

Characterization of self-assembled monolayers of thiols on gold using scanning tunneling microscopy

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Abstract — The formation and the structure at the molecular level of self-assembled monolayers of thiophenol and dodecanethiol molecules on gold surfaces were characterized by scanning tunneling microscopy. Highly ordered monolayer films were obtained for both thiols. The results suggest that the molecular ordering and packing depend on the adsorption time and on the solvent dipole moment. Longer adsorption times and polar solvents favor the saturation of surface coverage and molecular disorder.

I. INTRODUCTION

Thiols self-assembled monolayers (SAMs) on metal surfaces have attracted considerable attention due to their potential applications in molecular electronics [1,2]. In particular, aromatic thiol SAMs are being studied in various areas such as control of charge transfer [3], organic-based electronic functionality [4] or patterning at the nanometer scale [5]. The structural and electrical characterization of organic monolayers is therefore of importance and this is in fact an emerging area of study.

Thiols SAMs on gold are very stable due to the strength of S-Au bond. However, previous studies have demonstrated the high dependence of these monolayers formation and characteristics on the preparation conditions like temperature, adsorption time, solvent and concentration [6]. In these experiments, the characterization of the molecular organization of thiols SAMs and their electrical current characteristics were made using a Scanning Tunneling Microscope (STM).

STM is a powerful microscopy technique to investigate electrically conducting surfaces down to the atomic scale [7]. In STM, the sample is scanned by a metallic tip, usually made of Pt/Ir. The tip is connected to the scanner, an XYZ positioning device. A small bias voltage can be applied between the atomically sharp tip and the sample, and the current flowing between the tip and the conducting surface is recorded. The magnitude of that tunneling current is extremely sensitive to the gap distance between the tip and the sample. When the distance is large there is no current flow. But, if the tip is brought very close ($< 10 \text{ \AA}$), without physical contact, a current (in the range pA to nA) flows across the gap between the tip and the sample, as shown in scheme of Fig.1. During the current measurements, with the

tip moving across the surface, atomic information of the surface can be mapped.

The work we are currently carrying out aims to explore factors that influence the thiols SAMs characteristics, such as molecular structure of the thiol and the adsorption conditions, such as time, solvent and temperature. Ultimately we aim to relate the molecular structure of the thiol molecules with their electrical properties, determined at the single molecule level.

In this communication we report on preparation conditions and characterization of monolayers formed on Au(111) with two different thiol molecules: an aromatic (thiophenol) and an alkanethiol (dodecanethiol).

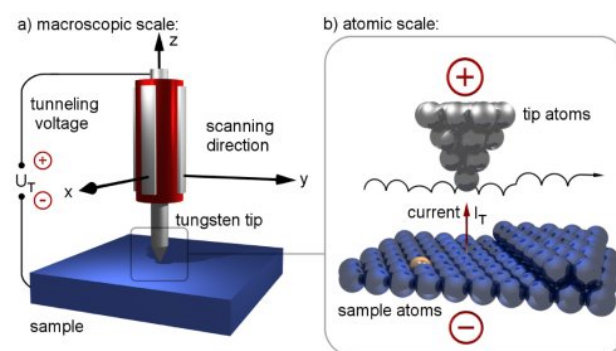


Fig. 1. Principle of scanning tunneling microscopy

II. EXPERIMENTAL

Flame annealed Au(111) on mica, purchased from Molecular Imaging, was used as substrate. Thiols self-assembled monolayers were prepared by immersing these Au(111) substrates in a solution containing the thiol molecules we want to assemble at the surface. Two types of thiols were used, the thiophenol (Aldrich, 97%) and dodecanethiol (Aldrich, $> 98\%$). The concentration of thiophenol and dodecanethiol solutions was 2mM and 5mM, respectively, and the solvents used were toluene, methanol or ethanol. In the case of thiophenol the adsorption time varied from 24h to 72h at room temperature. For the preparation of dodecanethiol SAMs, the substrates were either immersed for 5h in the solution at 70°C under inert atmosphere or 72h at room temperature. After adsorption, samples were carefully rinsed with the pure solvent and dried under a flow of nitrogen. STM measurements were performed using a Molecular Imaging STM (model 5100) with Pt/Ir (80/20) mechanically cut tips (diameter = 0.25 mm) purchased from Goodfellow. Images were recorded at room temperature and in the constant current mode with positive bias voltage typically between 0.05 and 1V. Data treatment included plan

subtraction, smoothing and adjustment of colour scale and brightness to enhance the contrast.

