The application of multiple spectroscopic techniques to the characterisation of self-assembled monolayers (SAMs) is essential for determining whether the desired surface functionalization was achieved, the molecules are integral after self-assembly and well-packed on the substrate. In this chapter we report on the use of surface enhanced Raman spectroscopy and X-ray photoelectron spectroscopy to characterise SAMs of a disulfide-functionalised nitrobenzene (i.e. 4-nitrophenyl-5-(1,2-dithiolan-3-yl)pentanoate). We showed that electron-induced damage during acquisition of photoemission spectra of the monolayer occurs through reduction of the nitro group. The use of roughened bulk gold substrates to enhance the SERS sensitivity resulted in an increase in the rate at which the reduction proceeds under the conditions used to obtain XPS data.

The results presented in this chapter were published in:

4.1 Introduction

The development of molecular and organic electronics is in large part based on the use of self-assembled monolayers (SAMs) of compounds that bear functional units; indeed often relatively complex organic compounds are used [1,2]. The characterisation of SAMs formed by these compounds is essential to understand the electronic properties of devices prepared from them and facilitated by the wide range of techniques available including electrochemistry, ATR FTIR, (spectroscopic) ellipsometry, etc. Ideally several techniques should be employed in the characterisation of SAMs and in this regard X-ray photoelectron spectroscopy (XPS) and surface enhanced Raman spectroscopy (SERS) are especially useful in the characterisation of non-redox active SAMs and submonolayer functionalized surfaces [3,4,5,6,7]. Characterising the same SAM modified surfaces with both these techniques is potentially useful as it allows for direct correlation of the results [8,9,10,11,12]. However, for SERS the range of suitable substrates, i.e. metal island films, colloids and roughened silver, gold or copper electrodes [13], is more limited than for XPS.

Nitrobenzene units are extensively used in the field of organic electronics, for instance as a key component in spiropyran molecular photo-switches [14]; as a part of systems that allow electrochemical switching of molecular conductance [15]; in molecular junctions [16,17,18]; as a monolayer linker for attachment of a functional units to a substrate [19,20,21,22]; as a reagent for surface electron-initiated polymerization [23]; and as a precursor in the preparation of electrodes for electrochemistry [24]. The wide range of applications requires that the compounds used are stable when the SAM formed from them is employed in devices. In the present report we focus on changes that occur in nitrobenzene based SAMs due to interactions with slow electrons; these changes could affect the performance of such SAMs in molecular-based electronic devices.

**Figure 4.1** Structure of 1 (a) and possible mechanism for reduction (b).
Rapid reduction of nitroaromatic SAMs on roughened Au surfaces during XPS measurements

Previous XPS studies on nitrobenzene-based self-assembled monolayers on gold [25,26,27] or silicon [28,29] demonstrated that when exposed to X-rays or electron beams, the nitro group can undergo reduction to, e.g., amines (Figure 4.1). This phenomenon was observed first by Grunze and co-workers [25,30] and attributed to the reduction to amines induced by slow electrons, promoted by hydrogen liberated from the phenyl moieties by secondary electrons. The resulting N 1s XPS spectrum of the fully reduced monolayer comprised a peak at ca. 400 eV binding energy (BE), consisting of a convolution of amine (399 eV) and protonated amine contributions (401 eV), while the original N 1s peak of the nitro-component at 406 eV was absent. A similar spectrum was observed when the monolayer was reduced electrochemically [26]. La et al. [28] observed reduction of nitroaromatic groups in monolayers on silicon, induced by primary and secondary electrons or by an electron beam (500 eV), in addition to extensive degradation/stripping of the nitro group when the monolayer was exposed to soft X-rays (550 eV). The source of hydrogen for the reduction was proposed to be protons released from the thiol anchors upon chemisorption, which are trapped within the monolayer when the self-assembly is carried out under UHV conditions [31], and which are absent for self-assembly from solution or for compounds bearing a disulfide anchor group. Roodenko et al. reported that oxygen liberated by the reduction of the nitro group can react with the Si/SiO2 substrate to form surface oxides [29]. Furthermore, it has been noted that during the three step reduction process (C-H splitting, N-O splitting, formation of N-Hx), polymerization is likely to occur yielding various cross-linked aromatic amines [30,32]. This reaction attracted significant attention in lithographic applications and surface patterned modification, where electron (<1 keV) or UV (<100 eV) beams were used to induce reduction and cross-linking [27,33].

