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Investigation of carboxylic-functionalized and *n*-alkanethiol self-assembled monolayers on gold and their application as pH-sensitive probes using scanning electrochemical microscopy

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Abstract

We investigated the insulating properties of *n*-alkanethiol self-assembled monolayers (SAMs) of varying chain lengths [$CH_3(CH_2)_nSH$; $n = 7, 9, 11, 15$] on polycrystalline gold electrodes using scanning electrochemical microscopy (SECM) and cyclic voltammetry. On the basis of SECM approach curves we examined the local ET through monolayers with increasing chain length in different redox mediators. We were able to distinguish the monolayers because of their different insulating properties and in addition, the status of SAM formation after immersion times of 2 h and 24 h, respectively, could be observed. Cyclic voltammetric measurements confirmed the SECM results and were in good agreement with other experimental data in the literature. High-resolution SECM images of hexadecanethiol SAM micropatterns down to 4 μm in diameter formed by microcontact printing (μCP) were obtained in the feedback mode. Furthermore, we studied the ET and the pH-dependent behavior of mercaptoundecanoic acid monolayers on gold at varying pH and in different redox mediator solutions to test their application as pH-sensors. An additional influence on the ET could be established based on Coulomb/ionic interactions between the charged monolayer and the redox mediator at changing pH. Therefore, we present a new approach for designing pH-sensitive SECM probes using 11-mercaptoundecanoic acid-coated 10 μm-diameter gold ultramicroelectrodes (HOOC–C_{11}SH/Au UMEs) in aqueous solutions containing hexacyanoferrate. Voltammetric measurements at HOOC–C_{11}SH/Au UMEs at different pH values enabled us to estimate the degree of dissociation of the carboxylic-terminated monolayers.

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1. Introduction

Self-assembled monolayers (SAMs) of both aliphatic and aromatic thiols on gold or silver electrodes have been intensively studied [1–3] in the last two decades because they provide an elegant approach for tailoring biological, physical and chemical properties of a solid electrode surface. This simple way of obtaining well-defined and organized surfaces covered with ultrathin films of a few nanometer thickness by dipping a substrate in a diluted solution containing thiols has many scientific and technological applications [4].

One important scientific application is the study of the long-range heterogeneous electron transfer (ET) through SAMs used as a model system of varying chain length, dielectric properties and molecular ordering [5,6]. Many other applications of SAMs take advantage of their highly organized conditions and electrically insulating (alkanethiols) or electrical properties (arenethiols) for use in molecular electronic devices such as dielectric for capacitors [7,8], self-assembled monolayer field-effect transistors (SAMFET) [9] or for developing single-molecule devices [10].

Another wide field of technical applications of SAMs, particularly in nanotechnology, is the development of new electroanalytical devices, for example selective filters for chemical sensors [11] and new biosensors [12] and the use as lithographic resists [13,14]. In particular, patterns of mixed SAMs with controlled different terminal functionality or chain length are very well suited to immobilizing proteins [15], antibodies [16], enzymes and other biological molecules [12].

Numerous studies using different analytical techniques such as ellipsometry and contact angle measurements [17], reflection/absorption infrared spectroscopy (RAIRS) [18], cyclic voltammetry [5], impedance spectroscopy (EIS) [6,19], second harmonic generation [20] and scanning probe microscopies [21–23] as well as molecular simulation studies were carried out to elucidate the kinetics and mechanism of self-assembly and SAM formation [24]. The qualitative conclusion that SAMs of alkanethiols are densely packed films was confirmed. However, the results for more quantitative aspects such as the number of adsorption steps (two or three), the time scales and the process of SAM formation were more ambiguous [25].

Since its introduction by Bard et al. in 1989 the scanning electrochemical microscope (SECM) has overcome a tremendous development regarding its spatial resolution, combinations with other microscopic/spectroscopic techniques and application areas [26]. The SECM demonstrates a versatile electrochemical tool and provides applications both for surface analysis and structuring in the micro- and nanometer range.

First investigations on a long-chain alkanethiol were carried out by Forouzan et al. [27] with different electrochemical techniques such as SECM, chronoamperometry and cyclic voltammetry. They observed the adsorption kinetics of hexadecanethiol onto a gold surface and its formation in a time range from 1 s to 1 h and found a two-step mechanism similar to results received with other measurement techniques and described in the literature [17,18,20]. In the first rapid step the gold surface is covered with a monolayer more than 90% within a few minutes. In contrast, the second step requires several hours for the ordering process of the alkyl chains and terminal end groups and thus to form highly organized SAMs.

Other research groups for example Wittstock et al. [28], Yasukawa et al. [29] and Turyan et al. [30] used SAM micropatterns of *n*- or functionalized alkanethiol mostly generated by the SECM to attach enzymes and other biological molecules. Besides they investigated the activity of the attached molecules by the SECM in the generation-collection or feedback mode.

Recently the generation of periodic enzyme patterns based on microstructured SAMs formed by microcontact printing (μCP) and related techniques was reported by Wilhelm and Wittstock [31]. The obtained micropatterns were used for