Growth of 4-aminothiophenol on iodine modified Au(100) studied by scanning tunneling microscopy

Tizoc F. Huerta [a,*], José Valenzuela [b]

[a] Posgrado en Ciencia e Ingeniería de Materiales, Universidad Nacional Autónoma de México, Km. 107 Carret. Tijuana-Ensenada, Ensenada, B.C. c.p. 22860, Mexico
[b] Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Km. 107 Carret. Tijuana-Ensenada, Ensenada, B.C. c.p. 22860, Mexico

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ABSTRACT

The adsorption and growth mechanism of 4-aminothiophenol (4-ATP) molecules on iodine modified Au(100) has been investigated by electrochemical scanning tunneling microscopy (ECSTM) and cyclic voltammetry in perchloric acid solution. The first stage of ATP adsorption is characterized by one dimensional molecular growth along the [001] of the Au(100) substrate, together with long and thin trenches between molecular lines that are present even after several layers of growth. At more positive potentials complete surface coverage and 3D growth is observed on the surface. Potential-induced molecular desorption forms randomly distributed pits or vacancies on the surface. This markedly different desorption mechanism from the adsorption process is explained in terms of the different molecular bonds during the oxidation of the ATP molecule. The role of the iodine layer on the growth of 4-ATP on Au(100) is discussed.

1. Introduction

Noble metals in general tend to readily absorb many types of organic molecules in a variety of environments, due mainly to a lower free surface energy. Adsorbed organic molecules also play several important roles, as electrostatic barrier against aggregation, decreasing the reactivity of the surface atoms, or even act as an electrical insulator or conductors [1]. But not all molecular coating are as effective if they lack reproducible chemical and physical properties (e.g. chemical reactivity, resistivity, wetting properties).

The use of Self Assembled Monolayers (SAMs) is a simple, convenient, and flexible route to modify the interfacial properties of metals or metal oxides. A commonly accepted definition of SAMs is that they are organic assemblies formed by the adsorption of molecular entities from a gas or liquid phase onto bare or modified surfaces of well-defined solid substrates, able to self-organize into crystalline or quasi crystalline structures depending on the interplay between molecule-molecule and molecule-substrate forces. Examples of metal substrates are silver [2,3], copper [4–6], iron [7], platinum [8,9], palladium [10], and mostly gold [11], or even liquids, like Hg [12].

An important advantage of organic molecules is their chemical selectivity due to functionality, which means they possess an specific affinity for a particular substrate, considering that a terminal group of the SAM can be chemically adapted in order to play an specific role on the modified surface [13]. The route to synthesize the selected organic molecule and the way to incorporate it into surfaces as SAMs or other forms of nanostructures with a particular set of desired properties is a major concern in SAM research.

The adsorption of thiols, alkanethiols and aromatic thiols as self-assembled monolayers on different substrates has been the subject of multiple research [14–20] and there is an interesting review on this topic [1]. In recent years, aromatic thiols have received special attention due to steristic considerations, particularly because their phenyl ring tends to reduce the molecular flexibility that affects packing [21], while providing a higher electrical conductivity due to the presence of their delocalized pi electrons [21,22]. This increased interest is not only attributed to the simplicity of preparation but also to their ability to serve as electrochemical biosensor. On this point, SAMs of 4-aminothiophenol (4-ATP, or p-ATP) have been used as electrochemical sensors for tolazoline on gold nanoparticles [23], on functionalized multi-walled carbon nanotubes for the determination of quercetin and rutin [24], for detection of dioxygen reduction [25], and even for biosensing DNA [13].

The most often used route for 4-ATP SAM preparation consist of ex-situ experiments like cyclic voltammetry (CV) [13,23,25–29], surface-enhanced Raman scattering (SERS) [30–34] and scanning tunneling microscopy (STM) [13,21,35]. Among these investigations, STM provides a visual imaging at molecular and atomic level; furthermore 4-ATP is one of the most studied molecules by SERS [36].

