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Introduction

Organic self-assembled monolayers (SAMs) are of great significance in surface technology since the presence of chemically bound molecules render the properties of an interface entirely different compared to those that are unmodified.¹⁻⁴ SAMs are typically formed by exposure of solid substrates to amphiphilic molecules with chemical groups that exhibit strong affinities for the substrate.

For example, alkanethiols adsorb spontaneously from solutions onto the surface of gold, silver, platinum, and copper. Gold is the most frequently used metal because it does not form a stable oxide layer under ambient conditions and potentially provides a reproducible, convenient, and robust method with which to incorporate functionality at the surface in a chemically and physically well-defined way.

SAMs on gold substrates have been characterized by various analytical techniques including Fourier transform infrared spectroscopy (FTIR)⁵⁻⁷, X-ray photoelectron spectroscopy (XPS)^{6,8}, surface plasmon resonance (SPR),^{5,7} ellipsometry,⁵ and quartz crystal microbalance (QCM)^{9,10}. FTIR with specular reflectance sampling mode has proven to be a feasible technique to obtain spectroscopic features regarding organic thin films on gold.⁵⁻⁷ Herein, the preparation and modification of representative alkanethiol-based SAMs on gold and their characterization via single reflectance FTIR are described.¹¹

Experimental and Results

Gold substrates were prepared by the deposition of gold films on single-crystal Si (100) wafers using a high vacuum thermal evaporator. First a chromium adhesion layer (~20 nm) was deposited on the pre-cleaned silicon wafer at a rate of 1 Å/s, followed by ~180 nm of gold at a rate of 3 ~ 4 Å/s.

SAMs were prepared by using three thiols, 1-dodecanethiol (DDT), 11-mercaptoundecanoic acid (MUA), and hydroxyl-terminated (hexaethylene glycol) undecane-

thiol (EG6OH). These thiols contain the same backbone, but different end groups, methyl (CH₃), carboxyl (COOH), and hydroxyl-terminated hexaethylene glycol (HO-(CH₂CH₂O)₆) for DDT, MUA, and EG6OH, respectively (see Fig. 1 for structures).

At biologically-relevant interfaces, a COOH-terminated SAM has been popularly used to introduce N-hydroxysuccinimide (NHS) groups via chemical modification. NHS groups are used for covalent immobilization of proteins via chemical coupling between NHS ester moieties on the surface and primary amine groups in proteins.^{12,13} Alternatively, EG6OH-terminated SAM has been used to prevent nonspecific protein adsorption.¹⁴

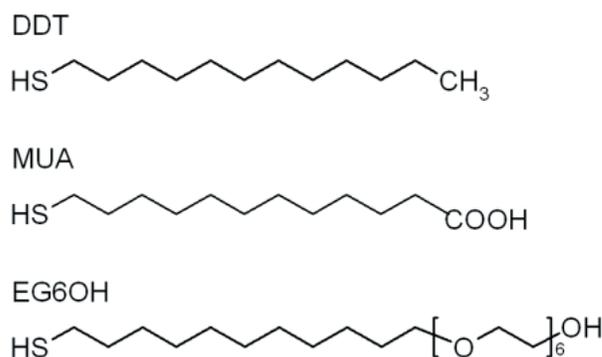


Figure 1. The structures of three thiols, DDT, MUA, and EG6OH.

In a first set of experiments, three SAMs were prepared by incubating gold substrates in freshly prepared thiol solutions using anhydrous ethanol (ca. 1.0 mM) for 48 h. After the formation of SAMs, gold substrates were rinsed with a copious amount of ethanol and deionized water, and finally dried using a stream of nitrogen gas before FTIR data collection.

A VeeMAX™ II (Fig. 2, PIKE Technologies) was placed into the sample compartment of a FTIR spectrometer. The angle of incident infrared was set ca. 70° with respect to the normal plane of the sample surface. Gold substrates were placed (face down) onto the sample

mask with an aperture of 1". For each FTIR spectrum, data was collected using 600 scans with 4 cm⁻¹ resolution. A *p*-polarized infrared beam was used and the output signal was collected using a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen.



Figure 2. VeeMAX II Specular Reflectance Accessory.

Fig. 3 shows FTIR data obtained from SAMs of DDT, MUA, and EG6OH on gold substrates in the range between 3600 and 1000 cm⁻¹. All FTIR spectra contain different features depending on the structure of the thiols in the SAMs.

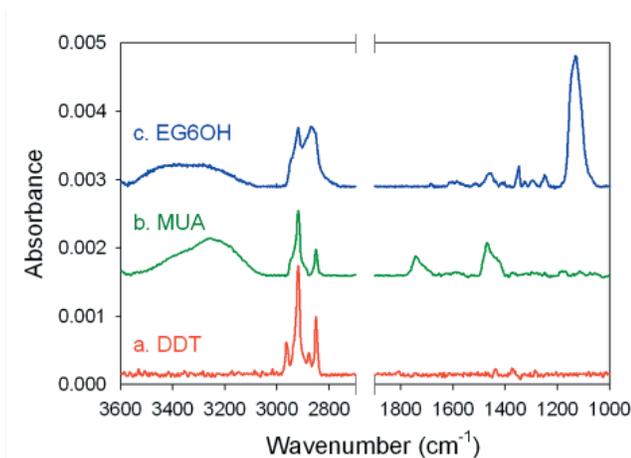


Figure 3. FTIR spectra of DDT, MUA, and EG6OH SAMs prepared on gold substrates.

