



# Chemisorption of alkyl thiols and S-alkyl thiosulfates on Pt(1 1 1) and polycrystalline platinum surfaces

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Received 21 September 2004; accepted for publication 4 February 2005

Available online 13 April 2005

## Abstract

The self-assembled monolayers prepared from 1-dodecanethiol ( $C_{12}SH$ ) or S-dodecylthiosulfate (Bunte salt,  $C_{12}SSO_3Na$ ) have been characterised on polycrystalline gold and platinum surfaces and on Pt(1 1 1). Contact angle and impedance measurements show that the film quality decreases in the order  $Au/C_{12}SH > Pt/C_{12}SH \sim Au/C_{12}SSO_3Na > Pt/C_{12}S SO_3Na$ . XPS measurements show that the S– $SO_3$  bond of organic thiosulfates is broken on platinum surfaces and the state of the surface-bound sulfur is indistinguishable from that of thiolate. On platinum three sulfur species are formed upon SAM formation and we suggest that the catalytic activity of platinum is responsible for their existence in pristine monolayers.

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**Keywords:** X-ray photoelectron spectroscopy; Platinum; Self-assembly; Chemisorption

## 1. Introduction

Self-assembled monolayers (SAMs) have become important in many areas of surface related studies. In particular, monolayers prepared on transition metal surfaces using molecules with a sulfur containing surface-active headgroup have

been intensively studied [1–7]. Thiols and disulfides are known to chemisorb on gold through a polar covalent Au–S bond and the structure and properties of SAMs on gold, formed using a wide variety of surface-active thiols and disulfides, have been extensively characterised. However, compared to the extensive literature on self-assembled monolayers on gold, very little is known about the structure and properties of thiol-based SAMs on platinum, which is another important electrode material in electrochemistry. The pioneering work by Soriaga

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and Hubbard [8] showed that thiophenol and 2,5-dihydroxymercaptobenzene chemisorb on platinum and their orientation depends on the solution concentration. The blocking efficiency against the platinum surface oxidation has been shown to increase with the alkyl thiol length [9]. Raman scattering studies have shown that the orientation of 4-mercaptopyridine is similar on polycrystalline platinum, gold and silver [10]. On adsorption, mercaptopyridines displace surface platinum oxide, implying a strong interaction with the adsorbate and the surface [11,12]. On the other hand, adsorbed oxygen on the platinum surface slows down the kinetics of thiol adsorption and the reorganization of the formed monolayer [13]. Auger spectroscopy proves that the initially adsorbed oxygen is replaced by thiols. The SAMs are, however, less ordered on platinum than on gold and a considerably high number of gauche defects in alkyl thiol monolayers on Pt(111) has been found by vibrational sum frequency generation (SFG) spectroscopy, making the film permeable to ions [14]. The alkyl thiol SAMs do not show the odd–even effect characteristic of the monolayers on gold and exhibit potential dependent conformational changes, which were attributed to a less ordered structure. No long range order in the alkyl thiol monolayers on Pt(111) was detected by LEED, contrary to gold, and the methylene moieties were more exposed on platinum than on gold, indicating more local defects [15].

The exact nature of the obviously inferior organic self-assembled monolayers on platinum, compared to gold, is not known at the moment because of very few studies concerning the thiol-based SAMs on platinum. We present here a comparison of alkyl thiol SAMs on Pt(111) and polycrystalline gold and platinum electrodes using conventional and synchrotron-based X-ray photoelectron spectroscopy (XPS), ac-impedance spectroscopy and contact angle measurements. We focus on SAMs formed on polished electrodes because they are the major form of platinum electrodes used in electrochemical measurements. In addition to thiol-based films on different electrodes, we compare monolayers prepared using S-alkyl thiosulfates (Bunte salts) on both metals. We have earlier shown that Bunte salts chemisorb

on gold through an identical gold-thiolate bond as thiols and disulfides [16].

## 2. Experimental

### 2.1. Substrate and film preparation

The polycrystalline platinum and gold electrodes were initially polished to a mirror finish. Immediately before modification with thiol or thiosulfate the electrodes were cleaned in oxygen plasma, followed by treatment in hydrogen plasma. This procedure has been shown to produce a clean metal surface [17]. The Pt(111) electrode (MaTecK, orientation accuracy  $<1^\circ$ ) was cleaned by repetitive  $\text{Ar}^+$  bombardment and heating in ultra high vacuum (UHV) until the characteristic LEED pattern was obtained and XPS indicated a clean surface. Electrodes were shortly exposed to air (less than 10 min) before inserting them to the solution. They were then placed in 1 mM solutions of the surface-active compounds in ethanol. All solutions were deaerated with argon and adsorption was carried out under an argon atmosphere. After an appropriate time the electrodes were removed from the solution and rinsed thoroughly with the solvent. Before measurements all electrodes were finally rinsed with Millipore water.

