Supporting Information

Alkanethiols on Platinum: Multicomponent Self-Assembled Monolayers

Dmitri Y. Petrovykh,*[,†,‡] Hiromi Kimura-Suda,[§,∥] Aric Opdahl,[§,£,#] Lee J. Richter,[§] Michael J. Tarlov,[§] Lloyd J. Whitman[‡]

[†]*Physics Department, University of Maryland, College Park, MD 20742;* [‡]*Naval Research Laboratory, Washington, DC 20375;* [§]*National Institute of Standards and Technology, Gaithersburg, MD 20899;* [∥]*Current address: PerkinElmer Japan Co., Ltd., Yokohama, Japan;* [£]*National Research Council Postdoctoral Associate at NIST;* [#]*Current address: Department of Chemistry, University of Wisconsin, La Crosse, WI 54601*

*Author to whom correspondence should be addressed: Dmitri Y. Petrovykh, Code 6177, Naval Research Laboratory, Washington, DC 20375-5342; E-mail: dmitri.petrovykh@nrl.navy.mil

RAIRS data for SAMs/TS-Pt. The spectra for the monolayers on TS-Pt substrates are intermediate between those for p-Pt and UVO-Pt (Figure SI1, Table SI1). The linewidths for TS-Pt are comparable to p-Pt, but the chain tilt, as reflected in the relative intensities of the CH_2 and CH_3 features, is comparable to UVO-Pt.

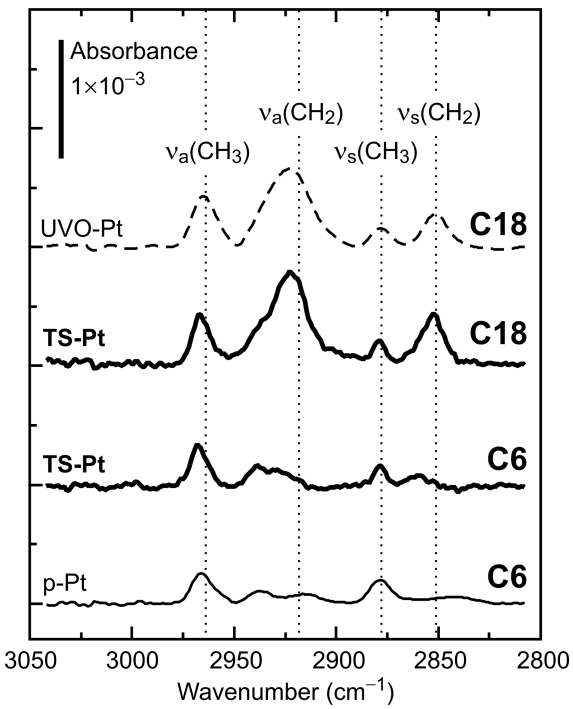

Figure SI1. RAIRS spectra of C-H region for C6SH and C18SH SAMs prepared on TS-Pt substrates compared to counterparts on p-Pt and UVO-Pt. Deposition from 1 mM ethanolic solutions, rinse in EtOH.

Table SI1. Vibrational Line Positions for C18SH/TS-Pt

Peak Assignment	ν, cm^{-1}	fwhm, cm^{-1}
$\nu_s(CH_2)$ sym str	2852	12
$\nu_s(CH_3)$ sym str	2879	6
$\nu_a(CH_2)$ asy str	2922	18
$\nu_s(CH_3)$ FR sym str	2939	12
$\nu_a(CH_3)$ op asy str	2966	8

Table SI2. Oxidation of SAMs/Pt Exposed to Air

Time in air	S 2p Components [a]				O 1s [a]
	S3	S2	S1	S 2p Total	
1.5 h					
C6	109	192	540	841	593
C12	99	147	531	777	637
C18	87	205	564	856	398
47 h					
C6	109	178	512	799	718
C18	70	152	555	777	505
5 days					
C6	129	174	491	794	1015
C12	206	158	426	790	1162
C18	95	143	428	666	1026
29 days[b]					
C12	452	74	263	789	2219
C18	318	92	289	699	1370

[a]Intensities for each element X are reported as Scofield-adjusted intensity ratios to Pt $4f_{7/2}$ substrate signal $(I_X/I_{Pt})(\sigma_{Pt}/\sigma_X)$ to enable direct comparison between S 2p and O 1s intensities.[36,37] In order to avoid multiple additional decimal characters, all the values are listed multiplied by a factor of 10^4.