III. RESULTS

A. Thiophenol

Fig. 2 shows a STM image of thiophenol adsorbed on Au(111) which has been immersed for 24h in a toluene solution. The topographic image shows a significant degree of molecular order. Thiophenol is organized by parallel stripes, separated by a distance of $11.9 \pm 1.3 \text{ \AA}$. Each stripe is constituted by a pair of rows at a distance of $5.0 \pm 0.1 \text{ \AA}$ from each other, as shown by the line profile 2 marked on the topographic image of Fig. 2. Note that one of the rows has a smaller height because the thiophenol makes a smaller angle with the surface. In profile 1 it is possible to observe a very regular distribution of the thiophenol molecules along each row.

For longer adsorption times, different types of molecular distributions can be identified. Fig. 3 shows STM images of thiophenol SAM prepared using an immersion time of 72h in a toluene solution. In this case, organized regions with dimensions in the range between 30 to 40 nm can be observed. These regions are separated by depressions with a depth corresponding to a single atomic Au layer ($1.8 \pm 0.1 \text{ \AA}$). The longer adsorption time has a great influence in thiophenol packing. In Fig.3 a) the region **A** presents the same type of thiophenol organization as that found in the SAM prepared using 24h adsorption time (Fig.2 a)), and the distance between each stripe and each thiophenol in the same stripe is also the same. However, in this case the degree of surface coverage is higher. Each two pairs of rows with the same height are separated by a third row with lower height. Other types of thiophenol organization are observed in these samples. For instance, the regions with well defined stripes are separated by thiophenol agglomerates, identified by **B** in Fig.3 a). This region **B**, which, in terms of surface morphology, appears as islands, is likely due to disordered molecules, as observed with other aromatic thiols [8].

Different results are obtained when the SAMs are prepared from methanol or ethanol solutions with 72h adsorption time. Fig. 4 a) and b) show the images of thiophenol SAMs prepared with methanol and ethanol, respectively. In both images any type of thiophenol ordering can be observed. In this case the molecules form agglomerates. This result suggests that the solvent dipole moment can influence the adsorption kinetics. Solvents with high polarity disturb the S-Au bond, in particular when the substrate is immersed in the solution during long periods of time.

B. Dodecanethiol

Fig. 5 shows topographic and current STM images of dodecanethiol monolayer. The images were obtained using 0.02 nA current and 0.68V tip bias voltage in a $50 \times 50 \text{ nm}^2$ area. Molecular order can be observed, which is characterized by parallel stripes identical to the ones observed in the thiophenol SAMs. According to the cross-section profile 4 shown in Fig. 5c), each stripe is composed by only one row

of dodecanethiol molecules separated by $1.32 \pm 0.01 \text{ (nm)}$. For this case an I/V curve of dodecanethiol was obtained by scanning tunneling spectroscopy (STS) to characterize the electronic properties of an individual molecule. A bias voltage between -0.5 to 0.5 V was applied during 10 sec, above the molecule, identified by an arrow in profile 4 of Fig. 5 c). Fig.5 d) shows the dodecanethiol I/V curve. In spite of the insulating character of this alkanethiol, this technique has sufficient resolution to measure low current values (ca. 0.01 nA as observed in Fig. 5 d)).

