Thiocyanate and thiol self-assembling process on platinum investigated by means of sum-frequency generation

Sartenaer, Yannick; Tourillon, Gerard; Louette, Pierre; Volcke, Cedric; Humbert, Christophe; Peremans, André; Thiry, Paul; Dreesen, Laurent

Published in:
Physicalia Magazine

Publication date:
2005

Document Version
Early version, also known as pre-print

Link to publication

Citation for pulished version (HARVARD):
Sartenaer, Y, Tourillon, G, Louette, P, Volcke, C, Humbert, C, Peremans, A, Thiry, P & Dreesen, L 2005, 'Thiocyanate and thiol self-assembling process on platinum investigated by means of sum-frequency generation', *Physicalia Magazine*, vol. 27, no. 4, pp. 405-413.

Thiocyanate and thiol self-assembling process on platinum investigated by means of sum-frequency generation

Yannick Sartenaer[1], Gérard Tourillon[1*], Pierre Louette[2], Cédric Volcke[1], Christophe Humbert[1], André Peremans[1], Paul A. Thiry[1] and Laurent Dreesen[1]

[1]Laboratoire de Spectroscopie Moléculaire de Surface
[2]Laboratoire Interdisciplinaire de Spectroscopie Electronique
University of Namur, 61 rue de Bruxelles, B-5000 Namur, Belgium

* Permanent address : IRC-CNRS Avenue A. Einstein, 2 – F-69626 Villeurbanne cedex - France

Abstract

In the field of self-assembled monolayers (SAMs), recent works have shown that thiocyanate functions seem to be a good alternative to the use of thiols groups for adsorption on gold surfaces. In order to check if this is also valid for platinum substrates, we use Sum-Frequency Generation spectroscopy (SFG) to study two similar SAMs: decanethiol (DT) and decyl thiocyanate (DTCN) adsorbed on platinum surfaces. By comparing the intensities of the methyl/methylene vibration modes, we can conclude that the DTCN SAMs are less ordered than the DT ones. These effects are related to the SAMs quality which depends on the molecular packing. In order to confirm these assumptions, we use other techniques of surface characterisation like Scanning Tunneling Microscopy (STM) and X-Ray Photoelectron Spectroscopy (XPS). This last one shows that DTCN SAMs are partially composed of cyanide free groups lying on the surface. Finally, we propose an adsorption mechanism for thiocyanate-based monolayers.

Introduction

Organic thiols have attracted considerable interest due to their ability to produce self-assembled monolayers (SAMs) on metallic surfaces [1][2]. These latter ones quickly became a major advance in disciplines ranging from electronics [3] to biochemistry [4][5][6][7]. By this way, we can obtain spontaneous structured films by simple chemisorption. However, thiols groups have also some limitations. For example, in the case of protective thiols, the deprotection can generate extraneous materials which can disturb the SAMs formation and quality [8]. Other drawbacks are the propensity of α,ω-dithiols, used in surface polymerisation, to form multilayers rather than monolayers [9]. Recently, Tour et al. have shown that thiocyanate function is an interesting alternative to the use of thiol groups for efficient self-assembly processes on gold surfaces [10].

The aim of this paper is twice: on one hand to determine if molecules possessing a thiocyanate group adsorb on platinum substrates as well as on gold surfaces, and, on the other hand, to compare the quality of the SAMs obtained by using these two different binding functions. To reach these goals, we mainly use infrared-visible sum-frequency generation (SFG) spectroscopy. This non linear optical spectroscopy has demonstrated to be a powerful technique for studying organic films organisation on various surfaces [11][12][13]. Finally, in order to complete the SFG data, we also use X-ray photoelectron spectroscopy (XPS) to identify the atomic species in presence and scanning tunneling microscopy (STM) to provide information on the surface morphology.