### 2.2. Film characterisation

The ac impedance and XPS measurements were carried out as described elsewhere [16]. A CAM 200 optical contact angle meter (KSV Instruments, Ltd., Espoo, Finland) equipped with a video camera was used to measure the static aqueous contact angles. Measurements were performed at five different locations with at least two different samples. All measurements were carried out on thoroughly rinsed samples (ethanol and 18 M $\Omega$  water) immediately after removing the substrates from the modification solutions. The XPS spectra were subtracted by the Shirley or linear background correction and fitted using Gaussian–Lorentzian as well as asymmetric line shapes. The S2p spectra were analyzed using a fixed splitting of 1.18 eV and equal FWHM value for both components of the

doublet. An intensity ratio of 2:1 for the  $2p_{3/2}$  and  $2p_{1/2}$  peaks was used. The Au $4f_{7/2}$  and Pt $4f_{7/2}$  binding energies of bulk metal (84.0 eV and 71.2 eV, respectively) agreed with the previously published values [18]. The synchrotron measurements were performed at MAX-lab (Lund, Sweden) using the beamline I411 equipped with a SX-700 PGM monochromator and Scienta SES-200 analyser [19]. The Fermi level of platinum was used for calibration of synchrotron-based measurements.

### 3. Results and discussion

#### 3.1. Contact angle and impedance measurements

Alkyl thiol monolayers have a profound effect on the wetting of the electrode surface. The hydrophobicity of the surface is enhanced with increasing alkyl chain length and with pronounced film order. Table 1 shows the static contact angles measured on the four systems studied in this work, Au/C<sub>12</sub>SH, Au/C<sub>12</sub>SSO<sub>3</sub>Na, Pt/C<sub>12</sub>SH, and Pt/C<sub>12</sub>SSO<sub>3</sub>Na. All the surfaces are hydrophobic although the contact angles are smaller than those reported for alkyl thiol SAMs on well-ordered crystal surfaces [13]. In addition, the differences between the surfaces are small, probably as a result of the levelling effect of the rough substrate surface. The electrochemical impedance data was best accounted for by the modified Randles equivalent circuit, in which the interface consists of a charge transfer resistance (denoted by  $R_{ct}$ ) in series with a Warburg impedance (described by  $Z_w$ ), which are in parallel with a constant phase element (CPU) [16]. The need to incorporate the CPU into the circuit instead of a simple capacitor reflects the low quality of the SAMs on these polished electrodes. An effective capacitance value can be calculated from the fitted circuit parameters according

to the method described by Brug et al. [20], assuming the CPU behaviour to originate from the surface inhomogeneity. However, as described elsewhere, the charge transfer resistance is a much more sensitive indicator of the film quality [16]. The effective capacitances for the Au/C<sub>12</sub>SH and Pt/C<sub>12</sub>SH systems were identical (Table 1) but the higher charge transfer resistance of the former indicated better quality (10.5 and 7 k $\Omega$  cm<sup>2</sup>, respectively). The capacitance of the Pt/C<sub>12</sub>SH interface is smaller than reported for the corresponding SAM of decanethiol on polycrystalline platinum, indicating that a better layer can be obtained with the longer aliphatic thiol [13]. As previously observed, the SAMs formed using Bunte salt exhibited greater variation in properties, especially in the  $R_{ct}$  values. The effective capacitances for the Au/C<sub>12</sub>SSO<sub>3</sub>Na and Pt/C<sub>12</sub>SSO<sub>3</sub>Na interfaces were 2.0 and 2.8  $\mu$ F cm<sup>-2</sup>, respectively (Table 1).

#### 3.2. XPS of the monolayers

Considering the vast literature dealing with the XPS measurements of thiol SAMs on gold a very limited number of work has been done on platinum. An early work with ferrocene thiols showed that the S2p binding energy (BE) of thiolate on platinum surface is ca. 163 eV [21], a value ascertained by more recent studies [11,12,22].

