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SELF-ASSEMBLED MONOLAYERS OF FERROCENYLTHIOLS ON GOLD. AN ELECTROCHEMICAL AND OPTICAL CHARACTERISATION

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Abstract

Short chain ferrocenyalkylthiols, $(C_5H_5)Fe(C_5H_4)CO(CH_2)_nSH$ (n= 3, 5 and 7), were self-assembled on gold (111). The influence of the chain length and adsorption time on stability, surface coverage and order of the monolayers were assessed electrochemically and by the use of optical ellipsometry. The redox behaviour and structure of the SAMs were strongly dependent on the chain length. Long adsorption times were required to obtain ordered monolayers with high surface coverage. Ellipsometry indicated that the thicknesses of the layers were dependent on the surface concentration of the ferrocene derivatives. The thickness of the monolayer with the longer alkyl chain was estimated to be 2.9 nm with a complex refractive index $\hat{n}$= 1.472-0.076i. Imaging Ellipsometry allowed the visualisation of the lateral thickness distribution of a monolayer deposited on gold.

Keywords: Self-Assembled Monolayers, Au, Ferrocenyalkylthiols, Voltammetry, Ellipsometry.

Introduction

Self-Assembled Monolayers (SAMs) are prepared by the spontaneous adsorption of organic molecules onto a substrate from homogeneous solution. Versatility, ease of preparation, stability and organisation contributed to the great popularity of self-assembly in the last two decades [1].
Alkanethiols used in the formation of SAMs generally contain three important parts [2]: (i) the surface active head group, which binds strongly to the substrate, (ii) the alkyl chain, responsible for the stability and order of the layer due to van der Waals chain interaction, and (iii) functionality. The latter plays a paramount role in controlling the redox behaviour of the monolayer and can be tailor-made to create the desired interfacial microenvironment. Self-assembly of thiol derivatives on gold is believed to occur in two stages [1-3]. Physisorption of the thiol, which after a short time on the surface, forms a strong covalent bond with the substrate via the formation of a thiolate,

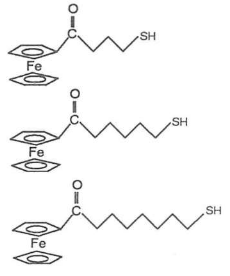
accompanied by the loss of a proton. This is followed by slow changes in the monolayer properties, suggesting an approach to a more highly ordered state.

Since their discovery, SAMs exhibit interesting properties pointing to a great promise in several areas, such as chemical sensors, electronic devices, electrocatalysis, and lubrication. These modified surfaces are also ideal models for the study of interfacial reactivity and fundamental charge transfer phenomena [2-4].

In this work, short chain ferrocenylalkylthiols with a carbonyl functionality, $(C_5H_5)Fe(C_5H_4)CO(CH_2)_nSH$ (n = 3, 5 and 7), were assembled on Au (111) surfaces. Effect of the adsorption time and alkyl chain length, on the structure and order of the monolayers, were studied by cyclic voltammetry and ellipsometry. There are few ellipsometric studies on ferrocene derivative monolayers [5, 6], and the majority of such studies were performed on long chain compounds (n > 10). In this paper we show that it is possible to deduce layer thicknesses for short chain monolayers (n = 5 and 7). The data indicate a strong dependence on the order and packing of the SAMs.

Experimental

Chemicals. The ferrocene derivatives (Figure 1) were synthesised using a previously described method [7]. Perchloric acid (Aristar, BDH) and absolute ethanol were used as received. Ultra pure water was obtained from an Elgaster UHQ II purification system (nominal resistivity 18MΩ cm at 25°C).



$FcCO(CH_2)_3SH$ **(FcC4)**

$FcCO(CH_2)_5SH$ **(FcC6)**

$FcCO(CH_2)_7SH$ **(FcC8)**

Fig 1. Structures of the ferrocenylalkylthiols used as electrode modifiers.
Fc corresponds to ferrocene, $(C_5H_5)Fe(C_5H_4)$.

Au Substrates. The gold slides used were made by the evaporation of 200 nm Au on glass slides (Tempax AF 45) which have been coated with a Cr layer (2-4 nm). Prior to use, the gold slides were heated in the cold part of a bunsen flame and quenched in ultra pure water. This treatment produces a flat gold surface with strong Au (111) characteristics [8]

Monolayer Preparation. After appropriate surface treatment, electrodes were rinsed with ethanol and immersed in ethanolic solutions containing the compounds of interest at a concentration of 1-2 mM. The immersion time varied between 5 minutes and three days. After self-assembly, the electrodes were rinsed prior to use with copious amounts of fresh absolute ethanol and ultra pure water.