Experimental section

The samples consist of decanethiol: CH_3-$(CH_2)_9$-SH (DT) or decyl thiocyanate: CH_3-$(CH_2)_9$-SCN (DTCN) self-assembled monolayers on Pt(111) single crystals. The ad-layers were prepared by immersing the substrates in a 2 mM ethanol solution of DT or DTCN during ~ 16 h. In order to perform SFG measurements, two laser beams, a visible one and an infrared one, are focused on the sample surface giving rise to a second order non linear optical process which generates a third beam at the sum of the frequencies of the incident ones. The vibrational fingerprint of the surface is obtained by recording the SFG signal as a function of the infrared frequency. This spectroscopic tool is sensitive to the breaking of inversion symmetry encountered at surfaces and interfaces. This characteristic not only implies interface sensitivity but also makes this technique sensitive to the conformation of molecular chains [14][15]. Practically, those beams are generated by two optical parametric oscillators (OPOs) built around $LiNbO_3$ and BBO non linear crystals. The visible and SFG beams are *s* polarised while the infrared one is *p* polarised. A detailed description of the SFG setup used in this work can be found elsewhere [16]. XPS analysis was performed on a SSX-100 spectrometer, using a hemispherical analyser and a monochromated Al $K_{\alpha1,2}$ X-ray (1486.6 eV). A commercial STM (Multimode Nanoscope IIIa, Digital Instuments) equipped with a "pico-amp" low-current amplifier and a "tip-view" STM head was used to image the Pt(111) surface covered by the molecules. The STM operates in the constant current mode and the measurements are performed at ambient air, i.e., in the same conditions as for SFG spectroscopy.

Results and discussion

We have restricted our measurements to the 2800-3000 cm^{-1} infrared spectral range in order to detect the CH_2 and CH_3 stretching vibration modes of the molecules forming the SAMs. Figure 1 shows the SFG spectra of decyl thiocyanate and decanethiol SAMs adsorbed on Pt(111). The occurrence of SFG resonances evidences that, in both cases, an ad-layer is formed on the platinum substrate. Both spectra are characterised by five spectral features characteristic of three terminal methyl (CH_3) and two methylene (CH_2) vibration modes, which are located at 2969, 2947, 2913, 2886 and 2850 cm^{-1}. More precisely, we can set that, on one hand, the two bands at 2850 and 2913 cm^{-1} are related to the symmetric (CH_2-SS) and asymmetric (CH_2-AS) methylene stretching vibration modes, respectively [17]. On the other hand, the 2886 and 2969 cm^{-1} bands are assigned to the symmetric (CH_3-SS) and degenerate (CH_3-DS) stretching vibration modes of the terminal methyl groups, respectively. The last resonance at 2947cm^{-1} is ascribed to a Fermi resonance (CH_3-

FR) between the methyl symmetric stretching mode and an overtone of a methyl bending mode.

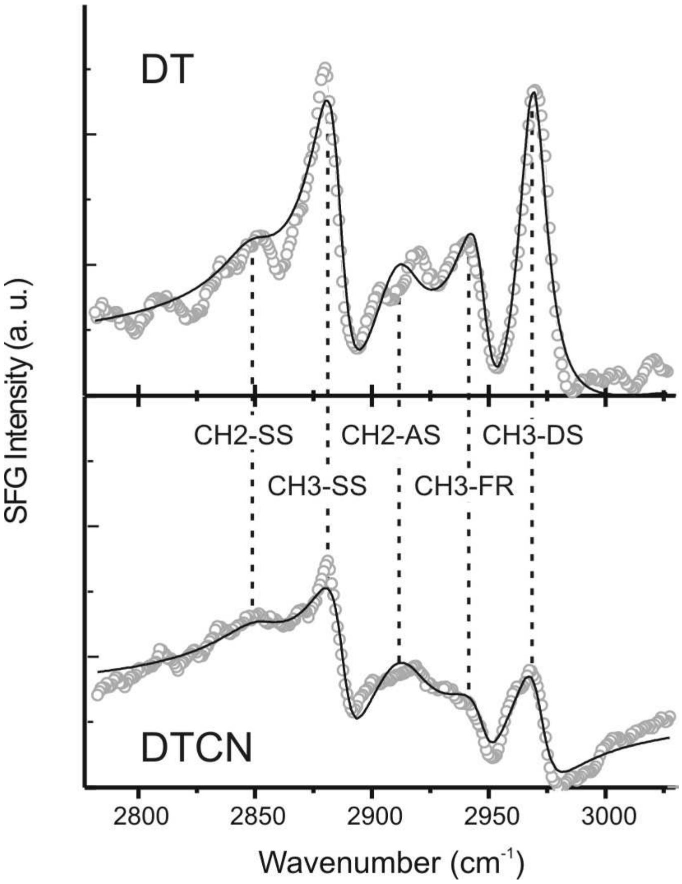

Figure 1: SFG spectra of DT and DTCN adsorbed on Pt(111) with ssp polarisation combination. Upper panel and lower panel present the data for DT and DTCN, respectively. Open circles and continuous lines represent experimental data and fits, respectively.