To our knowledge, for the case of roughened surfaces used for SERS analysis of SAMs information on the reactivity of nitrobenzene-based compounds under XPS analysis has not been reported to date. In this chapter this issue is addressed and the optimal conditions to utilize both SERS and XPS effectively are identified. For this we prepared self-assembled monolayers of the nitrobenzene-based compound 1 (4-nitrophenyl-5-(1,2-dithiolan-3-yl)pentanoate), (Figure 4.1) on several surfaces including smooth gold coated slides, and electrochemically roughened gold coated slides and gold beads. We demonstrate that with roughened gold beads and, to a lesser extent, with roughened, gold-coated slides as substrate, XPS spectra of SAMs with nitroaromatic groups are unrepresentative of the pristine composition of the SAM due to in situ reduction of the nitro group. We also found that the charge for the reduction originates from the gold substrate as primary and secondary electrons, and their effective yields are increased in the case of SERS-active roughened Au bead surfaces.
4.2 Results and discussion

**Solid state Raman spectrum**

Compound 1 was obtained by the esterification of thiooctic acid with \( p \)-nitrophenol in dichloromethane, using DCC as coupling reagent. The detailed synthesis and characterisation by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy and mass spectrometry of 1 are provided in [34].

In the solid state Raman spectrum of 1, shown in Figure 4.2, a band of benzene stretching mode at 1592 cm\(^{-1}\) and an intense band of the symmetric nitro stretching mode at 1346 cm\(^{-1}\) are observed [35]. The band at 865 cm\(^{-1}\) can be assigned to either the deformation mode of the NO\(_2\) group or the para-, nitro- substituted aromatic ring out-of-plane deformation [35]. The disulfide stretching mode is observed at 505 cm\(^{-1}\) [36].

**SERS of self–assembled monolayers on roughened gold bead electrodes**

The SERS spectrum obtained from a SAM of 1 on an electrochemically roughened Au bead (Figure 4.2) is remarkably similar to the solid state Raman spectrum of 1, testifying to the integrity of 1 in the SAM. Notably the disulfide stretching mode at 505 cm\(^{-1}\), present in the solid state spectrum of 1, is absent in the spectrum of the SAM, indicating that SAM formation involves breaking of the disulfide bond to form S-Au bonds.

**Core level photoemission spectra of a film and SAMs on roughened Au beads**

X-rays photoelectron spectra were acquired on SAMs of 1 formed on a roughened Au bead and compared with spectra of a film of 1 (representative of the bulk compound), to gain insight into the influence of the nature of the substrate on the composition of the SAM (Figure 4.3).

![Figure 4.2](image_url) Solid state Raman spectrum of 1 and SERS spectrum of a SAM of 1 on a roughened Au bead. The intense NO\(_2\) stretch at 1346 cm\(^{-1}\) is truncated to facilitate spectral comparison.
Rapid reduction of nitroaromatic SAMs on roughened Au surfaces during XPS measurements

Figure 4.3 Comparison of the (a) N 1s, (b) S 2p and (c) C 1s XPS spectra for a SAM of 1 on a roughened Au bead (lower spectra) and for the same compound drop-cast to form a film on a gold substrate, representative of the bulk compound (upper spectra). (a) The N 1s core level region of the SAM features of two contributions, a nitro peak at 406 eV binding energy and a contribution assigned to the reduced species at ca. 400 eV, while the film shows only the former. (b) The S 2p core level region of the SAM is composed of two doublets corresponding to a chemisorbed (R-S-Au) and a disulfide species, respectively, while for the film only the disulfide doublet is observed. (c) The C 1s core level region of SAM of 1 on the Au bead and in the film, deconvoluted with three components – C-C at 284.9 eV, C-S, C-N and C-O at ca. 286 eV (see text for details) and COO at 289 eV.