Notwithstanding these studies, there are few studies dealing with direct in-situ modifiable and controllable SAM formation of 4-ATP. Using electrochemical scanning tunneling microscopy (EC-STM), Batz

* Corresponding author.
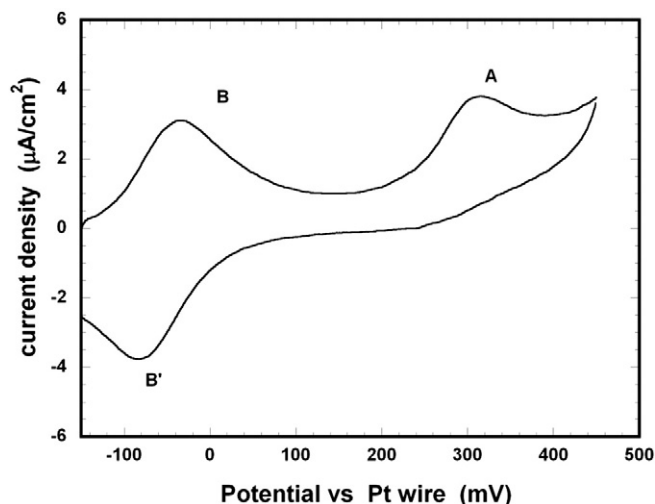E-mail addresses: thuerta@cnyn.unam.mx (T.F. Huerta), valenzue@cnyn.unam.mx (J. Valenzuela).

Fig. 1. Cyclic voltammogram of iodine modified Au(100) in 0.1 M HClO$_4$ solution containing 0.1 mM 4-ATP. Scan rate 15 mV/s.

Fig. 2. Scan rate dependence of the oxidation current peak B.

et al. [21] studied the electrochemistry and structure of the SAMs formed by o-ATP, m-ATP, and p-ATP on Au(111). Ganesh et al. [29] reported the SAM formation of thiophenol, o-ATP, and p-ATP on polycrystalline gold surface and analyze the effects of the potential cycling on the blocking ability of TP and o-ATP on polycrystalline gold.

With the discovery of highly ordered arrays of 5,10,15,20-tetrakis (N-methylpyridinium-4-yl)-porphyrin (TMyP) molecules on Au(111) by Itaya's group [37] there has been an increasing interest on using iodine-modified gold surfaces, since it was demonstrated that the iodine layer on Au(111) plays a crucial role on the formation of the highly ordered TMPyP arrays. The same route is effective to achieve SAMs of more complex molecules and substrates other than gold [38–42].

As ATP is a promising organic molecule in the field of organic sensors, and there are few experiments dealing with direct imaging of 4-ATP SAMs, we focus in a new alternative to obtain highly ordered arrays of this important organic molecule. In this sense, we provide the first EC-STM results, to our knowledge, of self-assembled molecules of 4-ATP on iodine modified Au(100) surfaces. The surface has been characterized by in-situ EC-STM in HClO$_4$ solution. The preparation methodology and analytical characteristic features are described and discussed.

2. Experimental

In-situ ECSTM measurements were carried out with a Nanoscope E (Digital Instruments, Santa Barbara CA). For tunneling tips we used 0.25 mm diameter W wire, electrochemically etched in 6N KOH solution, and coated several times with nail polish in order to minimize faradaic currents. Tip and sample potentials were independently controlled by means of a bipotentiostat, and all STM images were taken at a constant current operating mode. Pt wire was used for the quasi-reference and counter electrodes in the STM cell. All potentials are quoted with respect to the platinum reference electrode.

