was observed on GC- NO_2 , after further electrolysis a slowed redox system was observed, with peak currents reaching around 60% of those recorded on bare GC. The corresponding ΔE_p were 560 and 340 mV, respectively. $\text{Fe}(\text{CN})_6^{3-}$ redox mechanism being known to proceed via an inner-sphere mechanism, the observation of the partial reduction and re-oxidation peaks supported the presence of pinholes in the organic film. Although these pinholes were also

present in the GC- NO_2 film, the electrostatic repulsion between the nitro groups and the negatively charged redox probe, which strongly decreases or even disappears after reduction into NHOH and NH_2 , accounts for the almost totally blocking behavior in the NO_2 case.

3.2. SFG characterization of GC- NO_2

The SFG spectrum of GC- NO_2 recorded outside solution (Fig. 3, curve A) exhibited a clear signal located at 1349 cm^{-1} which corresponded to the symmetrical vibration mode of the NO_2 group. Therefore, SFG spectroscopy afforded a supplementary evidence for diazonium grafting at a potential as high as 0.3 V. The spectrum recorded on the same functionalized electrode in contact with a deuterium oxide solution containing 0.1 M HCl showed the same signal centered at 1353 cm^{-1} but twice higher (Fig. 3, curve B). This latter position depends on the nature of the substrate, the molecular structure of the probed molecules and their chemical surroundings in the $1330\text{--}1360 \text{ cm}^{-1}$ spectral range [61–68]. Since SFG is very sensitive to structure and organization of the considered system [69], the increase of the signal may be due to the higher order of organization in the film while immersed into solution compared to the same organic layer outside solution, in which the aromatic moieties may be collapsed. To the best of our knowledge, this is the first time that a diazonium compound grafted onto an electrode surface is observed by this technique.

3.3. Electrochemical study coupled to SFG spectroscopy

To get more information on the various reduction steps of 4-NBD, several experiments were conducted by combining electrochemical techniques and SFG spectroscopy.

A constant potential electrolysis at -0.1 V for 800 s was performed on the GC- NO_2 electrode in a deuterium oxide solution containing 0.1 M HCl, and the SFG signal at 1353 cm^{-1} corresponding to the NO_2 group was recorded in situ during the whole experiment (Fig. 4). SFG data clearly showed a decrease of the

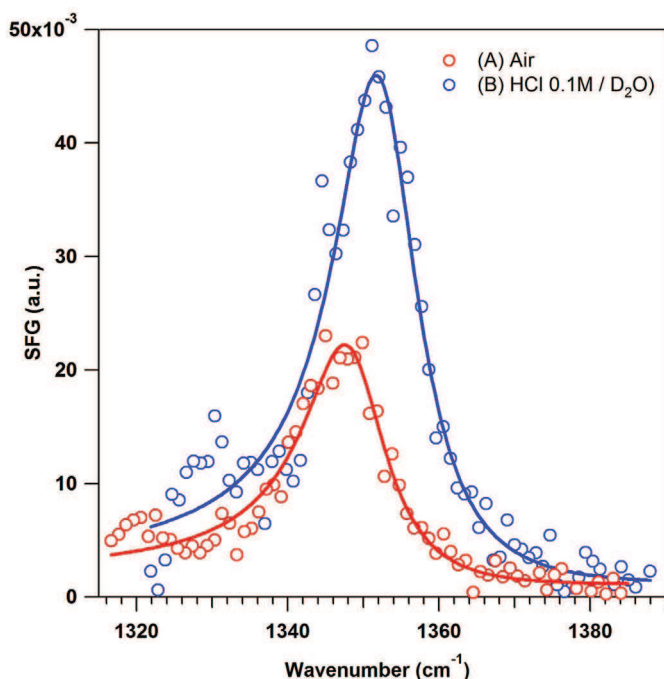


Fig. 3. SFG spectra recorded on a GC electrode functionalized by 4-NBD grafted by constant potential electrolysis at 0.3 V for 300 s. Spectra recorded outside (A) and into (B) 0.1 M HCl in D₂O. Lines are fit to the data following the mathematical procedure described in reference ⁵¹.

