



# Self-assembled alkanethiol monolayers on a Zn substrate: Interface studied by XPS

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## ABSTRACT

After having presented the organization and self-assembly of alkanethiols on zinc substrates, we focus here on the bond between the thiol sulfur and the metal. The interfacial bond between decanethiol and bulk Zn platelet has been investigated by X-ray photoelectron spectroscopy. In the presence of traces of oxygen, the Zn is oxidized and subsequently the thiolate  $\text{-Zn(II)-SR}$  is formed whatever the adsorption time  $t_{\text{ads}}$  and ageing conditions. This is attributed to the inability of the thiol to reduce the Zn(II). Results for the Zn substrate are discussed and we put into perspective the behaviour of Zn compared to other metals in the light of its great affinity towards sulfur and its complexing, soft acid and reducing properties.

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## 1. Introduction

Alkylthiols  $\text{CH}_3(\text{CH}_2)_n\text{SH}$  can graft and organize on metallic substrates leading to self-assembled monolayers (SAMs) notably on noble metals such as gold, silver, platinum or other oxidizable metallic substrates [1]. It is generally recognized that the presence of oxidized sulfur species adsorbed onto the surface, may drastically decrease the adhesion; this can be related to the poor organization of the monolayer and to the weak/undefined attachment to the surface or to ageing [2–4]. In the case of Fe [2], the oxidized species resulting from the interaction of thiols and unreduced metal oxide give poorly organized monolayers with many pinholes. In the case of Pt [5] adsorbed oxygen delays or hinders thiol chemisorption. The preliminary reduction of a superficial oxide such as CuO is required for the attachment of mercaptan [6] suggesting a stronger interaction of the thiol with Cu(I) or Cu(0) than with Cu(II).

Concerning SAMs properties and potential applications, these close-packed monolayers form effective barriers against ions, oxygen and water. Because SAMs are tunable with a relevant functionalization, they provide an original path for surface modification and open up new perspectives for applications in materials science [1]. Then SAMs can be envisaged as a primer before deposition of various coatings. Both the improvement of coating adhesion and enhancement of protection against corrosion can

be achieved by the use of SAMs [2] instead of primers based on chromium oxides [8]. This non-toxic approach is particularly promising. Thiols act as grafting agents if they possess a second terminal function able to bind chemically or electrochemically to a subsequent layer. Such bipolar molecules  $\text{HS-(CH}_2)_n\text{Y}$  have already been tailored and used successfully to graft conducting polymers/oligomers to noble metals [9] but also to Al [10] and Ti [11] or to improve the adhesion of polyisoprene to Zn wire [12].

Therefore, in a first study, the adsorption of simple alkanethiols on Zn is considered. In previous work [7], the orientation and self-assembly of alkanethiols on Zn or galvanized metal was demonstrated by IRRAS spectroscopy and wetting measurements. However, XPS is required in order to characterize the nature of interfacial binding between the thiol sulfur and metals [3], as has been shown for Au [13], Ag [3b,14], Cu [3b,15], Ni [16], Fe [2], Ti [17], Al [10], Zn [18] and Pt [19,20]. In this interfacial study, we focus on the chemical state, the oxidation number (o.n.) of the zinc and of the sulfur of decanethiol, and on the oxide present at the interface as a function of the adsorption time in neat thiol. We show that the thiol is bound only to Zn(II), forming a stable thiolate. By putting into perspective Zn metal and its thermodynamic properties compared to other common metals, we attempt to explain the absence of Zn(0)-SR and the unusual stability of Zn(II) thiolate.

## 2. Experimental

### 2.1. Preparation of Zn substrates

For XPS studies, Zn sheet (99.99%, Goodfellows) ( $1 \times 4 \text{ cm}^2$ ) was polished with 1200 and 4000 grit SiC abrasive paper (Struers).

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Ultrapure water for solutions and for rinsing was taken directly from an ELGSTAT UHQ II (18 M $\Omega$  cm) water purification system. Samples were sonicated in a Bioblock-Scientific T-460H ultrasonic bath at a frequency of 35 kHz and a power of 35 W. Conditions for contact angle measurements and the corresponding substrate preparation have been described elsewhere [7].

## 2.2. Preparation of monolayers

All vessels were carefully cleaned by immersion in hot sulfuric acid (Ultrapure, Merck) overnight and then rinsed with ultrapure water. *n*-Decanethiol, CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>SH (DT) (Aldrich 99%), was used as received.

For the spectroscopic study, the zinc sheets are first polished in the neat thiol in a glove box under argon with 4000 grit SiC abrasive paper. After 10 min the substrates are immersed in thiol for a few seconds to 48 h ( $t_{\text{ads}}$ ). The preparation of the spherical electrode used for contact angle (CA) measurements has been described [7,20]. All Zn samples were subsequently rinsed twice with dichloromethane (Aldrich 99%) in the ultrasonic bath for 2 min to remove molecules that were not strongly grafted. No presence of SiC or contamination due to the polishing in the neat thiol was detected on the substrate. Moreover this method decreases the atmospheric contamination and limit the oxygen adsorption.