2.1. Materials used

Hydrogen peroxide (30 wt%) and NH$_4$OH (28–30%, ACS reagent) were used as provided by Sigma-Aldrich. Deionized water (18 MΩ-cm) was used in the preparation of all solutions and H$_2$SO$_4$ (95–98%, ACS reagent) provided by Jalmek, and HNO$_3$ (70%, ACS) by Fermont were used as received. KI (99.999%, puratronic), HClO$_4$ (68%, environmental grade), and 4-aminothiophenol (97%) were obtained from Alfa-Aesar and used without further purification. Prior to our experiments all glassware was cleaned with a H$_2$SO$_4$:HNO$_3$ (1:1) solution at 60–70 °C for 1 h and rinsed several times under distilled water.
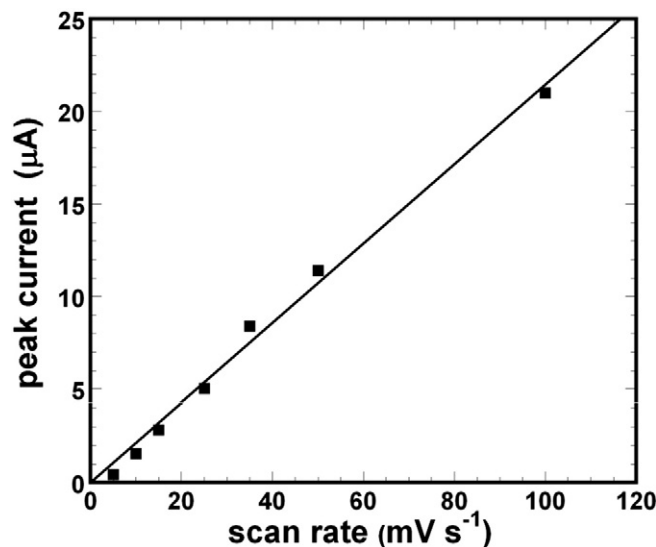
The electrochemical cell was cleaned using a H$_2$O$_2$:NH$_4$OH:H$_2$O (1:1:5) solution heated at a temperature between 60 and 80 °C for at least 1 h and rinsed generously with distilled water, at the end of the process the cell was kept on pure water until the experiments were developed.

2.2. Preparation of gold surfaces

The Au(100) electrode was a 10 mm diameter single-crystal disk. Before surface modification, the gold single-crystal was cleaned in a heated "piranha" solution bath (H$_2$O$_2$:H$_2$SO$_4$, 1:3 @ 60–70 °C), thoroughly rinsed with deionized water (18 MΩ-cm resistivity) and dried under room conditions. At this point the cleaned surface is flame-annealed using a butane torch, using the method developed by Clavilier et al. [43] and adapted by Hamelin and Katayama [44], a process that
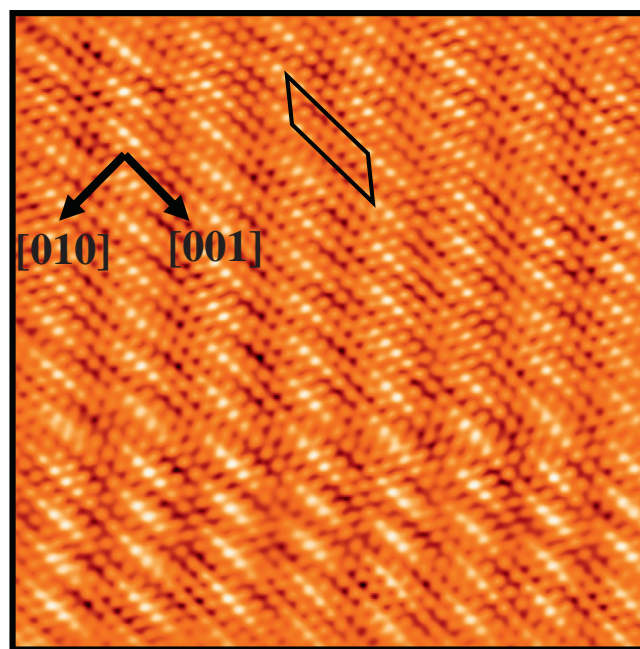

Fig. 3. Filtered 17 × 17 nm^2 in situ image of the I layer on Au(100). The height modulation results from the mismatch between the pseudo-hexagonal iodine layer on top of the square Au(100) lattice.