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Alkanethiol self-assembling on gold: Influence of high frequency ultrasound on adsorption kinetics and electrochemical blocking

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ABSTRACT

Self-assembling of undecanethiol (C11SH) on polycrystalline gold was investigated under two different conditions. The kinetics of C11SH grafting was studied without and under high frequency ultrasound irradiation. Two electrochemical experiments were extensively carried out in order to determine electrochemical surface blocking of adsorbed layers as a function of grafting time: chronoamperometry in-situ monitoring and cyclic voltammetry. Interestingly, the grafting process is highly accelerated under sonication, and C11SH modified substrates of good quality are obtained after 3 h' immersion under ultrasound irradiation. This would allow elaboration of high-quality alkanethiol modified samples within much shorter times. Water contact angle measurements and X-ray Photoelectron Spectroscopy (XPS) confirmed the presence of adsorbed undecanethiol on the gold surface. A very close link between electrochemical blocking, surface hydrophobicity and species chemical grafting was established.

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1. Introduction

Chemical grafting of self-assembled monolayers (SAMs) by adsorption of organic molecules on metal substrates has received considerable interest over the last three decades. Simple immersion of the substrate in a solution containing active molecules leads to spontaneous formation of covalent bonds between molecules and metals. The triviality of use and the possibility of fabricating interfaces with a well-defined composition, structure and thickness enable numerous applications in different areas, barriers against corrosion [1,2], adhesion [3,4], and lubrication [5]. To permit such spontaneous and strong grafting molecules, various types of SAMs have been developed with different reactive headgroups depending of metal affinity (e.g., phosphonic [6,7], carboxylic [8,9], or sulfonic acids [10] which can be grafted on titanium [7,11], copper [12] or stainless steel [8,9,13]. In the literature, the system alkanethiol on gold is the most commonly studied. The grafting process on gold has been described as an exothermically homolytic cleavage of the S–H bond [14,15] with formation of H₂ [16]. Thanks to inertness of gold, recent years have witnessed the development of [17,18] biosensor thiolate SAM-DNA. Forma-

tion of compact and well-organized monolayers requires long-term modification (i.e. 16–24 h), which makes their industrial application impossible. To overcome this problem, ultrasound can be used as a grafting kinetics accelerator.

Low frequency ultrasound is frequently used during the SAM grafting process. It can be used for metal cleaning [19] before substrate immersion and to clean the surface after SAM formation to remove physisorbed species or other impurities that may have formed during the immersion process. Few studies have been conducted on the use of ultrasound during SAM grafting [20–22]. An increase in the rate and saturated amount of self-assembled adsorption of aromatic thiolate species (4-pyridinethiolate and phenylthiolate) on polycrystalline gold under low frequency ultrasound irradiation (20 kHz) has been reported by Atobe et al. [21]. Dai et al. showed that low frequency ultrasonic irradiation (40 kHz) formed a very low ionic permeability and almost defect-free structure of dodecanethiol SAMs on polycrystalline gold in a short period of time (15 min) [20]. Even if it is well known that cavitation and mechanical activities are far less aggressive at high frequencies [23–27], no study has ever been reported on formation of SAMs on gold under high frequency ultrasound.

In this paper, grafting of undecanethiol on gold under high frequency ultrasound irradiation was investigated. In the first part, the formation of a well ordered and compact monolayer after 19 h' modification is verified. High frequency ultrasound is then

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used during grafting, as a tool to decrease modification time. To explore this grafting mechanism, the influence of each effect of ultrasound has been investigated. Characterization of undecanthiol SAM by water contact angles, X-ray photoelectron spectroscopy (XPS) and polarization modulation infrared reflection spectroscopy (PM-IRRAS) was carried out. Cyclic voltammetry and in-situ chronoamperometry were also used to investigate electron transfers through grafted layers in order to determine covering rates and study adsorption kinetics.

2. Experimental

2.1. Chemicals

De-ionized water (Milli-Q, resistivity 18 M Ω -cm) was distilled twice before use. Sulfuric acid (VWR, 98%, 7664-93-9), potassium hexacyanoferrate (II) trihydrate (ALFA AESAR, 98+%, 14456-95-1), sodium sulfate (SIGMA-ALDRICH, 99+%, 7757-82-6), ferrocene (ALFA AESAR, 99%, 102-54-5), sodium perchlorate anhydrous (ALFA AESAR, 95%, 7791-03-9), absolute ethanol (ACROS, pure, 64-17-5), 1-undecanthiol, (SIGMA-ALDRICH, 98%, 5332-52-5) were used as received.

2.1.1. SAM preparation

A polycrystalline gold electrode (0.24 cm²) was mechanically polished (grain size 10, 1 and 0.25 μ m) and rinsed twice with de-ionized water. The substrate was then cycled in 0.5 M H₂SO₄ solution from 0 to 1.7 V (vs Ag/AgCl) at 0.1 V s⁻¹ for 50 cycles. The real surface area was calculated with the method reported by Dai et al. [20]. The substrate was finally immersed in modification solution (1 mM undecanthiol in absolute ethanol).

