Stability of self-assembled monolayers of organothiol mono and bipode on copper in presence of another organothiol solution

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ABSTRACT

The stability of alkanethiol self-assembled monolayers (SAMs) on metallic substrates is an important aspect for further application. Some studies point out the poor stability of this coating and the displacement of alkanethiol from the monolayer by immersion in another alkanethiol solution.

The aim of this work consists in a comparative investigation of self-exchange of three organothiols: 11-perfluorobutyl-1-thiol-undecane (or R_fSH), 2-dodecylpropane-1,3-dithiol (or $R(SH)_2$) and n-decanedithiocarboxylic (or RS_2H).

The immersion of RS_2H monolayer into R_fSH solution (first approach) leads to the incorporation of thiol molecules into the defects of the initial SAMs followed by the displacement of RS_2H molecules by R_fSH. While for R_fSH SAM in presence of $R(SH)_2$ solution (second approach), longer time of immersion is required to observe the incorporation of dithiol molecules into the coating as well as the displacement of thiol molecules.

1. Introduction

Self-assembled monolayers (SAMs) have been extensively studied over the past two decades [1–3]. These organic thin films are potentially useful in many areas by controlling the chemical and physical surface properties. In the literature, many studies are devoted to a better understanding of the interface substrate/SAMs but few investigations are reported about SAMs stability, while the long term stability is a key factor for further applications.

Some studies [4,5] point out the displacement of alkanethiolate molecules from the surface by immersion into another solution of alkanethiol (RSH). This poor stability of aliphatic alkanethiol limits their use in technological application. Shon et al. [6] suggest that the self-assembly of 2-monoalkylpropane-1,3-dithiol $(R(SH)_2)$ on gold affords enhanced stability than alkanethiol monolayer. The preformed SAM of $R(SH)_2$ is not displaced by immersion in alkanethiol solution, while, the dithiol molecules are able to displace alkanethiol SAM [6]. The self-assembly of $R(SH)_2$ on gold brings thus improvement for long term applications.

In other applications, SAMs are used as a sacrificial structure to perform patterns on a metal. For this purpose, the monolayers have to provide initially robust films but which degrade rapidly under mild conditions. Previous studies [7,8] of self-assembly of aliphatic dithiocarboxylic (RS_2H) on gold surface show the formation of high quality SAMs but with lower stability than alkanethiol. They are removed faster and with greater ease, without the use of UV radiation [9,10].

Recently, our research was focused on the relative stability of alkanethiol, dithiocarboxylic and dithiol adsorbed on copper [11]. It comes out that $R(SH)_2$ monolayers are the more stable SAM when subjected to both anodic and cathodic desorption tests, while the dithiocarboxylic acid leads to the less stable coating. The trends are thus similar to those found in the case of gold substrates.

Understanding the stability and reactivity of mono- and bipodal alkanethiol monolayers on copper is essential before further application. In this paper, we compare the stability of decanedithiocarboxylic $(RS_2H$, Fig. 1a), 2-dodecylpropane-1,3-dithiol $(R(SH)_2$, Fig. 1b) and 11-perfluorobutyl-1-thiol-undecane $(R_fSH$, Fig. 1c) by self-exchange reaction. The experiments are carried on with a functionalized normal alkylthiol in order to have a tag molecule and make easier the detection of the different molecules.

The first approach (Fig. 2a) investigates the relative ease of displacement of RS_2H by the immersion of the modified substrate in R_fSH solution. The higher stability of dithiol SAMs is, for its part, investigated in a second approach by immersing R_fSH SAM in $R(SH)_2$ solution (Fig. 2b).

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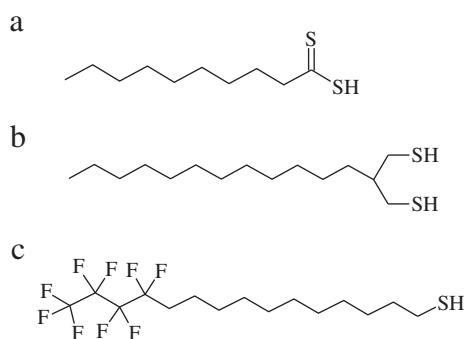
Fig. 1. Molecular structure of (a) *n*-decanedithiocarboxylic RS$_2$H (b) 2-dodecylpropane-1,3-dithiol R(SH)$_2$ (c) 11-perfluorobutyl-1-thiol-undecane R$_f$SH.

2. Experimental details

2.1. Materials

The substrates were prepared from pure polycrystalline copper (Goodfellow, 99.99 + %, CU000749). NaOH and HClO$_4$ were purchased from Acros Organic and are used without further purification. Absolute ethanol (Norma pur, Analytical reagent) is also used as received. The synthesis of the 2-dodecylpropane-1,3-dithiol (R(SH)$_2$), 11-perfluorobutyl-1-thiol-undecane (R$_f$SH) and *n*-decanedithiocarboxylic (RS$_2$H) are described in previous papers [8,11–13].