Both SAM and film were exposed for 10 min to X-rays to accumulate the spectrum of the N 1s core level region. The N 1s spectrum of the thin film shows only the component at 406 eV indicating that the nitro groups at the surface of the physisorbed film are not affected by such a short X-ray exposure. The N 1s spectrum the SAM of 1 on a roughened Au bead consists instead of two contributions at 406 eV and 400 eV binding energy, where the latter is attributed to nitrogen in a lower oxidation state than that of Ar-NO$_2$, i.e. to contributions from amine and protonated amine nitrogen atoms at 399.7 and 401 eV {e.g., Ar-N=O (400 eV), Ar-NH$_2$ (399.5 eV) or Ar-NH$_3^+$ (401 eV) [37,38]}. The reduced species account for ca. 30 % of the total N 1s intensity after 10 min exposure to X-rays [39]. To the best of our knowledge, neither X-ray induced reduction of the nitro group on a roughened bead surface nor the rate at which the reaction proceeds there have been reported to date. The relative intensity of the reduced nitrogen species increases over time, reaching half of the total N 1s intensity after 2 h of exposure to X-rays.

A similar picture emerges from spectra of the S 2p region: after 20 min of exposure to X-rays, the thin film showed only one type of sulfur species at a binding energy of 163.3 eV, typical of free disulfide groups [40], while for the SAM, next to the signal of the chemisorbed species (R-S-Au) at a binding energy of 161.8 eV, a second signal at 163.6 eV was observed. This additional signal, which accounts for 48 % of the total S 2p intensity, is assigned to disulfides, in agreement with results obtained after exposure to a deep UV beam (21.2 eV) by Turchanin et al. [22,40]. Continued exposure of the SAM to X-rays did not induce further changes in S 2p spectra over time. However, the ratio between the N 1s intensity originating from the reduced nitrogen species, $N_{\text{red}}$, and the total S 2p intensity, corrected for the respective sensitivity factors, increased with time and reached $I(N_{\text{red}})/I(S)=0.25$ after 2 h of accumulation; this is more than twice its initial value of 0.11.

The C 1s spectrum of the film of 1 was composed with three components – aromatic and
aliphatic C-C contribution at 284.9 eV, C-S, C-N and C-O component at 286 eV and a COO peak at 289.1 eV [41]. Comparison of the C 1s spectrum of the film and the SAM shows a difference mainly in the component related to the C-S, C-N, C-O carbon, which appears to be shifted to higher binding energies at 286.4 eV. The observed shift is attributed to the diminishing of C-S contribution to the peak due to the attenuation in the monolayer. This results in the observation of the higher BE components – C-N and C-O. Furthermore, the C 1s spectrum remained relatively unaffected over the accumulation time.

Taking into account that during the measurement X-rays and photoelectrons travel through the monolayer, it is important to identify the source of the electrons necessary for the reduction of the nitro group.

**Core level photoemission spectra of a SAM on flat and roughened Au surfaces**

We carried out XPS measurements for SAMs of 1 on flat and roughened Au/Cr/glass to investigate how the morphology of the substrate on which the SAM is formed influences the extent of reduction during exposure to X-rays. Figure 4.4 shows the N 1s core level region of the SAM of 1 assembled on the flat substrate (top line a), where after 10 min of exposure to X-rays only one peak at 406 eV BE was observed, as for the film of 1 (vide supra). Analogous results were obtained for a SAM of 1 assembled on flat Au/mica (not shown). In contrast, the N 1s spectrum measured on a SAM of 1 formed on a SERS-active roughened Au/Cr/glass substrate, presented in Figure 4.4 (middle line b), featured an extra component corresponding to a reduced species at 400 eV BE, with an intensity that accounted for ca. 11 ± 2% of the total N 1s intensity. If the accumulation was continued at the same spot of the roughened surface for several hours, a broadening at the lower BE side was observed as well as a gradual increase of the intensity of the component corresponding to the reduced species, ultimately reaching 39 ± 1% of the total N 1s intensity (not shown). For this system, the ratio between the intensity of the N 1s peak originating from the reduced nitrogen species, N_red, and the total S 2p intensity, I(N_red)/I(S) increased from 0.13 to 0.26, similar to that observed for the SAM of 1 formed on a roughened gold bead.