corresponding signal as the result of the reduction of nitro moieties, in accordance with our previous results [44]. The intensity reached zero after 500 s electrolysis, suggesting at this time the reduction reaction was almost quantitative. The resulting decay was satisfactorily fitted using the following equation (Equation (1)):

$$\Gamma(t) = \Gamma^{\circ} e^{-kt} \quad (1)$$

where $\Gamma(t)$ (mol cm⁻²) is the NO₂ surface concentration at time t , Γ° (mol cm⁻²) is the NO₂ surface concentration at initial time and k (s⁻¹) is the electron transfer rate constant from the cathodic part of the Butler-Volmer equation, that is (Equation (2)):

$$k = k^{\circ} e^{-\frac{\beta n F (E - E^{\circ'})}{RT}} \quad (2)$$

where k° (s⁻¹) is the intrinsic heterogeneous transfer rate constant, β is the cathodic transfer coefficient, n is the number of electron exchanged per mol of reduced NO₂, F is the Faraday constant (96500 C mol⁻¹), E (V) is the applied potential, $E^{\circ'}$ (V) is the apparent standard potential, R is the gas constant (8.314 J K⁻¹ mol⁻¹) and T is the temperature (K).

Equation (1) is the solution of the differential mass balance Equation (3), which is consistent with a species immobilized at the electrode surface and a charge transfer-limited, first order reaction rate $v(t)$, and may be expressed (Equation (3)):

$$v(t) = -A \frac{d\Gamma(t)}{dt} = k A \Gamma(t) \quad (3)$$

where A (cm²) is the electrode active surface area.

The fact that Equation (1) satisfactorily fits the SFG signal decay indicates that the reaction rate is limited only by the amount of adsorbed species ($\Gamma(t)$).

Considering the potentiostatic conditions used for this experiment, k is constant and the differential equation (3) may be solved to give a first order kinetic rate constant for NO₂ reduction with respect to surface concentration $k = 0.006$ s⁻¹.

In the present experiment, the SFG signal is expressed as arbitrary units, thus making it impossible to access the Γ° value by this technique. The global amount of charge consumed during the electrolysis at -0.1 V was found to be 28 ± 3 μ C. In order to evaluate the contribution of the aromatic skeleton to this latter value, the same electrolysis was performed on a GC electrode functionalized by an unsubstituted phenyldiazonium. The corresponding amount of charge was 4.8 ± 0.7 μ C, and may be associated to phenyl groups cleavage from the surface and loss of material, as reported by Ortiz et al. [42]. Thus, the charge that actually relied on NO₂ reduction was $Q_{-0.1} = 23 \pm 4$ μ C. From the relationship between $Q_{-0.1}$ and the reaction rate v , and taking into account the expression of $\Gamma(t)$, it is possible to express (Equation (4)):

$$Q_{-0.1}(t) = n F \int_0^t v(t) dt = -n F A \Gamma^{\circ} (e^{-kt} - 1) \quad (4)$$