2.2. Sonochemical cell

High frequency ultrasound irradiation was carried out using commercial equipment (Meinhardt Multifrequency system 575/856/1135 kHz) at a frequency of 575 kHz. Solution volume for experiments conducted under ultrasound was 8 mL in a beaker immersed in 120 mL of water (Fig. 1). Calorimetry measurements showed a transmitted power of 19 W i.e. 2375 W/dm⁻³ in the reactor inner cell.

2.3. Characterization methods

Electrochemical experiments were carried out using an AUTO-LAB PGSTAT30 potentiostat driven by Nova.10 software. A classical three-electrode setup was used with Ag/AgCl/KCl 3 M as the reference electrode (210 mV/SHE), platinum wire as the counter-electrode and modified polycrystalline gold electrode as the working electrode (0.24 cm²). Cyclic voltammetry in water was carried

out in 10 mM Potassium hexacyanoferrate (II) with 0.2 M in sodium sulfate (background salt) in pure water. Ethanol's electrolyte was made up of 1 mM in ferrocene with 0.1 M in lithium perchlorate in absolute ethanol. The process of in-situ following of steady state current during grafting is described by Kye and al. [28,29]. All cyclic voltamograms were performed at 100 mV/s.

XPS was used to measure the elemental composition of elements. Spectra were acquired using monochromatized Al K α radiation (1486.6 eV). The X-ray radiation source operated in a vacuum of 3 $\cdot$ 10⁻⁹ mbar. Binding energies of core levels were calibrated as a function of the C1s binding energy set at 284.8 eV, a characteristic energy of alkyl moieties. Deconvolutions were performed using mixed Gaussian-Lorentzian curves (80% of Gaussian character).

Polarization Modulation Infrared Reflection Absorption Spectroscopy data were collected from a Bruker VERTEX 70 PMA 50 equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a photoelastic modulator PMA: ZnSe. The infrared light, reaching the sample surface at an angle of 82°, was modulated between s- and p-polarizations at a frequency of 50 kHz. Signals generated from each polarization (R_s and R_p) were detected simultaneously by a lock-in amplifier and used to calculate the differential surface reflectivity $\Delta R/R = (R_p - R_s)/(R_p + R_s)$. The spectra were taken by collecting 250 scans with a spectral resolution of 2 cm⁻¹.

3. Results

3.1. Characterization of the C11SH monolayer on polycrystalline gold

To graft well-organized monolayers on gold, a long-term modification is studied. To evaluate coverage and packing in monolayer structures, a PM-IRRAS spectroscopic measurement was undertaken. Fig. 2 shows IR spectra of the C–H stretching region for C11SH grafting over 19 h. The peak positions of symmetric and asymmetric vibration frequencies of CH₂ and CH₃ groups give information on analyzed layer organization. As shown in Fig. 2, bands appearing at 2849 and 2916 cm⁻¹ correspond to CH₂ asymmetric and symmetric vibration, respectively (ν_a CH₂ and ν_s CH₂), and bands at 2871 and 2959 cm⁻¹ are assigned to CH₃ symmetric and asymmetric vibration frequencies (ν_s CH₃ and ν_a CH₃), which is in agreement with a well-organized adsorbed alkyl chain [30–34].

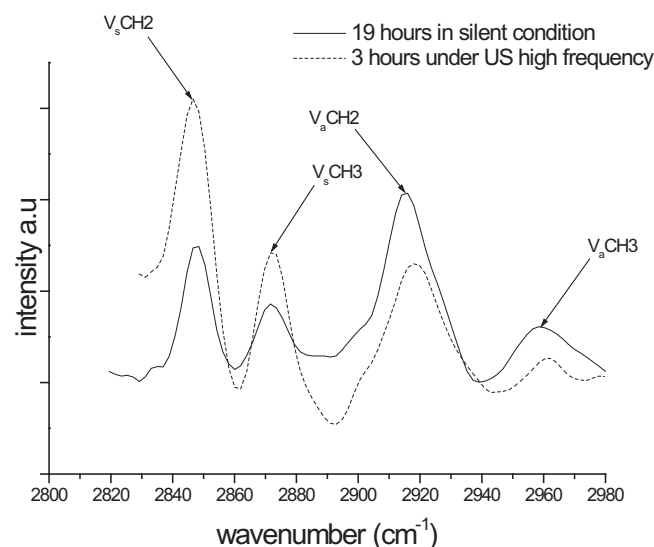


Fig. 2. 2800–3000 cm⁻¹ region from PM-IRRAS spectrum C11SH gold modified for 19 h in silent condition and 3 h under high frequency ultrasound irradiation.

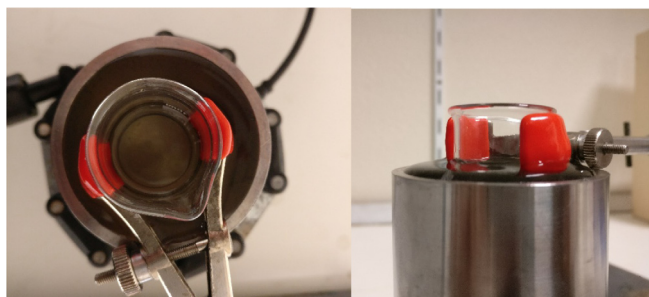


Fig. 1. Experimental set-up with an inner embedded into the multifrequency sonoreactor.

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