After 3.5 h of accumulation degradation of the monolayer was evident; a decrease in the total intensity of the N 1s (-15%), O 1s (-20%) and C 1s (-1%) signals was observed together with an 11% increase in the intensity of the S 2p line. This result can be rationalised as a loss of the outermost atoms of the SAM, which consequently leads to a reduction in the attenuation of the S 2p signal from chemisorbed sulfur. In addition, a shoulder at lower binding energies appeared in the O 1s core level region and was assigned to Ar-NO and the original nitro peak with an overlapping contribution from NHOH (Figure 4.4).
Rapid reduction of nitroaromatic SAMs on roughened Au surfaces during XPS measurements

Figure 4.4 Left: N 1s photoemission spectra of a SAM of 1 on a smooth (a) and a roughened (b) Au/Cr/glass substrate. The bottom curve (c) was collected on the SAM of 1 on a roughened Au/Cr/glass substrate after exposure to electrons with a kinetic energy of 0.5 eV for 30 min. Right: X-ray photoemission spectrum of the O 1s core level region of 1-Au/Cr/glass before (a) and after extensive reduction under X-rays (b). The additional component at 531.5 eV which appears after extensive exposure to X-rays, is assigned to either Ar-NO or Ar-NOH reduced groups.

From these results one can conclude that reduction occurs at a much slower rate for a SAM of 1 formed on a roughened Au-covered glass slide than on a roughened bead but with more substantial loss in coverage if a certain region was irradiated continuously.

To confirm the hypothesis that reduction occurs due to photoelectrons and secondary electrons from both the metal substrate and the monolayer, a SAM of 1 on roughened Au/Cr/glass was irradiated with low kinetic energy (0.5 eV) electrons for 30 min in the absence of X-rays and other ionizing sources. The spectrum of the N 1s core level region of the sample (Figure 4.4, bottom line c) acquired subsequently showed only the signal originating from the reduced nitrogen species, at ~ 400 eV BE. The reduction of the nitro peak under slow electron bombardment demonstrates the origin of the electrons as low energy secondary electrons that escape from the substrate. Remarkably the energy of the electrons (0.5 eV) that caused reduction is far below the energy threshold (7 eV) necessary to cleave C-H bonds by dissociative electron attachment [42,43,44]. This observation leads us to conclude that the reduction proceeds either with H obtained from the cleavage of C-H bonds if the energy of electron is sufficient or involving electron attachment at antibonding orbitals.

Integrated intensities of Au 4f photoemission peak of SAMs on various substrates

The measured intensities of the Au 4f photoemission doublet of SAMs of 1 on the different types of Au substrates were quantified to gain further insight into the reduction process (Table 1). The lowest intensity of the Au signal was measured for the SAM of 1 on smooth Au/Cr/glass. Electrochemical roughening of this substrate increases the geometrical
surface area (see optical and AFM images of the slide and bead substrates in Figure 4.5); however, the limited thickness of the Au film restricts the roughness that can be achieved and therefore only a 22% increase in Au intensity was observed. The Au 4f photoemission doublet observed for smooth and electrochemically roughened Au bead electrodes by contrast was 75% and 125% more intense, respectively. The increase in the intensity of the Au 4f photoemission line is attributed to a higher photoemission yield from the rougher gold bead, based on the expected change of the work function, which decreases with increasing roughness of the interface [45,46]. This results in higher amount of secondary electrons (Figure 4.6). Remarkably the secondary electron background of both smooth (RMS roughness 6 ± 1 nm) and roughened (RMS roughness 81 ± 3 nm) Au slides did not differ as much; the same is true in the comparison of the smooth (RMS roughness 10 ± 1 nm) and roughened beads (RMS roughness 418 ± 10 nm), however a large difference in background between slides and beads is observed. This indicates that the roughness, which is required for SERS, plays a minor role in the reduction process. Indeed rapid reduction of nitro groups was observed on smooth beads as well. The rate of the reaction is influenced by the number of gold atoms which, in a particular experimental geometry, can contribute to the generation of photoelectrons and secondary electrons.