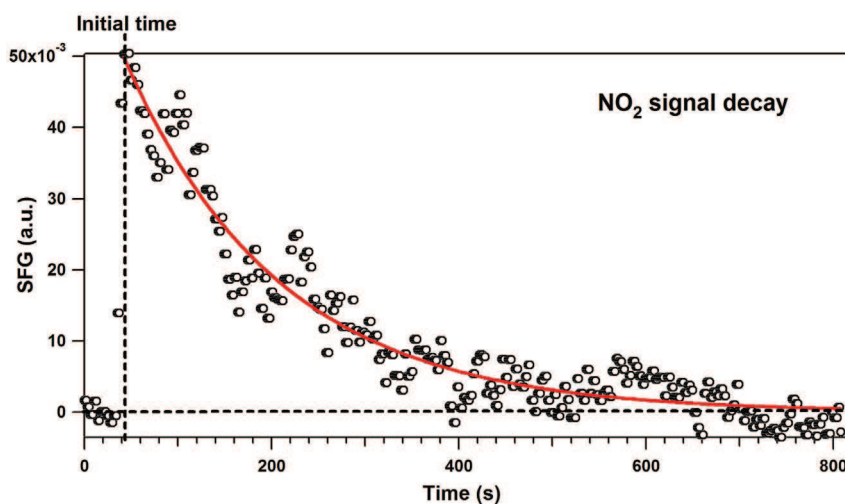


Fig. 4. Decay of the NO₂ SFG signal located at 1353 cm⁻¹ recorded in a D₂O solution containing 0.1 M HCl during constant potential electrolysis performed at -0.1 V during 800 s on a GC-NO₂ electrode and corresponding fit. Curve fitting (red) performed using Equation (1). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Thus, for long electrolysis times, $Q_{-0.1}$ may be approximated as $Q_{\infty} = nFA\Gamma^{\circ}$. Taking into account that n may be 4 or 6, depending on whether the reduction product is NHOH or NH_2 , respectively, two different values of Γ° were obtained: $(8 \pm 1) \times 10^{-10}$ and $(6 \pm 1) \times 10^{-10} \text{ mol cm}^{-2}$. Both were higher than the values commonly reported for monolayer coverage (ca. $2.5 \times 10^{-10} \text{ mol cm}^{-2}$) [44,45,57], which suggested that the electrolysis process at -0.1 V did not only affect the most easily reducible NO_2 groups in our multilayered films. The comparison of these values with $\Gamma_{4\text{-NBD}}$ (lower limit: $8.1 \times 10^{-10} \text{ mol cm}^{-2}$) showed that the electrolysis at -0.1 V actually reduced at most 100% or 75% of the total NO_2 groups for final product being NHOH and NH_2 , respectively. The 100% value may be considered keeping in mind that $\Gamma_{4\text{-NBD}}$ is underestimated (ratio 62% and 46% were obtained if using the upper limit: $\Gamma_{4\text{-NBD}} = 13 \times 10^{-10} \text{ mol cm}^{-2}$). In summary, the reduction at -0.1 V affected at least half the nitro groups, but was not exhaustive. This observation is apparently in contradiction with the SFG data, which showed complete disappearance of the NO_2 signal. The comparison of in situ SFG and electrochemical data suggests that part of the NO_2 groups are silent for SFG spectroscopy on one side, and another part silent for the reduction process on the other side. The two parts, defined by their positions inside the film, may a priori be distinct, partially overlap or be equal. As for the SFG spectroscopy, its symmetry properties require that the investigated chemical moieties possess a net alignment at the surface to appear on the spectra. Considering that the NO_2 groups in the grafted films experience a weaker interfacial electrical field as they are located farther from the electrode surface and taking into account the natural disordered structure of the films, only the nitro moieties close to the carbon surface contribute to the SFG spectra, the others being too randomly oriented or simply too far. As for the reduction process, the silence of some NO_2 groups depends on the scenario, or equivalently the limiting steps, involved in the electrolysis. Brooksby and Downard suggested the electron transfer throughout the film to occur via site-to-site hopping [45]. The reduction of NO_2 groups being an irreversible process, it was assumed that, for thick films, electron tunneling was inefficient. Consequently, NO_2 moieties far from the electrode surface were unaffected by the reduction process and, thus, silent from the electrochemical point of view. Moreover, the nature of the reduction product, namely NHOH or NH_2 , was proposed to depend on proton availability into the film [45]. On the contrary, Ceccato et al. considered the electron transfer process to be independent from the film thickness and to occur via a NO_2 self-mediated mechanism throughout the film [39]. They made evidence for the “inner” NO_2 groups, i.e. those located very close to the electrode surface, to be reduced first, but suggested that only a part of these groups are effectively reduced, this part corresponding to moieties easily solvated because of the presence of defects or pinholes in the film. Here, the complete disappearance of the SFG NO_2 signal proves that all the NO_2 groups located in the close vicinity of the electrode surface are actually reduced. Moreover, the fact that $\Gamma(t)$ verifies Equation (1), which satisfactorily fits the decay of the SFG signal without taking into account any mass transport phenomenon, shows that there is no limitation from a lack of solvation for the reduction of the inner NO_2 groups. The k value found here (ca. 0.006 s^{-1}) is in the same order of magnitude as those reported by Ceccato et al., but can be definitely ascribed to a first order kinetics, excluding any “cumulative effect of several types of inner-layer groups”, as invoked by Ceccato et al. On the contrary, the fact that the electrolysis yield was not quantitative demonstrates that all the NO_2 groups present in the film are not reduced, but only the closest ones from the electrode surface. This strengthens the hypothesis of an electron tunneling process, the efficiency of which decreases throughout the organic film while

increasing the distance to the electrode, in accordance with Brooksby and Downard [45].