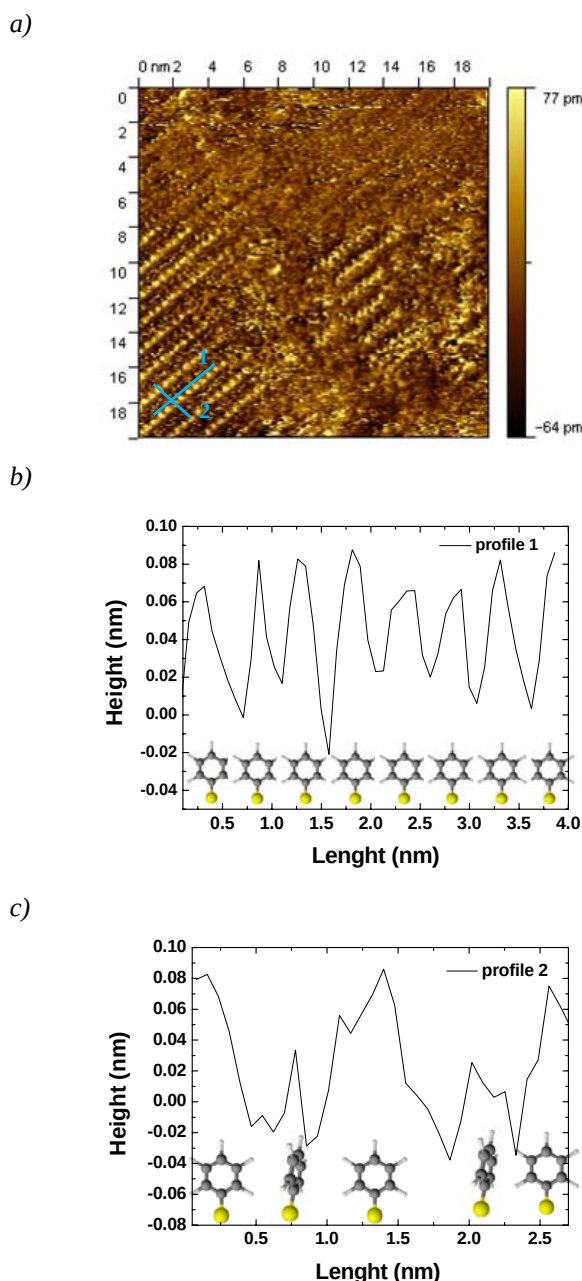


Fig. 2. a) Topographic image of thiophenol SAMs with 24h adsorption time in a toluene solution. Imaging conditions: tunneling current of 1.15 nA and bias voltage of 0.52 V. b) cross-section profile 1 marked in topographic image that represents the thiophenol molecules along each row. c) cross-

section profile 2 marked in topographic image that represents the thiophenol distribution across parallel rows.

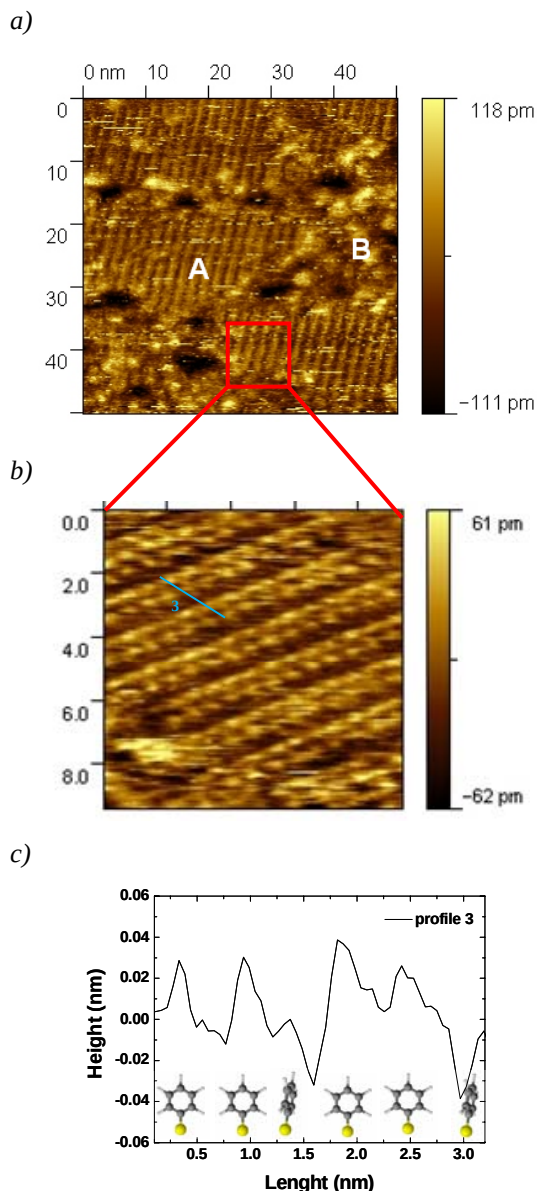


Fig. 3. *a)* Topographic image of thiophenol SAMs with 72h adsorption time in toluene. Two types of thiophenol organization can be observed: **A** – parallel lines and **B** – islands. Imaging conditions: tunneling current 1.27 nA, bias voltage 0.60 V; *b)* higher resolution image obtained by zooming in the square marked in *a)*. Imaging conditions: tunneling current 1.48 nA, bias voltage 0.28 V; *c)* cross-section profile of thiophenol across parallel rows marked in *b)*.

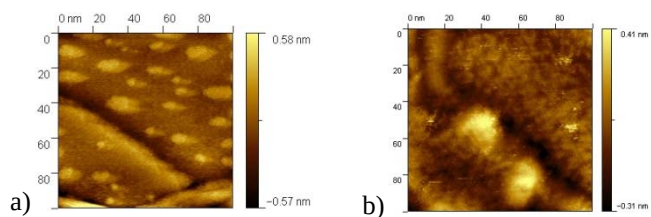


Fig. 4. Topographic images of thiophenol SAMs with 72h adsorption time in *a)* methanol and *b)* ethanol. Imaging conditions: *a)* tunneling current 0.49 nA, bias voltage 0-10 V; *b)* tunneling current 0.44 nA, bias voltage 0.59 V.