2.2. Substrate and monolayer preparation

The substrates were rectangular-shaped (15 mm × 10 mm) 1 mm thick coupons cut from commercially available polycrystalline copper foils. The samples are mechanically polished on a Buehler-Phoenix 4000 instrument using a silicon carbide paper (P1200) followed by three diamond pastes of different granulometry (9, 3 and 1 μm). At the end of the polishing steps, all coupons were treated with UV-ozone for 15 min (Jelight 42–220), immersed for 15 min in an ethanolic sonication bath, copiously rinsed with absolute ethanol and blown dried in a nitrogen stream. They were then electrochemically reduced (−820 mV/SCE) for 10 min in an aqueous solution of HClO$_4$ (0.5 M).

At the end of their preparation, copper coupons were immersed for 2 h in 10^{-2} M organothiols (RS$_2$H or R$_f$SH) ethanolic solutions to allow surface modification. The protocol used has been previously reported for the modification of electrochemically reduced copper surfaces with alkanethiols [14]. After reaction, all modified substrates were copiously rinsed with ethanol, then immersed for 2 h or 2 days in another organothiol (R$_f$SH or R(SH)$_2$ respectively) 10^{-2} M ethanolic solution. After this period, the samples were immersed for 15 min in an ethanolic sonication bath to remove physisorbed molecules and dried under a nitrogen flow.

2.3. SAMs characterizations

SAMs were characterized by X-ray photoelectron spectroscopy (XPS), Polarization Modulation Infrared Reflection Adsorption Spectroscopy (PM-IRRAS), contact angle goniometry and cyclic voltammetry (CV).

2.3.1. X-ray photoelectron spectroscopy (XPS)

XPS is used to reveal the type of surface chemistry occurring between the organothiol derivatives and the copper surface. Spectra are collected on a Surface Science SSX-100 spectrometer. The photoelectrons are excited using AlK$_\alpha$ radiation as the excitation source (1486.6 eV), collected at 35° from the surface normal and detected with a hemispherical analyzer. The spot size of the XPS source on the sample is of the order of 600 μm, and the analyzer is operated with a pass energy of 20 eV. During data acquisition the pressure is kept below (1.33 × 10^{-7} Pa), and the binding energies of the peaks obtained are referenced with respect to the binding energy of the C1*s* line, set at 285.0 eV. The spectrum was fitted using an 80/20 linear combination of Gaussian and Lorentzian profiles. The S^{RfSH}/Cu ratio is calculated by normalising the F/Cu ratio in function of the molecule structure (S^{RfSH}/Cu = F/9Cu).
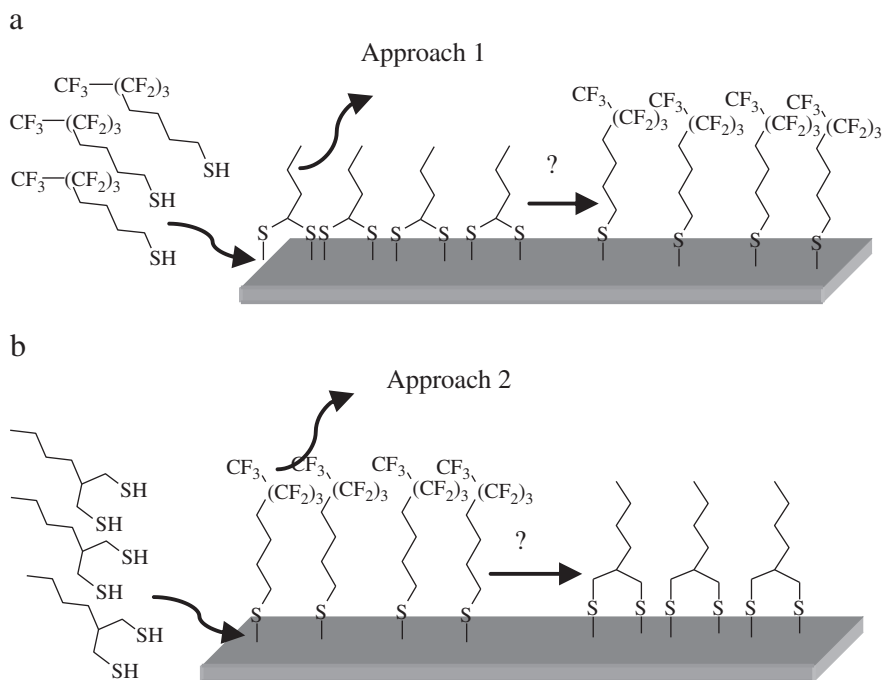
Fig. 2. Scheme of self-exchange reaction by the first (a) and by the second approach (b).