The main difference between the vibrational fingerprints of those two molecules is observed in regard of the SFG intensity of the corresponding vibration modes. More precisely, the intensity of each methyl DTCN resonance is clearly weaker than the corresponding DT one. SFG being a coherent process, the intensity of a resonance is directly proportional to the amount of identical chemical functions pointing in the same direction. We can then deduce a poorer order for the thiocyanate-based monolayer.

The next conclusion can be addressed by examining the methylene vibration modes. Indeed, the observation of these features is indicative of gauche defects which are commonly observed on alkane thiol SAMs adsorbed on Pt [18][19]. In a SAM with a high degree of molecular order, all the methylene chains adopt an "all trans" conformation. With this configuration, the molecular skeleton is globally centrosymmetric and then SFG inactive. When the Van der Waals interactions between the chains become too weak, a folding of the top of the chains, called a "gauche defect", is observed. This symmetry breaking activates the methylene vibration modes in the SFG spectra. This type of defect, resulting from weaker interactions between alkane chains, indicates that the molecular packing is less dense in the DTCN ad-layer. In our spectra, the symmetric and asymmetric methylene stretching vibration modes are more intense (with respect to the methyl resonances) for the DTCN SAM than for the DT one, meaning a larger occurrence of gauche defects in the ad-layer.

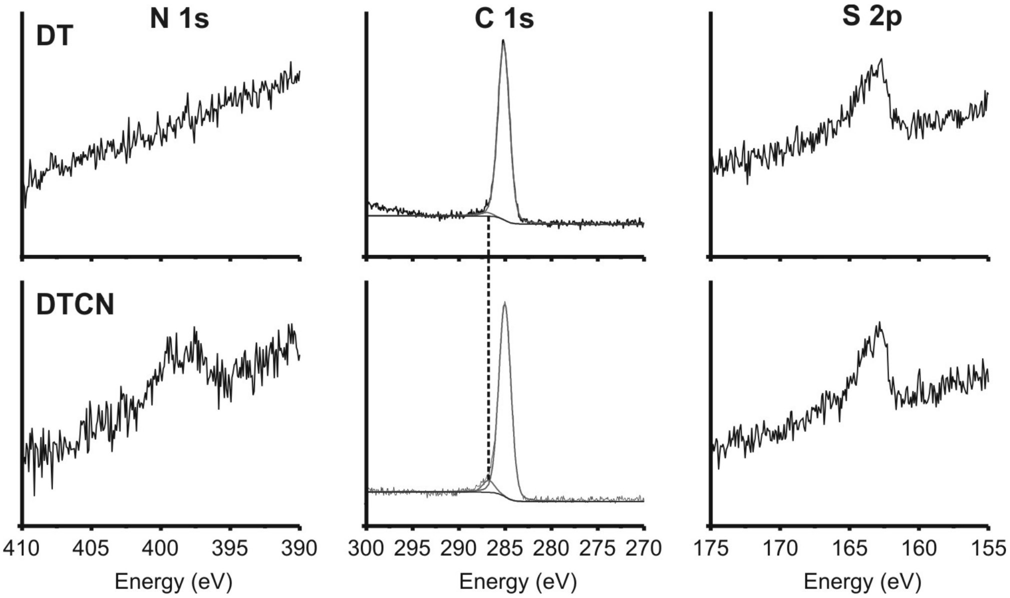

Figure 2: XPS spectra in the N1s, C1s and S2p binding energy ranges.