[b]For the "29 days" samples, the three highest BE components (Figure 5, bottom) are included in the S3 intensity.

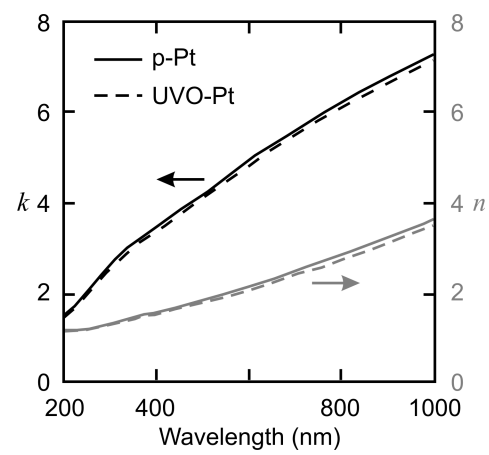

Figure SI2. P-Pt and UVO-Pt substrate refractive index. Real (n) and imaginary (k) parts of the Pt substrate refractive index $n + ik$ derived from the multiple sample SE analysis.

Sulfur Coverage Quantification and EALs for Pt Substrates

The standard XPS formalism used to calculate an absolute S coverage from an experimental I_S/I_M intensity ratio is described in the Appendix A2. The formalism used to derive eq 1 (Appendix A2) has been developed and examined over the last three decades and its reliability is generally accepted.[77-80] In Appendix A2, we validate this approach by the reference measurements of SAMs/Au, which agree with previously published results for both intensity ratios and absolute coverages.[22]

The direct application of eq 1 (Appendix A2) to experimental S/Pt intensity ratios however runs into unexpected complications. It is important to emphasize the distinction between the conversion of relative peak intensities into absolute coverage

values and the relative intensities themselves. The relative intensities in Figures 2, 7, and Tables 3, SI2 are obtained directly from the raw data, and thus are independent of the absolute quantification. Therefore, the conclusions from Sections 3 and 4 on monolayer thickness, stoichiometry, S 2p components, and relative coverage changes are not affected by any discrepancy in the absolute coverage quantification. As elaborated in the following, the unexpected failure of the quantitative EAL formalism in the Pt case defies simple explanations and thus represents a subject of a completely unrelated study, but fortunately we had enough reference data to identify and implement a practical solution in the form of an empirical sensitivity factor.

For S/Pt coverage eq 1 (Appendix A2) can be re-written as:

$$n_S = \left(\frac{I_S}{I_{Pt}}\frac{\sigma_{Pt}}{\sigma_S}\right)\left(\frac{T_{Pt}}{T_S}L^Q_{Pt}N_{Pt}\right) \quad (2)$$

Formal parameters analogous to the Au case in Appendix A2 are: T_{Pt}/T_S =2831/2931, N_{Pt}=6.622×10^{22} cm^{-3}, and L^Q_{Pt}=1.647 nm (L^Q_{Pt} calculated using NIST SRD-82 software[77-79]), which gives the second term in eq 2 as 10.53×10^{15} cm^{-2}. The first term in eq 2 suggests Scofield-adjusted S/Pt intensity ratios as a natural representation for the experimental intensity ratios.[36,37] A Scofield-adjusted intensity ratio of 0.0455 represents a unit of 1 in Figure 2 and Table 3, from eq 2 for Pt the corresponding coverage is 4.8×10^{14} cm^{-2} ("Pt reference" in Table SI3).

Inspection of the "Pt reference" absolute coverage values in Table SI3 reveals that they are physically impossible, even if packing with density of HDPE is assumed for the alkyl chains in the SAM. What is the source of this discrepancy?

The two numerical factors that could contribute to the coverage discrepancy are the S 2p/Pt 4f$_{7/2}$ intensity ratio itself and the estimate of the absolute number of Pt atoms contributing to the XPS signal (second term in eq 2). Another factor, albeit more difficult to quantify, is the structure (morphology) of the Pt substrate.