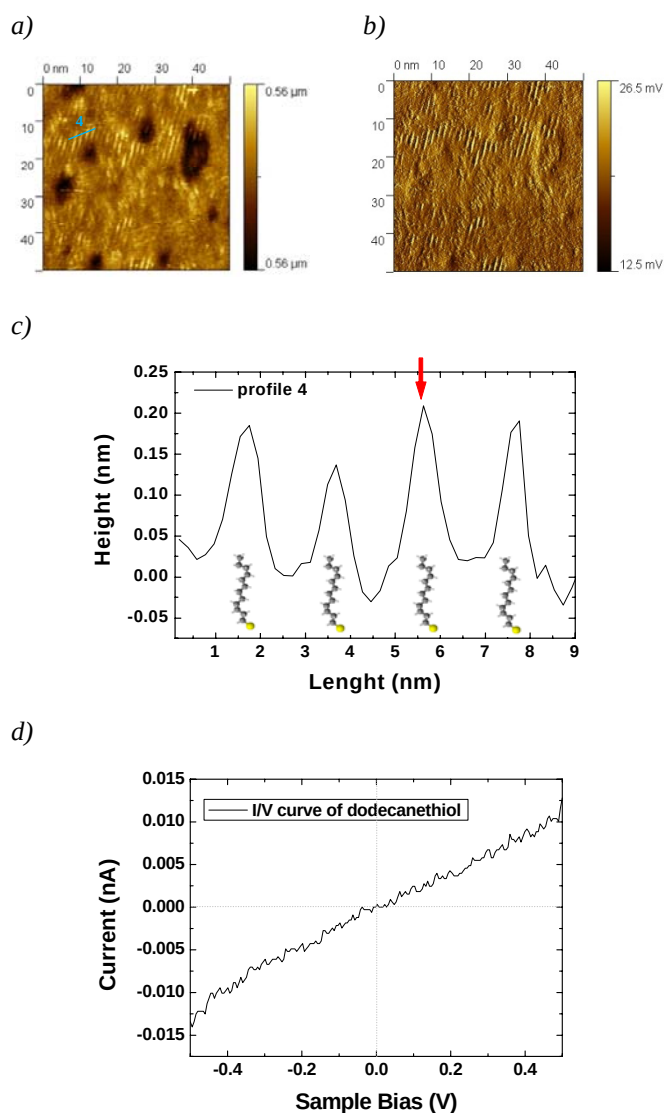


Fig. 5. *a)* Topographic and *b)* current images of dodecanethiol SAMs with 5h adsorption time, in toluene, at 345K under inert atmosphere. Imaging conditions: tunneling current 0.02 nA, bias voltage 0.68 V; *c)* cross-section profile 4 identified in *a)*; *d)* I/V curve of dodecanethiol at the "peak" position marked by an arrow in the cross-section profile 4, obtained at an applied bias voltage between -0.5 to 0.5 V and during 10 sec.

The effect of the adsorption time was also investigated for dodecanethiol. In this case, longer adsorption times are destructive for the molecular order independent of the solvent polarity. This happens in SAMs formed with either toluene or ethanol with 72h immersion time at room temperature. Fig.6 shows STM images of dodecanethiol SAMs prepared from toluene (Fig. 6a) and ethanol (Fig. 6b) and it is possible to observe islands of alkanethiol.

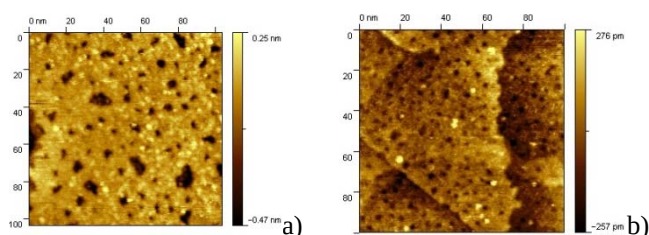


Fig. 6. Topographic images of dodecanethiol SAMs with 72h adsorption time at room temperature in: a) toluene and b) ethanol solutions. Imaging conditions: a) tunneling current 0.20 nA, bias voltage 0.55 V; b) tunneling current 0.03 nA, bias voltage 0.94 V.

IV. CONCLUSIONS

With this study some conditions of SAMs preparation were tested. The adsorption kinetics of aromatic and alkanethiol is different, influencing the packing density. The coverage of thiophenol is higher than that observed for the dodecanethiol and is in agreement with the strong interaction between aromatic thiols and gold.

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