Fig. 1a and b show the S2p XPS spectra of SAMs prepared from 1-dodecanethiol and S-dodecylthiosulfate, respectively, on polycrystalline platinum. The only peaks appear around 163 eV with no signal at higher binding energies indicating that no oxygen containing sulfur species are present. In addition, the O1s spectra displayed no traces of oxygen on the surface. Sodium was not detected, either. In all cases, the C1s spectra show only one component at 285 eV, characteristic for hydrocarbon chains [23]. We have previously shown that

Table 1  
Static contact angles and effective capacitances of different SAMs

SAM	Au/C <sub>12</sub> SH	Au/C <sub>12</sub> SSO <sub>3</sub> Na	Pt/C <sub>12</sub> SH	Pt/C <sub>12</sub> SSO <sub>3</sub> Na
Static contact angle	101.7°	100.8°	101.2°	100.5°
Effective capacitance	1.9 $\mu$ F cm <sup>-2</sup>	2.0 $\mu$ F cm <sup>-2</sup>	1.9 $\mu$ F cm <sup>-2</sup>	2.8 $\mu$ F cm <sup>-2</sup>

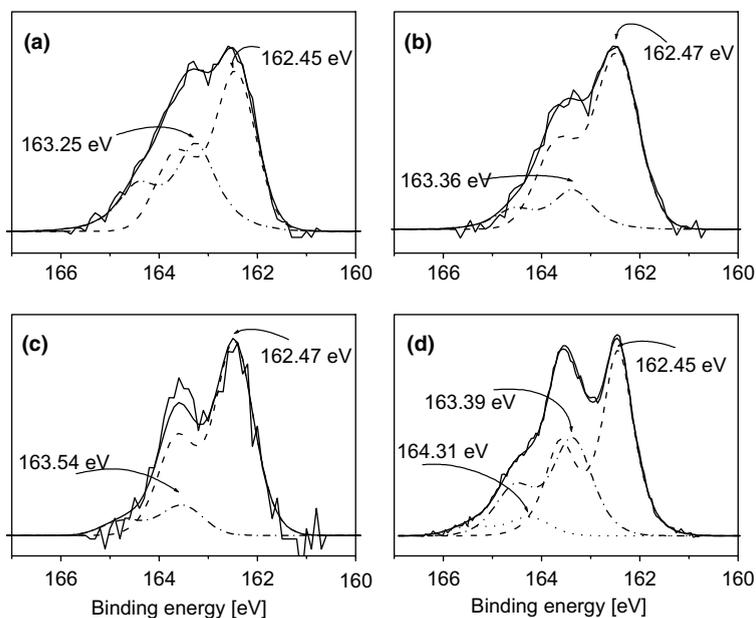


Fig. 1. The S2p XPS spectrum (Al K $\alpha$  excitation) of SAMs prepared from (a) 1-dodecanethiol on polycrystalline platinum, (b) S-dodecylthiosulfate on polycrystalline platinum, (c) 1-dodecanethiol on Pt(111) and (d) HRXPS spectrum (250 eV excitation) of SAM prepared from 1-dodecanethiol on polycrystalline platinum.

on gold the chemisorption of organic thiosulfates produces SAMs with sulfur in a chemical state indistinguishable from thiolate [16]. The results in this work show that Bunte salts and thiols behave similarly also on platinum surfaces. However, two closely spaced doublets (at  $\sim 162.5$  and  $\sim 163.4$  eV for both Pt/C<sub>12</sub>SH and Pt/C<sub>12</sub>SSO<sub>3</sub>Na) were needed to characterise the XPS S2p signal from monolayers on platinum while on gold only a single doublet assigned to gold-thiolate is generally observed at 161.9 eV [16,23,24]. In order to ascertain that the appearance of the extra peak was not due to the nonideal nature of the polished polycrystalline electrode surface we have also measured the S2p spectrum on similar gold electrode (not shown) and on a single crystal Pt(111) surface (Fig. 1c). On gold, only one doublet characteristic of surface thiolate was observed but the spectrum of the SAM on Pt(111) was similar to that observed on polycrystalline platinum. The proportion of the component at higher BE (ca. 15% of the total sulfur) was, however, smaller than on the polycrystalline electrodes (ca. 33%). In case of Au, two doublets have been observed with

poorly rinsed samples, the one at higher BE (ca. 163.5–164 eV) being attributed to unbound thiol or disulfide [24]. In this work, the surfaces were very thoroughly rinsed and unbound sulfur species can not explain the two signals observed. Extensive treatment in ultrasonic bath (15 min in ethanol followed by 15 min in water) in order to remove all physisorbed material resulted in the decrease of both doublets. For thiol SAMs on gold and silver, radiation induced changes in the S2p spectra have been reported [25–27] but we have shown that on platinum the relative intensity of the two spectral features does not change during irradiation [27]. In gold-based SAMs prepared using very short adsorption times isolated thiols exhibit BE at 161 eV [23] but the immersion time was at least 12 h for all films studied in this work. Therefore, the appearance of two doublets due to sulfur seems to be an inherent feature of SAMs prepared from thiol or thiosulfate on platinum surfaces.

