



Self-assembled alkanethiol structures on gold: A further insight into the origins of structural rearrangement phenomena

Dimitrios A. Lamprou^a, James R. Smith^a, Thomas G. Nevell^a, Eugen Barbu^a, Corinne Stone^b, Colin R. Willis^b, Richard J. Ewen^c, John Tsibouklis^{a,*}

^a Biomaterials and Drug Delivery Group, School of Pharmacy and Biomedical Sciences, University of Portsmouth, St. Michael's Building, White Swan Road, Portsmouth PO1 2DT, UK

^b Physical Sciences Department, Dstl Porton Down, Salisbury SP4 0JQ, UK

^c Faculty of Applied Sciences, University of the West of England, Coldharbour Lane, Frenchay, Bristol BS16 1QY, UK

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ABSTRACT

Self-assembled structures of alkanethiols that have been deposited on gold from ethanolic solutions are susceptible to both chemical and physical changes: ethanol provides a medium for the formation of S-alkyl hydrogen thiocarbonates and related compounds *via* reaction with dissolved, atmospheric, CO₂. Deposition from ethanolic solutions results in multilayered structures incorporating these compounds, which at room temperature are susceptible to time-dependent structural rearrangement and molecular migration.

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1. Introduction

The formation of self-assembled monolayers (SAMs), particularly those of alkanethiols on gold, provides well-defined, ordered surfaces [1,2]. Under ambient conditions, the physicochemical stability of such structures is determined by the relative strengths of the Au–S bond and the van der Waals forces and Lewis acid/base interactions that operate between neighbouring molecules, with the implication that SAMs structures are susceptible to thermal and environmental ageing [3,4]. It has been reported that some alkanethiol SAMs detach from the gold surface even within a few hours from deposition [5]. As early as 1992, Tarlov and Newman used static secondary ion mass spectrometry (SSIMS) experiments to demonstrate the susceptibility of SAMs to oxidation [6]. The oxidative degradation was later attributed to reaction with atmospheric ozone [7]. Infrared spectroscopic investigations showed progressive lowering of the intensities of the $\nu(\text{C–H})$ bands, which was interpreted as being indicative of the tilting of the alkyl chain away from the surface normal as a result of the progressive oxidation of the sulphur moiety [8]. Other infrared studies, including work involving reflection–absorption IR spectroscopy (RAIRS), have shown that heating under ultra-high vacuum (UHV) induces increasing disorder in SAMs [9,10], with heating above 100 °C resulting in the loss of structural order [11]. X-ray photoelectron spectroscopy (XPS) has revealed a discrepancy between the calcu-

lated and detected values for CO₂H functionalisation in plasma-activated surfaces of 3-mercaptopropionic acid SAMs [12]. Mixed poly(ethylene oxide)-thiol SAMs containing CO₂H and OH groups are reported to be stable for at least 30 days if stored in air or under N₂, but their storage in ethanol has been found to result in partial oxidation at the thiol [13]. XPS studies have shown dodecanethiol SAMs to be stable in water for 24 h [14].

As part of our work on the suitability of self-assembled structures as coatings for gold-coated AFM cantilevers [15], we now employ contact angle goniometry (CAG), atomic force microscopy (AFM), scanning electron microscopy (SEM), and a combination of spectroscopic techniques (FTIR, GC–MS, HPLC–MS, XPS and NMR) to investigate the stability of self-assembled structures of a range of alkanethiols with molecular features which give rise to differences in the strength of interactions involving the Au–S bond and van der Waals and Lewis acid / Lewis base forces.

2. Experimental details

2.1. Surface preparation

Gold-coated glass microscope slides (Au.1000. ALSI, Platypus Technologies, Madison, WI, USA, cut to 1.25 cm × 1.25 cm) and gold-coated AFM cantilevers were cleaned by immersion in Gold Surface Cleaning Solution (thiourea 1%w/v in 10% aqueous sulphuric acid; Sigma–Aldrich, Poole, UK; 1 h), rinsed with filtered water (Millipore, 16.5 MΩ cm), and dried (nitrogen).

* Corresponding author. Tel.: +44 (0) 23 9284 2131; fax: +44 (0) 23 9284 3565.
E-mail address: john.tsibouklis@port.ac.uk (J. Tsibouklis).