### Table 1
Au 4f doublet intensity of SAMs of 1 on Au substrates and their RMS roughness values

<table>
<thead>
<tr>
<th>Substrate</th>
<th>I (Au 4f) (10^5 \text{ counts})</th>
<th>Roughness RMS values (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat Au/Cr/glass</td>
<td>1.4</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>Roughened Au/Cr/glass</td>
<td>1.7</td>
<td>81 ± 3</td>
</tr>
<tr>
<td>Smooth Au bead</td>
<td>2.4</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>Rough Au bead</td>
<td>3.1</td>
<td>418 ± 10</td>
</tr>
</tbody>
</table>
Rapid reduction of nitroaromatic SAMs on roughened Au surfaces during XPS measurements

Figure 4.5 Optical (a-d) and AFM (e-h) images of the Au substrates used for monolayer preparation. (a, e) smooth Au/Cr/glass, (b, f) roughened Au/Cr/glass, (c, g) smooth Au bead, (d, h) roughened Au bead.

Figure 4.6 Survey XPS scan of the SAMs on Au substrates studied. A strong increase in the secondary electron background can be observed. The increase in C 1s intensity found in the spectra collected on the beads is related to a higher coverage by 1 and different photoemission geometry (spot size increases on the curved beads’ surfaces). The Na Auger line originates from the sample holder.

**SERS of a SAM on an electrochemically roughened Au surface after exposure to X-rays**

The SERS spectrum of a SAM of 1 on an electrochemically roughened Au/Cr/glass substrate, presented in Figure 4.7a, was similar to that measured for a SAM of 1 on a roughened Au bead and the solid state Raman spectrum of 1 (Figure 4.2). However, the SERS spectrum acquired after reduction with low energy electrons, until the nitro N 1s component was depleted in the XPS spectrum (Figure 4.4), shows several differences.
Spectra collected from different regions of such a sample and also presented in Figure 4.7a, show a significant intensity decrease of all Raman bands of 1 and the appearance of a new band at 1553 cm\(^{-1}\) (Figure 4.7a middle spectrum). Furthermore, in many areas of the SAM the aromatic stretching mode at 1592 cm\(^{-1}\) and the symmetric nitro stretching mode 1346 cm\(^{-1}\) are no longer observed (Figure 4.7a bottom spectrum) and only the peak at 1553 cm\(^{-1}\) is discernible in the spectrum. The intensity decrease of the band at 1346 cm\(^{-1}\) can be rationalised by conversion of the nitro group to amines, while the decrease of the 1593 cm\(^{-1}\) mode supports the breaking of C-H bonds of the aromatic ring to deliver protons for the reduction. In addition, the spectrum of the reduced SAM of 1 is not similar to the spectra of aniline or nitrosobenzene (Figure 4.7b), which excludes the formation of a significant population of these species. Therefore we tentatively assign the new band at 1553 cm\(^{-1}\) to cross-linked or polymerized species [47].

**Figure 4.7** (a) SERS spectrum of a SAM of 1 on electrochemically roughened Au/Cr/glass (top). The middle and bottom spectra were recorded at different points on the same SAM-modified slide after extensive reduction by exposure to an electron beam (kinetic energy = 0.5 eV). (b) Solid state Raman spectra of aniline and nitrosobenzene.
4.3 Conclusions

Self-assembled monolayers of compounds bearing nitroaromatic moieties, in particular nitrospiropyrans [48], are often used in organic electronic applications. We have demonstrated here that if these molecules are assembled on substrates such as roughened gold beads, XPS measurements (or exposure to an electron beam) can induce extensive reduction/polymerization of the nitroaromatic groups. This effect does not occur to the same extent on flat surfaces such as Au/Cr/glass or Au/mica, but on these substrates surface enhancement of the Raman spectrum is either weak or totally absent. The optimal substrate for the combined study of such SAMs with SERS and XPS is a roughened Au/Cr/glass slide, where a satisfactory enhancement of Raman spectrum can be achieved but only limited photoemission-induced reduction occurs, allowing for the collection of XPS data that are representative of the pristine SAM. The observed effect is directly related to the high electron emission efficiency on gold beads, where photoelectrons and secondary electrons of the substrate convert nitroaromatic species to amines and cross-linked/polymerized species. In a broader context such reduction processes may need to be considered also in organic devices where current passes through the hybrid organic/inorganic systems.

4.4 Acknowledgements

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4.5 References