In order to clearly understand the origins of those features, we performed XPS experiments on both SAMs. Figure 2 shows the photoelectron spectra performed in selected binding energy ranges, i. e. the N1s, C1s and S2p domains. We can extract three important points from those data. Firstly, in both SAMs, only one sulphur doublet, characteristic of thiolate species and located at 162-163 eV, is observed (SCN^- species should give a second doublet around 165 eV). This observation evidences the formation of a DTCN thiolate. Secondly, we observe nitrogen species in the DTCN SAMs while they are not identified in the DT ones. Moreover, the C1s peak is composed of two distinct contributions for the DTCN monolayer. The first one at 285 eV is due to the C-C aliphatic chain when the second one at 286,8 eV comes from the C-N groups [20]. From all those points, we can deduce that the DTCN SAMs are partially composed of cyanide free groups lying on the surface. It seems obvious that these CN adsorbed species perturb the DTCN self-assembly process by giving rise to a lower DTCN surface packing and consequently a more disorder DTCN layer.

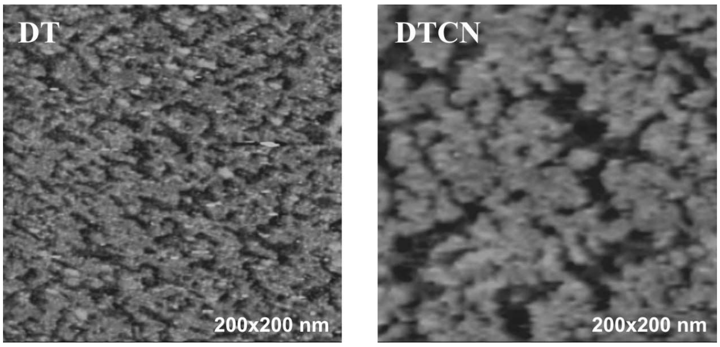

Figure 3: STM images of DT and DTCN on platinum surfaces.

The STM images of DT and DTCN SAMs on platinum substrates are presented in Figure 3. The bias and the current values are 950 mV and 10 pA, respectively, in the first case; 1000 mV and 2 pA, respectively, in the second one. Both images are quite similar: an ad-layer covers the platinum surface. The surface coverage may be estimated by using a simplified computing procedure. First, a height threshold is determined in the height histogram of the STM image in order to obtain a two-colour picture: one represents the molecules while the other one the substrate. Second, the number of pixels is calculated for each colour. By this way, we estimate the surface coverage of about 62% and 70% for the DTCN and DT SAMs, respectively.

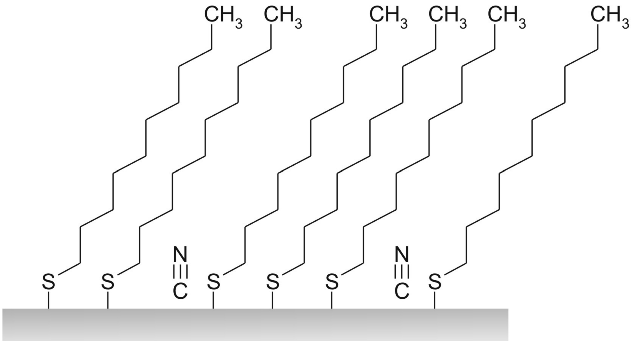

Figure 4: Mechanism proposed for DTCN assembly on Pt(111).

From all those points, we can try to understand the mechanism of assembly that occurs during the formation of thiocyanate-based monolayers. As presented in Figure 4, the DTCN SAMs are partially composed of cyanide free groups contrary to what is observed on gold substrates. We can then conclude that some of them are lying on the metal. Indeed, several works showed the affinity of those groups for platinum interfaces [21][22]. These chemical species act as contaminants and perturb the DTCN assembly giving rise to a weaker surface coverage as confirmed by STM analysis. Consequently, the average distance between two molecules in the SAMs is larger, which means a decrease of the inter-chains interactions and thus a poorer molecular order in the DTCN/Pt SAMs.

Conclusions

By using various techniques of surface characterisation like SFG, XPS and STM, we compared the adsorption properties of decanethiol and decyl thiocyanate molecules on platinum. SFG measurements showed that both molecules form thiolate self-assembled monolayers on the metallic surface. This was confirmed by the XPS spectra. The resonances intensities in the SFG spectra were less intense for DTCN molecules indicating that the DT SAM was more structured than the DTCN one. The STM images confirmed this assumption by showing a weaker surface coverage. Finally, the XPS experiments revealed that DTCN SAMs are partially composed of free cyanide groups. These ones act as a perturbation, impinging efficient Van der Waals interaction between adjacent carbon skeletons.