Electrochemistry. Cyclic voltammetry was performed using a DT 2101 Hi-Tek potentiostat, a PP RI Hi-Tek Waveform Generator, and a Yokohama 3023 X-Y recorder. The experiments were carried out in a one compartment Teflon cell, with an Au wire spiral counter electrode and a saturated calomel reference electrode (SCE). The Au slide was clamped against an o-ring, which defined the geometric area of the working electrode (0.64 cm^2). The electrolyte solution ($HClO_4$ 0.1 M) was degassed for 15 minutes before the electrochemical measurements were initiated.

Glassware and electrochemical cell were bathed in freshly prepared 1:1 mixture of concentrated sulphuric acid and nitric acid (Fisher Chemicals), thoroughly rinsed with ultra pure water and transferred to a steam bath for 20 min.

Ellipsometry. Ex-situ ellipsometric results were obtained using a rotating analyser type SENTECH Ellipsometer (SENTECH Instruments GmbH, Berlin, Germany) fitted with a He-Ne laser (632.8 nm). The measurements were carried out at an angle of incidence of 70°. The gold electrodes were dried with N_2 and measured before and after immersion in the coating solution. Imaging ellipsometry [9] was performed in a conventional null ellipsometer where an expanded light beam is used instead of the conventional narrow beam. The source was a Xenon lamp with a 632.8 nm interference filter and a collimating system to ensure a uniform intensity distribution over the beam area. The photomultiplier or photodiode detector was replaced by a CCD video camera (752 × 582 pixels) and suitable optics allowing more than 4×10^5 surface areas on a 15×25 mm^2 sample surface to be measured at the same time. The video signal is digitised, captured and stored in a greyscale format.

Results and Discussion

Electrochemical Studies.

As expected, the redox behaviour exhibited by the monolayers was wholly dominated by the ferrocene/ferricinium couple. Effect of chain length and deposition time on the stability, packing and order of the monolayers were analysed by evaluating the following parameters: 1) surface coverage, Γ_{Fc}, obtained by the integration of the area under the redox peaks of ferrocene; 2) half wave potentials ($E_{1/2}$); 3) full width at half maximum (ΔE_{FWHM}) and 4) redox peak separation ((ΔE_p).

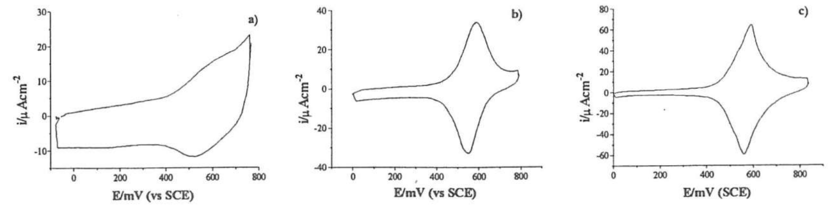


Figure 2. Representative cyclic voltammograms of SAMs prepared from 1-2 mM solutions of compounds FcC4 (a), FcC6 (b) and FcC8 (c), after 24 hours immersion. The voltammograms were recorded at 100 mV/s.

Figure 2 shows the typical cyclic voltammograms obtained for SAMs of compounds FcC4, FcC6 and FcC8, prepared under the same experimental conditions. Only a slight decrease (5-10%) of the surface coverage, with no changes in the shape or position of the voltammograms, was detected after repetitive potential cycles. This behaviour illustrates the inherent stability of these monolayers. As is characteristic for an adsorbed redox centre, the anodic peak current for the three monolayers studied was found to increase linearly with the sweep rate [10]. However, there was a significant difference between the shape of the voltammetric peaks for a monolayer of compound FcC4 when compared to compounds FcC6 and FcC8. The observed redox behaviour is intimately related to the structure and organisation of the monolayer. The electrochemical data obtained from the voltammetric curves are summarised in Table 1.