More accurate spectra can be obtained with high resolution photoelectron spectroscopy (HRXPS) using synchrotron radiation excitation.

The HRXPS S2p emission line is presented in Fig. 1d and it displays three doublets. The smallest doublet (S2p<sub>3/2</sub> component at about 164 eV) could not be observed in the conventional XPS spectra but it is apparent in all synchrotron-based measurements of thiol SAMs on Pt. Our earlier results show that it can be observed also on irradiated Cu and, occasionally, Au surfaces [28].

### 3.3. Adsorption mechanism

In order to explain the splitting of the sulfur spectrum different factors may be considered. The component at ~162.5 eV has been assigned to monomeric thiolate species whereas the component with higher BE has been attributed to dimerised species [11,12]. On gold, the thiolate sulfur atom may have either sp<sup>3</sup> or sp hybridization with a small energy difference [29]. The S2p<sub>3/2</sub> binding energy of the sp<sup>3</sup> sulfur should be ca. 1 eV higher than that of the sp sulfur [30], which is relatively close to the observed difference between the two lower sulfur doublets on platinum. Chemisorbed sulfur from the gas phase on Pt(111) exhibit two S2p doublets at 162.31 eV and 161.37 eV [31,32]. They have been attributed to sulfur chemisorbed at threefold hollow sites and bridge sites, respectively. According to theoretical calculations the difference in the fractional charge on the adsorbed sulfur atom is ca. 0.11 eV between hollow and bridge sites [32]. This difference implies a shift of ca. 0.5 eV in the S2p binding energy, which is reasonably close to the observed value [33]. On Pt(111), the chemisorption site of methanethiol has also been shown to be the fcc hollow site at high temperatures [34] but at room temperature the order decreases, which is in accordance with the failure to obtain a LEED pattern of an alkyl thiol SAM on Pt(111) [16]. These results imply that the binding site of sulfur may not be unique on platinum. It should also be emphasized that platinum has a very high catalytic activity. This fundamental chemical property of the metal has not been taken into account previously. On the reconstructed Pt(110)-(1 × 2) surfaces a rapid dissociative adsorption of alkanes takes place, resulting in the C–H bond activation and hydrogen abstraction well below room temperature under

UHV conditions [35,36]. The produced partially dehydrogenated hydrocarbon fragments remain adsorbed on the surface. Thiols are well known radical scavengers, which readily donate hydrogen, thus forming thiyl radicals [37]. Thiyl radicals can rapidly react with each other, with carbon radicals or add to carbon–carbon double bonds.

Although the extrapolation from high vacuum conditions to a solution phase is not straightforward we tentatively put forward a following mechanism for the origin of the new sulfur species on platinum surfaces (see Scheme 1; only the hydrocarbon chains of surface-aligned thiols are shown and no attempt has been made to show bonding to platinum). Oxidative dehydrogenation, another well known process on platinum group metals [38], can be ruled out because of the high temperature usually required and the absence of oxygen in our XPS spectra. During the first stage of the SAM formation the alkyl thiol molecules form a dense, flat surface-aligned phase [5,39]. The catalytically active platinum substrate interacts strongly with flat lying molecules. The fragmentation of carbon chains may take place (upper level on the Scheme 1). Platinum partially dehydrogenates the adsorbed hydrocarbon chains forming hydrocarbon radicals and, possibly, adsorbed alkenes (second level on Scheme 1). The thiols in solution effectively scavenge the radicals and produce thiyl radicals, which rapidly react with hydrocarbon radicals, alkenes or with each other (third level on Scheme 1). Both surface reactions lead to the formation of dialkyl sulfides (lowest level in Scheme 1), which have been identified as the species produced by X-ray irradiation in monolayers on gold [25]. On the other hand, the Pt(111) surface exhibits much lower catalytic activity [35] and thiosulfates are not radical scavengers although they can produce thiols in situ during the film preparation. These facts are well in accordance with the lower relative proportion of the 163.4 eV sulfur species on Pt(111) surface and in thiosulfate-based SAMs (Fig. 1b and c). In addition, the BE of the third, enigmatic sulfur species coincides with that of dialkyl disulfides, a probable reaction by-product [25]. This complex series of reactions results in self-assembled layers of low quality.



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