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Electrochemical stability of self-assembled monolayers of biphenyl based thiols studied by cyclic voltammetry and second harmonic generation

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Abstract

The reductive desorption of self-assembled monolayers (SAMs) of ω-(4′-methyl-biphenyl-4-yl)-alkanethiols (CH_3–C_6H_4–C_6H_4–$(CH_2)_n$–SH, BPn) on Au(111) on mica was studied in 0.5 M KOH solution as a function of the length of the aliphatic spacer chain ($n = 1$–6 and 12) and for two different preparations temperatures (295 K and 343 K). Second harmonic generation (SHG) was applied in situ parallel to cyclic voltammetry (CV). Odd–even differences in the structure of the BPn monolayers are clearly reflected in the electrochemical stability, as well as by the charge and shape of the desorption peak. For $n = 1$–5 a single desorption peak is detected whereas multiple peaks occur for BP6 similar to hexadecane thiol which was also studied for comparison. An increased preparation temperature affects the shape and width of the desorption peak but not the position. BP1 exhibits a temperature dependence different from the other homologues. The relationship between coverage monitored by SHG and desorption charge determined from the CVs is found to be linear and surprisingly independent from the details of the SAMs. The combined SHG and CV experiments suggest that capacitive and faradaic current are always closely coupled even for BP6 and hexadecane thiol which exhibit multiple desorption peaks.
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1. Introduction

Control of charge transfer [1,2], template directed electrometallization [3–5], or sensors [6,7] are a few examples where self-assembled monolayers of

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thiols are applied as modifiers to tailor electro-chemical properties of electrodes. An additional aspect which makes electrochemistry and thiol SAMs an attractive combination is that thiol SAMs can be manipulated via the electrochemical potential as the selective desorption of one thiol species from a mixed monolayer [8], the electro-chemical shrinking of SAMs [9], or the influence of the potential on the film formation kinetics [10] demonstrate.

While detailed electrochemical studies of thiol SAMs have overwhelmingly focussed on aliphatic thiols [1,11–20] aromatic thiol SAMs have been studied far less [21–29]. This is surprising as aro-matic SAMs offer some advantages with respect to SAM design. A rigid aromatic system might offer a better control of the structure and, thus, of defects in SAMs, an aspect of particular impor-tance for electrochemical applications. Together with the significantly higher conductivity of aro-matic compared to aliphatic systems [2] aromatic thiol SAMs promise to get around the dichotomy of increasing structural perfection with increasing chain length but at the same time large decrease in conductivity.

The present paper focuses on a particular class of biphenyl based thiol SAMs (ω-(4′-methyl-biphenyl-4-yl)-alkanethiols (CH_3–C_6H_4–C_6H_4–$(CH_2)_n$–SH, $n = 1$–6 and 12, BPn)) which are characterized by an aliphatic spacer unit bet-ween the aromatic moiety and the sulfur head group. Spectroscopic [30] and scanning tunneling microscope studies [31,32] have revealed that the structure of the BPn SAMs shows a pro-nounced odd–even alternation, i.e., the molecular orientation and, thus, packing density depends on the number of methylene units. On Au(1 1 1) substrates a denser molecular packing was found for $n = $ odd compared to $n = $ even which was explained by an sp^3 type bonding geometry of the sulfur. While both a favourable bonding geometry and an optimized molecular packing can be realized for $n = $ odd, a conflict results for even numbered spacer chains. As discussed in detail previously [30–32], the film structure for $n = $ even is determined by a balance of competing forces and interactions, thus, producing SAMs which are energetically less favourable compared

to $n = $ odd. This is reflected by a distinct odd–even alternation in stability against exchange by other thiols [28] and electrochemical stability [29].

The work presented here extends a previous study on the reductive desorption of BPn SAMs in several ways. Firstly, SAMs prepared differently and, thus, differing in their structural perfection are compared. Secondly, epitaxial (1 1 1) gold on mica was used rather than gold on silicon which has the advantage that the structure of the BPn SAMs can be characterized at the molecular level by scanning tunneling microscopy (STM) [31,32] and, thus, allows correlation of the elec-trochemical behaviour with the structure of the SAMs. Thirdly, second harmonic generation (SHG) was applied to monitor thiol desorption/adsorption in situ and in parallel to cyclic vol-tammetry. Since SHG monitors the thiol cover-age via the thiol–substrate bond [33] faradaic currents are reflected by changes of the SHG sig-nal, in contrast to the measured current which comprises both faradaic and capacitive currents. Another advantage of SHG might be stressed at this point. In contrast to electrochemical quartz microbalance (EQCM) as another coverage sensi-tive techniques [17,34,35], it can be applied to well defined Au(1 1 1) surfaces. This allows direct corre-lation with the SAM structure as analysed by STM.

2. Experimental

2.1. Sample preparation

Substrates of mica with an epitaxial (1 1 1) gold layer 300 nm thick (Au/mica) and evaporated gold on silicon (Au/Si) with titanium adhesion layer were purchased from Georg Albert PVD, Heidel-berg, Germany. The synthesis of the biphenyl thiol molecules has been described elsewhere [30,36]. Hexadecanethiol was purchased from Aldrich and used as received. Samples were prepared by immersing a flame annealed Au/mica substrate into a 1 mM thiol solution in ethanol (BDH, Ana-laR) and storing overnight in a sealed jar at 295 K or at 343 K.