Results confirmed that longer alkyl chains adsorbed preferentially and in a more ordered structure than the equivalent shorter chain compounds [1]. The amount of molecules adsorbed on the surface for the same deposition time and solution concentration increases with the chain length. The coverage of the monolayer formed by compound FcC8 is 4.7×10^{-10} mol cm^{-2}, if calculated using a roughness factor of 1.2 determined by the iodine chemisorption method [11]. This value is very close to the maximum theoretical value of 4.5×10^{-10} mol cm^{-2} estimated by Chidsey et al. [5] for a ferrocene derivative monolayer, based on a close packed layer of 6.6 Å diameter spheres.

The half wave potential values for the ferrocene redox process of compounds FcC4, FcC6 and FcC8 were positively shifted from the values observed for ferrocene monolayers without the carbonyl group (ca. 300 mV vs. SCE) [1]. This is expected due to the presence of the electron withdrawing carbonyl group in the compounds used here. Although the differences between experimental $E_{1/2}$ values for the three compounds are very small, they seem to indicate that short chain monolayers are more easily oxidised than the correspondent longer ones. On the other hand, the voltammetric peak separation decreases significantly with the number of CH_2 groups. The value for compound FcC8 was very close to the ideal 0 mV, for adsorbed species showing a reversible electron transfer process. The small ΔE_p values obtained for monolayers of FcC6 and FcC8 indicate that the ferrocene is surface-confined and that the rate of electron transfer is relatively fast.

Table 1. Effect of chain length on the electrochemistry of the investigated SAMs.

Compound	Γ_{Fc} (molcm^{-2})	E (mV)	ΔE_{FWHM} (mV)	ΔE_p (mV)
FcC4	8.6×10^{-11}	565	---[a]	80
FcC6	3.2×10^{-10}	570	115	40
FcC8	5.7×10^{-10}	580	100	5

[a] Broad and ill-defined oxidation peak.

The value of full width at half maximum of the oxidation peak provides a qualitative measure of the relative interaction between redox centres attached to the monolayer. For an ideal case, where the interactions between the electroactive adsorbates are minimal, a value of 90.3/n mV at 24°C can be expected [10]. The redox peak for oxidation of the ferrocene groups belonging to the monolayer of compound FcC8 was sharper than the peaks for the other monolayers and the value observed for ΔE_{FWHM} was very close to the ideal value. This reinforces the presence of a very ordered and packed layer of relatively short alkyl chain, with minimal lateral interactions between the ferrocene moieties. On the other hand, the shape of the voltammogram of FcC4 can be explained in terms of different adsorption sites [1,10]. It has been suggested that the relatively hydrophobic ferrocenes occupy sites both inside and on the surface of the SAM, a conformation that would cause multiple formal potentials to exist in the ensemble of redox centres.

Electrochemical parameters obtained for different adsorption times of compound FcC6 are summarised in table 2. The results clearly show that at a millimolar concentration, longer deposition time leads to higher surface coverage. After three days the amount of compound deposited on the gold was identical to the observed after 24 hours. Both the half wave potential and peak separations do not change significantly with the deposition time. This fact seems to indicate that the mechanism of electron transfer is somewhat independent of the amount of compound at the electrode surface for a given chain length. The values of ΔE_{FWHM} were larger than the theoretical value, which are possibly due to the existence of attached ferrocene tail molecules with different microenvironments within the monolayer. However, longer deposition times and higher surface coverage produced sharper oxidation peaks. This behaviour indicates the presence of a more organised layer with increasing adsorption time.

Table 2. Electrochemical data obtained for monolayer of FcC6 at different times of adsorption.

Adsorption time	Γ_{Fc} (molcm^{-2})	$E_{1/2}$ (mV)	ΔE_{FWHM} (mV)	ΔE_p (mV)
5 min	1.4×10^{-10}	580	---[a]	30
30 min	2.3×10^{-10}	570	180	25
1 h	2.3×10^{-10}	570	150	20
4 h	2.5×10^{-10}	570	120	25
24 h	3.2×10^{-10}	570	115	40

[a] Broad and ill-defined oxidation peak

Ellipsometric Studies

Ex situ ellipsometry was applied as a convenient and powerful mean of evaluating the average monolayer thickness and for following the adsorption process.