To get further information on NO_2 reduction in the film, the same experiment as before was conducted in a classical three-electrode cell using similar conditions. In this case 40 successive electrolyses were performed at -0.1 V during 15 s (total electrolysis time: 600s) and a CV was recorded between 0 and 0.4 V at the end of each electrolysis (Fig. 5). Before electrolysis, no peak was observed in the potential range from 0 to 0.4 V (Fig. 5, dashed line), as the result of a 4-NBD grafting which does not affect NO_2 groups. On the contrary, the first CV recorded after 15 s electrolysis exhibited the reversible signal characteristic of the NO/NHOH redox couple. Both cathodic and anodic peak currents increased during the electrolysis up to a maximum after 120–135 s. Then longer electrolysis times did not allow the signals to significantly increase. The surface coverage corresponding to NHOH groups was obtained by coulometric integration of the anodic peak (Fig. 5, inset). Considering a 4-electron process, its maximum value was found to be $\Gamma_{\text{NHOH}} = 1.2 \times 10^{-10} \text{ mol cm}^{-2}$ which is in accordance with values reported in the literature for a nitro active organic monolayer [43,45,70]. The amount of charge consumed during NO_2 reduction process and corresponding to this Γ_{NHOH} value was found $Q' = 3 \mu\text{C}$. Since the global amount of charge consumed during this latter electrolysis was $Q_{-0.1} = 23 \mu\text{C}$, it clearly appeared that NHOH was not the main reaction product. From the $\Gamma_{4\text{-NBD}}$ value, it may be deduced that barely 15% of the grafted NO_2 groups were actually reduced into NHOH by the electrolysis at -0.1 V . Assuming a nearly quantitative faradic yield for NO_2 reduction, the rest of the charge consumed, ca. $20 \mu\text{C}$, concerned the 6-electron process leading to NH_2 formation. The amine surface concentration was thus $\Gamma_{\text{NH}_2} = 4.9 \times 10^{-10} \text{ mol cm}^{-2}$ which corresponded to at most 60% of the initial NO_2 groups. Keeping in mind that it was demonstrated that the first NO_2 groups to be reduced are the closest ones from the electrode surface, and that there is no limitation by proton availability into the film, all these results pointed out to the formation of a stratified layer. After electrolysis, the NO_2 groups close to the electrode surface were reduced into NH_2 , then the inner NO_2 groups farther from the electrode surface were only partially reduced to give NHOH and finally the outer NO_2 , i.e. the NO_2 moieties located close to the film/solution interface, remained unaffected by the reduction. Once again, this is consistent with an

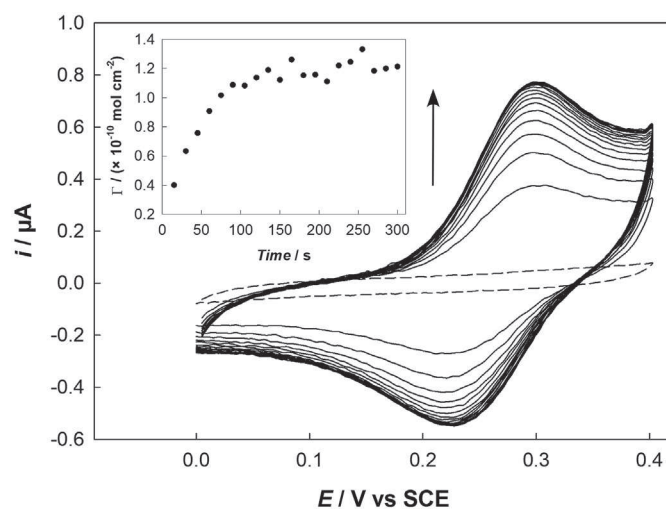


Fig. 5. CVs recorded in 0.1 M HCl on a GC- NO_2 electrode before (dashed line) and after (solid lines) successive electrolyses performed at -0.1 V during 15 s (total electrolysis time: 600 s). Scan rate: 50 mV s^{-1} . Inset: NHOH surface concentration extracted from anodic peak current integration as a function of total electrolysis duration.