2.2. Formation of self-assembled monolayers

Unless otherwise stated, organised molecular layers were deposited from ethanolic solutions (1 mmol dm⁻³; absolute EtOH, AR grade, Fisher, Loughborough, UK) of 1-undecanethiol (98%; referred to here as 'CH₃'), 11-mercapto-1-undecanol (97%; 'OH') and 11-mercaptopundecanoic acid (95%; 'CO₂H') from Sigma–Aldrich, Poole, UK, and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiol (>99%; 'CF₃') from Fluka, Poole, UK. Immediately after cleaning, each gold substrate was immersed in thiol solution (16 h), rinsed (EtOH), dried (nitrogen) and placed in a closed polythene box for storage.

2.3. Contact angle and surface energies

To probe liquid–surface interactions at maximal resolution, contact angles (θ at 20 °C) of small drops ($\times 4$ on each substrate) of water (surface tension $\gamma_l = 73.4$ mN m⁻¹ at 18.8 °C, literature [16] = 73.05 mN m⁻¹ at 18.0 °C; *ca.* 2 μ L), diiodomethane (>99%; $\gamma_l = 48.7$ mN m⁻¹ at 18.8 °C, literature [16] = 50.76 mN m⁻¹ at 20 °C; *ca.* 1 μ L) and 1,2-ethanediol (ethylene glycol, >99%; $\gamma_l = 47.7$ mN m⁻¹ at 18.8 °C, literature [16] = 48.40 mN m⁻¹ at 20 °C; *ca.* 1 μ L) placed on horizontal substrates ($\times 2$) were measured using a goniometer with an enclosed thermostated cell (Kruss G10, Hamburg, Germany). Advancing (θ_A) and receding (θ_R) angles ($\pm 0.1^\circ$; with syringe needle removed to enable curve fitting of drop-shape image) were obtained for both 'left' and 'right' contact angles at 20–30 s after placement of the drop [17]. Surface energies of substrates (γ_s) were calculated from the contact angles and the interfacial energies of the three probe liquids from Eqs. (1) and (2) [18,19] using a Visual Basic program (University of Portsmouth).

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB} = \gamma_s^{LW} + 2(\gamma_s^+ \gamma_s^-)^{1/2} \quad (1a)$$

$$\gamma_l = \gamma_l^{LW} + \gamma_l^{AB} = \gamma_l^{LW} + 2(\gamma_l^+ \gamma_l^-)^{1/2} \quad (1b)$$

$$\gamma_l(1 + \cos \theta) = 2 \left[(\gamma_s^{LW} \gamma_l^{LW})^{1/2} + (\gamma_s^+ \gamma_l^-)^{1/2} + (\gamma_s^- \gamma_l^+)^{1/2} \right] \quad (2)$$

where superscripts denote components of surface energy: Lifshitz–van der Waals *LW*, acid–base *AB*, Lewis acid γ^+ and Lewis base γ^- . (In mJ m⁻², FW: $\gamma_l^{LW} = 21.8$, $\gamma_l^+ = \gamma_l^- = 25.5$; DIM: $\gamma_l^{LW} = 50.8$, $\gamma_l^+ = \gamma_l^- = 0$; EG: $\gamma_l^{LW} = 29$, $\gamma_l^+ = 1.92$, $\gamma_l^- = 47$) [20].

2.4. Atomic force microscopy

AFM experiments were performed using a MultiMode/NanoScope IV Scanning Probe Microscope (Digital Instruments, Santa Barbara, CA, USA; Veeco software Version 6.11r1). Force vs. distance plots were obtained using a single gold-coated silicon nitride probe (NPG-20 'C' V-shaped cantilever; nominal length (l_{nom}) = 115 μ m, width (w_{nom} , measured perpendicular to long axis) = 17 μ m, resonant frequency (ν_{nom}) = 56 kHz, spring constant (k_{nom}) = 0.32 N m⁻¹; Au thickness = 60 nm on a 15 nm Cr adhesion layer (Veeco Instruments SAS, Dourdan, France). The laser alignment was not altered during measurements (deflection sensitivity = 60 $\pm$ 8 nm V⁻¹). The radius *R* of the tip (76 $\pm$ 4 nm) was determined by analysing the artefact image obtained by scanning, in contact mode (scan size 4 μ m, scan rate 1.03 Hz), an etched silicon surface that possessed features that were sharper than those of *R* (TGT01; MikroMasch, San Jose, CA, USA). An accurate value of *k* (0.236 $\pm$ 0.004 N m⁻¹) was obtained from measurements by scanning electron microscopy (JSM-6060LV, JEOL Ltd, Japan; 10 and 25 keV, 35 μ m spotsize, working distance 12–14 mm) of the thickness *t* (0.59 $\pm$ 0.02 μ m), length *l* (104.0 $\pm$ 0.1 μ m) and width

w (17.2 $\pm$ 0.1 μ m) of the cantilever (Young's modulus *E* = 175 GPa; Eq. (3)) [21,22].