Acknowledgements

L.D. acknowledges the Walloon Region for financial support. C.V. acknowledges the Belgian Fund for Agricultural and Industrial Research (FRIA) for financial support. C.H. and A.P. are Postdoctoral Researcher and Senior Research Associate of the Belgian National Fund for Scientific Research (FNRS), respectively. This work is supported by the Ministry of the Walloon Region, by the Belgian Fund for Joint Basic Research (FRFC), and by the Belgian Interuniversity Program on 'Quantum size effects in nanostructured materials' PAI/IUAP 5/1 initiated by the Belgian Office for Scientific, Technical, and Cultural Affairs (OSTC).

References

[1] A. Ulman, Chem Rev **96**, 1533 (1996).
[2] G. E. Poirier, Chem Rev **97**, 1117 (1997).
[3] J. Chen, M. A. Reed, A. M. Rawlett and J. M. Tour, Science **286**, 1550 (1999).
[4] R. M. Crooks and A. J. Ricco, Accounts Chem Res **31**, 219 (1998).
[5] R. M. Crooks, H. C. Yang, L. J. McEllistrem, R. C. Thomas and A. J. Ricco, Faraday Discuss, 285 (1997).
[6] D. G. Castner and B. D. Ratner, Surf Sci **500**, 28 (2002).
[7] L. Dreesen, Y. Sartenaer, C. Humbert, A. A. Mani, C. Methivier, C. M. Pradier, P. A. Thiry and A. Peremans, Chemphyschem **5**, 1719 (2004).
[8] J. J. Stapleton, P. Harder, T. A. Daniel, M. D. Reinard, Y. X. Yao, D. W. Price, J. M. Tour and D. L. Allara, Langmuir **19**, 8245 (2003).
[9] J. M. Tour, L. Jones, D. L. Pearson, J. J. S. Lamba, T. P. Burgin, G. M. Whitesides, D. L. Allara, A. N. Parikh and S. V. Atre, J Am Chem Soc **117**, 9529 (1995).
[10] J. W. Ciszek, M. P. Stewart and J. M. Tour, J Am Chem Soc **126**, 13172 (2004).
[11] L. Dreesen, C. Humbert, Y. Sartenaer, Y. Caudano, C. Volcke, A. A. Mani, A. Peremans, P. A. Thiry, S. Hanique and J. M. Frere, Langmuir **20**, 7201 (2004).
[12] C. Humbert, Y. Caudano, L. Dreesen, Y. Sartenaer, A. A. Mani, C. Silien, J. J. Lemaire, P. A. Thiry and A. Peremans, Appl Surf Sci **237**, 462 (2004).

[13] C. Humbert, L. Dreesen, A. A. Mani, Y. Caudano, J. J. Lemaire, P. A. Thiry and A. Peremans, Surf Sci **502**, 203 (2002).

[14] M. Himmelhaus, F. Eisert, M. Buck and M. Grunze, J Phys Chem B **104**, 576 (2000).

[15] A. Rao, H. Rangwalla, V. Varshney and A. Dhinojwala, Langmuir **20**, 7183 (2004).

[16] A. A. Mani, L. Dreesen, C. Humbert, P. Hollander, Y. Caudano, P. A. Thiry and A. Peremans, Surf Sci **502**, 261 (2002).

[17] L. Dreesen, C. Humbert, M. Celebi, J. J. Lemaire, A. A. Mani, P. A. Thiry and A. Peremans, Appl Phys B-Lasers O **74**, 621 (2002).

[18] C. D. Bain, J Chem Soc Faraday T **91**, 1281 (1995).

[19] M. A. Hines, J. A. Todd and P. Guyot-Sionnest, Langmuir **11**, 493 (1995).

[20] G. Beamson and D. Briggs *High resolution XPS of organic polymers*, 1992.

[21] A. Tadjeddine, A. Peremans, A. LeRille, W. Q. Zheng, M. Tadjeddine and J. P. Flament, J Chem Soc Faraday T **92**, 3823 (1996).

[22] B. Ren, X. Q. Li, D. Y. Wu, J. L. Yao, Y. Xie and Z. Q. Tian, Chem Phys Lett **322**, 561 (2000).