The FTIR spectrum for DDT SAM in Fig. 3a shows that there are four vibrational modes around 2855, 2875, 2940, and 2960 cm⁻¹. They are assigned to the CH₂ symmetric stretch, CH₃ symmetric stretch, CH₂ asymmetric stretch, and CH₃ asymmetric stretch modes, respectively.^{15,16} The FTIR spectrum obtained from MUA SAM is shown in Fig. 3b. Since MUA contains the CH₂ backbone, its spectrum shows CH₂ symmetric and CH₂ asymmetric stretch modes around 2855 and 2940 cm⁻¹.

In addition, the FTIR spectrum contains features around 1470 and 1750 cm⁻¹ which are related to the COOH moieties.^{17,18} In Fig. 3c, the FTIR data for EG6OH SAM contains a cluster of bands between 2800 and 3000 cm⁻¹, which arise from the overlap of several CH symmetric and asymmetric stretch modes from backbone and ethylene glycol moieties.⁶ One conspicuous vibrational mode is observed around 1110 cm⁻¹, which is responsible for the C-O-C stretching mode in ethylene glycol moieties.

In a second set of experiments, the COOH group in MUA was converted into a N-hydroxysuccinimide (NHS) ester group via chemical reaction using 1-ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide.^{13,19} NHS ester groups in SAMs were utilized to covalently immobilize immunoglobulin G (IgG) by the reaction with primary amine groups in IgG. The unreacted NHS ester groups could be removed by a quenching agent (ethanolamine). Fig. 4 shows FTIR spectra for SAMs after a series of surface modification reactions.

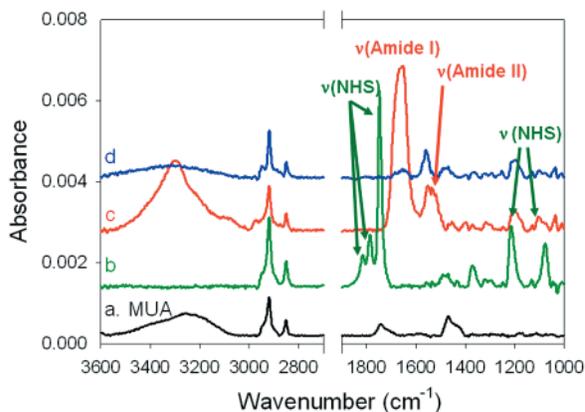


Figure 4. FTIR spectra of NHS-terminated SAM (b) prepared from MUA (a), followed by IgG immobilization (c). NHS groups were deactivated by a quencher, ethanolamine (d).

In the case of the FTIR data from the NHS-terminated SAM, two features around 2850 and 2940 cm⁻¹ are assigned to the CH₂ symmetric and CH₂ asymmetric modes from the carbon backbone, respectively (see Fig. 4b). Compared to the data from MUA (Fig. 4a), three characteristic bands appeared around 1815, 1790, and 1750 cm⁻¹ which are responsible for the carbonyl stretch modes in the COO-NHS ester moiety.^{17,20} After IgG immobilization new amide bands appeared around 1550 and 1670 cm⁻¹ (amide I and amide II), indicating the existence of IgGs on the surface (see Fig. 4c). The unreacted NHS groups on the surface could be deactivated by treatment with the quencher, ethanolamine (see

Fig. 4d).

This work has shown that specular reflectance FTIR using the VeeMAX II has proven to be a powerful technique to obtain vibrational spectroscopic fingerprints of SAMs on gold substrates. Compared to conventional surface analytical tools, presented single reflectance FTIR provides an easily accessible, feasible, and convenient way to monitor the formation and modification of SAMs on gold substrates.

References

- (1) Smith, R. K.; Lewis, P. A.; Weiss, P. S. *Prog. Surf. Sci.* 2004, 75, 1-68.
- (2) Ferretti, S.; Paynter, S.; Russell, D. A.; Sapsford, K. E. *Trends Anal. Chem.* 2000, 19, 530-540.
- (3) Blawas, A. S.; Reichert, W. M. *Biomaterials* 1998, 19, 595-609.
- (4) Netzer, L.; Sagiv, J. J. *Am. Chem. Soc.* 1983, 105, 674-676.
- (5) Vanderah, D. J.; Meuse, C. W.; Silin, V.; Plant, A. L. *Langmuir* 1998, 14, 6916-6923.
- (6) Harder, P.; Grunze, M.; Dahint, R.; Whitesides, G. M.; Laibinis, P. E. *J. Phys. Chem. B* 1998, 102, 426-436.
- (7) Frutos, A. G.; Brockman, J. M.; Corn, R. M. *Langmuir* 2000, 16, 2192-2197.
- (8) Pale-Grosdemange, C.; Simon, E. S.; Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* 1991, 113, 12-20.
- (9) Nakano, K.; Sato, T.; Tazaki, M.; Takagi, M. *Langmuir* 2000, 16, 2225-2229.
- (10) Kawaguchi, T.; Yasuda, H.; Shimazu, K.; Porter, M. D. *Langmuir* 2000, 16, 9830-9840.
- (11) The data shown here are not published and paper is in preparation for publication.
- (12) Patel, N.; Davies, M. C.; Hartshorne, M.; Heaton, R. J.; Roberts, C. J.; Tendler, S. J. B.; Williams, P. M. *Langmuir* 1997, 13, 6485 -6490.
- (13) Jiang, K. Y.; Schadler, L. S.; Siegel, R. W.; Zhang, X. J.; Zhang, H. F.; Terrones, M. J. *Mater. Chem.* 2004, 14, 37-39.
- (14) Herrwerth, S.; Eck, W.; Reinhardt, S.; Grunze, M. *J. Am. Chem. Soc.* 2003, 125, 9359-9366.
- (15) Himmelhaus, M.; Eisert, F.; Buck, M.; Grunze, M. *J. Phys. Chem. B* 2000, 104, 576-584.