$$k = \frac{Et^3 w}{2l^3} \quad (3)$$

Measurements of the force of adhesion (*F_{ad}*) between tips and SAM-functionalised substrates were obtained in air (temperature, *T* = 22 $\pm$ 1 °C; relative humidity, *RH* = 38 $\pm$ 2%). Force curves (10 $\times$ 10 force measurements; lateral separation, 100 $\pm$ 5 nm; ramp size, 800 nm; scan rate, 1.03 Hz) were obtained from 10 areas on each surface over 21 days period. Measurements were repeated twice using SAM surfaces that had been formed sequentially on the same gold-coated glass substrate. An in-house Visual Basic program was used to extract adhesion data from each of the force curves.

2.5. Fourier-transform infrared spectroscopy

IR experiments were performed using a Nicolet 6700 FTIR spectrometer coupled to a Nicolet Centaurus FTIR microscope (Thermo-Scientific, Madison, USA) with transmission, reflection and attenuated total reflectance (ATR) capabilities. The microscope was equipped with a camera, which provided a 20 μ m $\times$ 20 μ m optical image. Spectra (4000–650 cm⁻¹; 128 interferograms, 4 cm⁻¹ resolution) were recorded in left μ scope reflection mode (*R*%) using a single element mercury cadmium telluride (MCT/A) detector. Spectra (*n* = 2, 10 different areas in each surface) of the CH₃-terminated self-assembled structure (16 h, 40 mmol dm⁻³) were recorded every 7 days over a 21 day period.

2.6. X-ray photoelectron spectroscopy

X-ray photoelectron spectra (XPS) were obtained using a VG Scientific ESCALAB Mk. II spectrometer (Al-K α 1486.6 eV) at low power (10 kV, 5 mA = 50 W; to minimise sample damage); the take-off angle (between surface and analyser lens) was fixed at 60°. Spectra ($\times 2$; the data reported are averaged values), recorded within 2 days from preparation of the self-assembled structure (day 0) and again after 7 days and after 14 days for samples that had been stored in the instrument chamber (atmospheric pressure), were deconvolved using line-shape analysis; atomic percentages were calculated from the peak areas using standard atomic sensitivity factors [23].

2.7. Other analytical techniques

To assess the reactivity of the alkanethiol functionality (nucleophilic) towards atmospheric CO₂ (electrophilic), a solution of 1-undecanethiol in ethanol-d (CH₃CH₂OD; 40 mmol dm⁻³) was left in the laboratory for 16 h, under conditions similar to those used for the preparation of one of the CH₃-terminated self-assembled structures, and the sample was examined using a JEOL GSX nuclear magnetic resonance (¹³C-NMR, 100.52 MHz; δ relative to TMS) spectrometer, gas chromatography–mass spectroscopy (GC–MS; Agilent Technologies 7890A GC system with 597C VL MSD, Foster City, US; 1 μ L injection volume, 1.197 mL min⁻¹ flow rate, 300 °C injection heater, 50:1 split ratio, 9.5016 psi pressure; using Agilent 190915–433 column: 325 °C; 30 m $\times$ 250 μ m $\times$ 0.25 μ m and high performance liquid chromatography–mass spectroscopy (HPLC–MS; HPLC Agilent 1100 Series LC/MSD, Palo Alto, CA, USA; flow rate 0.5 μ L min⁻¹; stop time 30 min; sample volume 15 μ L; mobile phase acetonitrile:ammonium acetate (90:10, 10 mmol dm⁻³, isocratic); dual detection diode array (254 nm) and MS (Agilent; electrospray on positive and negative polarity; gas temperature 300 °C; flow rate 10 L min⁻¹; nebuliser

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