The thickness of the monolayers was estimated from the change in the ellipsometric parameters between the bare gold and the monolayer covered surfaces. Before depositing the layer the substrates were measured and their complex refractive indices ($\hat{n} = n - i\,k$, where n is the refractive index and k the extinction coefficient) calculated from the optical parameters Ψ and Δ, using Fresnel's and Drude's [12] equations. The values of n, k and thickness of the monolayers deposited on gold could be then estimated from the values of $\delta\Psi$ and $\delta\Delta$, using a computer program based on a three-phase model. Since the determination of three unknowns from two measurable parameters is mathematically impossible, one of the unknowns had to be reasonably introduced to deduce the other two. Since the layers were not transparent (k small but different from zero), the calculations were not straightforward, and the refractive index and layer thickness were deduced in two steps. First assuming n as 1.45, which is the value estimated for the index of refraction of alkanethiols [1,5], k and the thickness were calculated. The other step, consisted of predicting the thicknesses for compounds, also based on previous studies performed for alkylthiols (20 Å for $CH_3(CH_2)_{10}SH$; 1.07 Å per CH_2 and 7 Å for ferrocene group [6]), comparing them with the previous values, and introducing a series of thicknesses close to the average to evaluate n and k variations. Ellipsometric data obtained for the monolayers of ferrocenylalkylthiols are shown in table 3, and are a final result of the two steps mentioned above. The predicted thicknesses for the monolayers formed by compounds FcC4, FcC6 and FcC8 are 2.1, 2.3 and 2.5 nm respectively. After 24 hours immersion, the electrochemical data indicates that the monolayers are packed and ordered. The experimental thickness values obtained for monolayers of FcC6 and FcC8, were slightly larger than the predicted ones, but still in good agreement with them. However, immersion for 4 hours resulted in thinner films, which is indicative of the fact that the adsorption process occurs in two stages. The first step consists of rapid formation of the monolayer followed by slow approach to a more organised stage [1], where the molecules become more perpendicular to the gold surface and the ferrocene centres maintain a well-defined distance from the surface. Our electrochemical results have shown that further thiol adsorption occurs during the organisation stage.

Reasonable values for complex refractive index and thickness of FcC4 monolayer, could not be obtained after 4 hours immersion. Furthermore, the average thickness deduced for this monolayer after 24 hours immersion, was higher than the values found for the longer chain compounds. This fact is most probably related with the low coverage and loosely packed structure of the monolayer as observed in the voltammetric studies. One possible factor contributing to these observations is the thiol chemisorption as a thiolate, which may produce changes in electron density at the gold surface, shifting its optical constants relative to the bare unmodified substrate [1,6,13]. Such effect could be coverage dependent, which can explain its larger influence in the ellipsometric parameters on SAMs formed from FcC4.

Table 3. Ellipsometric data obtained for the three SAMs under study after 4 and 24 hours of immersion in 1-2 mM solutions of FcC4, FcC6 and FcC8.

Compound	Adsorption Time (hours)	n	k	Thickness (nm)
FcC4	4	---[a]	---[a]	---[a]
	24	1.466	0.141	**3.1**
FcC6	4	1.457	0.004	2.0
	24	1.459	0.045	**2.7**
FcC8	4	1.478	0.095	2.0
	24	1.472	0.076	**2.9**

[a] No reasonable values were obtained

Imaging ellipsometry was performed on a monolayer formed by FcC6 (figure 3). This recent technique provides the visualisation of the thickness distribution of a layer deposited on a substrate. The distribution is measured as a difference in the reflected light intensity between the bare substrate and the layer, with the thickness being proportional to the square root of the intensity. Imaging ellipsometry does not give absolute values of thickness, so an independent measure of the optical parameters in the conventional ellipsometer was performed. The complex refractive index and the layer thickness obtained for the monolayer visualised in figure 3 were respectively 1.455-0.095i and 2.6 nm.

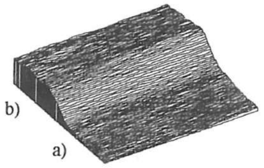


Figure 3. Image (15×20 mm^2) of thickness distribution of a monolayer of FcC6 (a) on Au (111) (b) obtained with imaging ellipsometry.

Conclusions

We have demonstrated that the redox behaviour and structure of short chain monolayers is strongly dependent on the chain length, even when they differ of two methylene groups. Longer alkyl chains produce more oriented and packed monolayers. At millimolar solution concentration long adsorption times (up to 24 hours) were required to obtain more organised SAMs with higher surface coverage. This result, together with ellipsometric thicknesses obtained at different deposition times, confirm that adsorption of thiol molecules on gold occurs in two steps.

We are currently investigating using *in situ* IR spectroscopy and *in situ* ellipsometry, possible structural changes occurring within the monolayers of short chain ferrocenylalkylthiols.

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