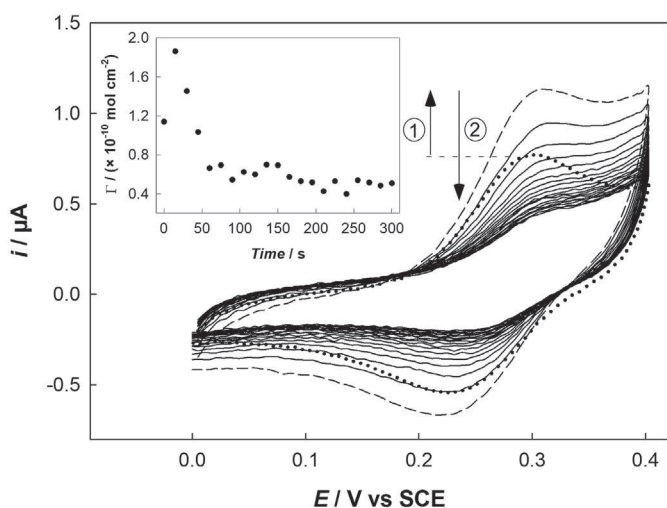


Fig. 6. CVs recorded in 0.1 M HCl on a GC-NO₂ electrode (which previously experienced a constant potential electrolysis at -0.1 V for 600 s) before (dotted line) and after one (dashed line) and further (solid lines) successive electrolyses performed at -0.8 V during 15 s (total electrolysis time: 600 s). Scan rate: 50 mV s^{-1} . Inset: NHOH surface concentration extracted from anodic peak current integration as a function of electrolysis duration.

electron tunneling, the efficiency of which decreases far from the electrode surface [45].

A last electrolysis was performed applying a constant potential -0.8 V for 600 s on the same electrode that previously experienced electrolysis at -0.1 V. As before, the electrolysis was stopped every 15 s to record a CV in the range 0 – 0.4 V (Fig. 6). During the first 15 s, the signal corresponding to the reversible NO/NHOH redox system increased, thus confirming that all NO₂ groups were not reduced by the previous electrolysis at -0.1 V, even after 600 s. The maximum surface coverage was $\Gamma_{\text{NHOH}} = 1.9 \times 10^{-10} \text{ mol cm}^{-2}$. This value was very close to that reported by Brooksby and Downard for NO₂ reduction operating at -0.65 V, ca. $2.5 \times 10^{-10} \text{ mol cm}^{-2}$ [45]. This represents a 60% increase compared to the maximum value obtained during the first electrolysis at -0.1 V. However this maximum surface coverage value of NHOH groups only represents 23% of the initially grafted NO₂ groups (using $\Gamma_{4\text{-NBD}} = 8.1 \times 10^{-10} \text{ mol cm}^{-2}$). Then, the redox response decreased together with NHOH surface concentration as the result of subsequent reduction into NH₂ moieties. This may be explained considering that at such large overpotential the remaining NO₂ groups are directly reduced into NH₂ whatever their localization in the organic film. The global amount of charge consumed during this latter electrolysis at -0.8 V once the contribution of the aromatic skeleton subtracted was $55 \mu\text{C}$ which would correspond to a surface concentration $\Gamma = (13 \pm 2) \times 10^{-10} \text{ mol cm}^{-2}$. This value was higher than $\Gamma_{4\text{-NBD}}$, which suggests an almost quantitative reduction of the NO₂ groups this time. It was verified using redox probes that the resulting organic film still exhibited a blocking behavior, hence showing that phenyl groups cleavage from the surface was negligible.

4. Conclusion

In this work we reported new insights upon 4-NBD reduction once grafted onto a GC electrode. In particular, the signal decay of the NO₂ groups was for the first time monitored in situ by means of SFG spectroscopy performed at the GC electrode with the CLIO FEL, allowing the first order kinetic rate constant of NO₂ reduction to be determined (ca. $k = 0.006 \text{ s}^{-1}$). We also demonstrated that NO₂ reduction is effective at potentials as high as -0.1 V and that the

whole reaction rate is limited rather by the charge transfer process than by proton availability into the organic layer. As a consequence, the first NO₂ groups to be reduced are those located close to the electrode surface and during the electrolysis, the organic film exhibits a stratified structure bearing NH₂ at the electrode surface, then NHOH and finally remaining NO₂ at the interface between the film and the solution.

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