## 2.3. Analytical methods

XPS experiments were performed using a physical electronics (PHI) Quantum 2000 Spectrometer with a monochromatic Al K $\alpha$  X-ray source (energy: 1486.6 eV). The analysis chamber was always maintained below 4.10–10 Torr. Sputtering was performed with an ionic argon beam (energy: 2.5 keV). The binding energy (BE) of the C<sub>1s</sub> of the alkyl chain (C10) at 285 eV was taken as reference. The S<sub>2p</sub> peaks were fitted with a Gaussian function with provision for 1.2 eV spin-orbit splitting for the 2p<sub>1/2</sub> and 2p<sub>3/2</sub> components [24]. Curve fitting was performed using the peak-fitting module software (Microcal Origin, version 5.1). The take-off of photoelectrons was 45°. A general survey spectrum was recorded first; then high-resolution spectrum for each element (C<sub>1s</sub>, S<sub>2p</sub>, O<sub>1s</sub>, Zn<sub>2p</sub> core levels and Auger Zn<sub>LMM</sub> feature) were acquired with an analyzer pass energy scan of 29 eV. Peak positions obtained after deconvolution are defined, given the signal-to-noise ratio, with an accuracy of  $\pm 0.2$  eV.

## 3. Results

Monolayers of CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>SH/Zn were formed by mechanically polishing the substrate in neat thiol and immersing it also in neat thiol for a time  $t_{\text{ads}}$ . XPS spectra were recorded just after sonication in dichloromethane.

Whatever the adsorption time, there is a S<sub>2p</sub> peak at  $162.5 \pm 0.2$  eV and a shoulder at  $163.6 \pm 0.2$  eV (Fig. 1).

The decomposition of the S<sub>2p</sub> line into two components with 2:1 intensity ratio ( $\pm 5\%$ ) and a difference in BE of 1.2 eV are in agreement with the presence of one sulfur species characterized by a doublet due to spin-orbit coupling S(2p<sub>3/2</sub>) at 162.5 eV and S(2p<sub>1/2</sub>) at 163.7 eV except for the shortest time  $t_{\text{ads}}$  (see below). The larger peak S(2p<sub>3/2</sub>) at 162.5 eV is characteristic of thiolates: Zn-SR (Zn "0" or "II"). Such a value has already been found on a "metallic" Zn substrate or with an oxidized Zn substrate [18]. We can exclude the presence of unbound decanethiol, since this species has an S(2p<sub>3/2</sub>) BE centered at  $163.5 \pm 0.3$  eV, as we have checked on free thiol RSH (not shown) and in agreement with the literature [3a]. In the case of the shortest immersion time

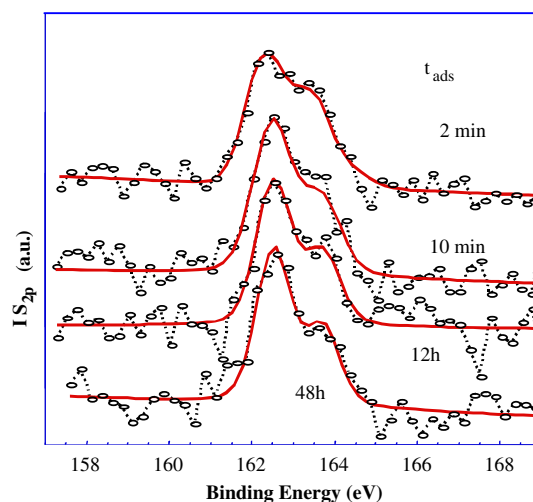


Fig. 1. Evolution of S<sub>2p</sub> for increasing adsorption times  $t_{\text{ads}}$  of CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>SH adsorbed on Zn substrate (the full line is the fitting curve).

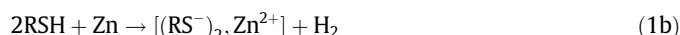
and with a single doublet, the ratio is slightly less than 2:1. Then, a second doublet was introduced into the decomposition at BE S(2p<sub>3/2</sub>) = 163.3 eV with a relative intensity of 17%. As proposed in the literature, this may indicate different adsorption sites [3a,19,21] or disulfide that appears after beam-induced damage [3a,13f].

Assuming initially the presence of Zn(0), we can propose the following reactions:

(i) covalent bond formation:

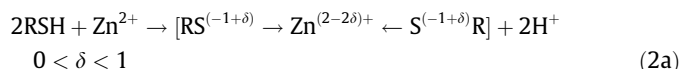


(ii) total charge transfer (ionic bond):

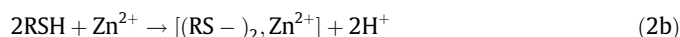


If Zn is previously oxidized because of traces of O<sub>2</sub> or H<sub>2</sub>O, the thiol could adsorb onto Zn<sup>2+</sup> or Zn(II) and give:

(i) with a partial charge transfer:



(ii) as in Eq. (1b):



Whatever the initial state of Zn, the final state after molecular interaction might be intermediate between the two final states with partial electron transfer from sulfur to Zn. The S(2p<sub>3/2</sub>) BE has been used as a probe of the charge density of the sulfur atom [22]. According to [22], the sulfur is partially "reduced" here with a small negative charge density:  $(-1+\delta) = -0.2e$  where  $e$  is the absolute value of the electron charge ( $e > 0$ ).

The integrated areas of both the S<sub>2p</sub> and C<sub>1s</sub> peaks do not depend on the adsorption time  $t_{\text{ads}}$  (Fig. 2, Table 1) within the detection limits (0.15 ML under our conditions). Since the total amount of adsorbed sulfur is constant, we conclude that chemisorption is fast and that total coverage occurs before  $t_{\text{ads}} = 2$  min. The ratio of intensities  $I(\text{S}_{2p})/I(\text{C}_{1s})$  remains also constant (Fig. 3), showing no breaking of the C-S bond. As observed with gold [1], the grafting reaction onto Zn is expected to be exothermic and fast and take place in the first seconds after immersion of the metal in the thiol.

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