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On the decisive role of the sulfur-based anchoring group in the electro-assisted formation of self-assembled monolayers on gold

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Abstract

A reproducible electro-assisted method is proposed to follow the influence of different sulfur-based anchoring groups on the adsorption kinetics and thermodynamics of SAM formation on gold electrodes. This has been made possible thanks to the preparation of several molecules containing various anchoring groups (thiol, thioester, acyclic and cyclic disulfides, thiosulfonate) while preserving the same spacer redox head group. In this paper we focus on the question of a substantial difference between SAMs derived from either alkylthiols or disulfides (symmetric or linear) using cyclic voltammetry. The comparison of equilibrium surface coverage, affinity constant toward gold surface and stability suggest a decisive role of the nature of the anchoring group in the formation of the monolayers. Moreover, a significant difference of the desorption behavior of SAMs on gold, pre-formed from either thiol or disulfide, has clearly been demonstrated.

Keywords

Redox-active monolayers, anchoring groups, modified electrodes, electrodeposition, chemisorption

1. Introduction

Chemisorption of organo-sulfur compounds on gold substrates for the preparation of self-assembled monolayers (SAMs) has been the subject of intense investigation [1-3]. Simple immersion of a gold substrate in a solution containing the sulfur derivatives still remains the most frequently used method for the preparation of SAMs [4, 5]. On the basis of this simple method, several studies comparing SAMs made either from alkylthiols or the corresponding symmetric

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