S 2p/Pt 4f$_{7/2}$ intensity ratio. For a fixed amount of S, the observed S 2p/Pt 4f$_{7/2}$ intensity ratio can be increased by S migration from the SAM/Pt interface to the top of the monolayer. There are four independent observations that rule out such a possibility in our case. First, the S1 component corresponds to alkylthiolates chemisorbed on Pt, thus only the S2 and S3 components can be associated with the hypothetical migrating molecules; for C18SH, the attenuation of the S signal by the monolayer is about 50% (Table 2), so even assuming that the entire S2 and S3 intensities represent S atoms on top of the monolayer is not sufficient to account for the observed S/Pt intensity ratio. Second, for molecules to migrate they must be weakly bound within the monolayer; the null result of the CH_2Cl_2 treatments argues against the presence of such weakly bound molecules. Third, any mechanism that artificially increases the S/Pt ratio must similarly affect the S/C ratio; it is extremely unlikely that any effect (e.g., adventitious carbon) could compensate for the hypothetical S enrichment for *all three* alkyl chain lengths in our study. Fourth, the thiol groups on migrating molecules must be subject to increased oxidation in the ambient; the data in Table SI2 and Figure 7 suggest that S1 rather than S2 and S3 is primarily oxidized during the first five days in air.

A sub-monolayer of oxide *between* the Pt substrate and the thiol groups can affect the measured S 2p/Pt 4f$_{7/2}$ ratio by attenuating the Pt signal. The total O 1s signal is less than the total S 2p signal for as-deposited monolayers (Table SI2 and Figure 7), therefore a full layer of Pt can be used to set a definite upper limit on attenuation of the substrate signal by the oxide, which corresponds to about 25%, i.e., again insufficient to account for the observed coverage discrepancy.

Table SI3. Sulfur Coverage for SAMs/Pt

Sample Description	Normalized S 2p Intensity[a]	Total Sulfur Coverage, 10^{14} atoms/cm^2	
		Pt reference[b]	Au reference[c]
p-Pt, EtOH			
C6SH	1.85	8.9	5.9
C12SH	1.71	8.2	5.5
C18SH	1.88	9.0	6.0
p-Pt, EtOH/CH_2Cl_2			
C6SH	1.70	8.2	5.5
C18SH	1.91	9.2	6.1
p-Pt, CH_2Cl_2			
C6SH	1.70	8.2	5.5
C18SH	1.94	9.3	6.2
UVO-Pt, EtOH/CH_2Cl_2			
C6SH	1.73	8.3	5.5
C12SH	1.82	8.7	5.8
C18SH	1.82	8.7	5.8
TS-Pt, EtOH, Ar			
C6SH	1.39	6.7	4.5
C18SH	1.52	7.3	4.9

[a]Intensities of S 2p components correspond to those in Figure 1 and are reported relative to the S 2p peak for C6SH/p-Au sample, i.e., as Scofield-adjusted[36,37] S 2p/Pt 4f$_{7/2}$ intensity ratios divided by 0.0455.

[b]From eq 2, one intensity unit used in the "Pt reference" column corresponds to the coverage of 4.8×10^{14} cm^{-2}.

[c]Absolute coverages calculated using a clean Au absolute reference and an empirical sensitivity factor to account for the difference between Pt and Au substrates (see text). Numerically, this corresponds to the "Pt reference" values divided by 1.5.

Pt reference. The absolute number of Pt atoms that contribute to the XPS signal is determined by the product ($N_{Pt}L^Q_{Pt}$) of the Pt atomic density N_{Pt} and the electron attenuation length (QEAL) within the Pt substrate L^Q_{Pt}. We used the standard value for Pt density. The actual density of the top layer (several nm thick) in polycrystalline Pt films clearly can differ from the tabulated bulk value, but by not more than a few percent, i.e., vastly insufficient to account for the observed coverage discrepancy.

The QEAL was calculated using NIST SRD-82 software.[77-79] The authors of the software estimated the combined uncertainty of these EAL calculations at about 20-25%. Moreover, both Pt and Au have been recently used in a systematic study of electron inelastic mean free paths (IMFPs), which found no significant discrepancies either between these two metals or between experimental data and model predictions.[81] Systematic differences between calculated and measured EALs, attributed to surface effects not included in the model, have been previously reported to be on the order of 10%.[82,83] In other words, the IMFP calculation in NIST SRD-82 is carried out using the same TPP-2M predictive formula[80] that has been independently tested in ref 81 for both Au and Pt, therefore the 50% discrepancy between XPS signals from Au and Pt that we observed in this work is not likely to be caused by systematic discrepancies in the underlying formalism. Perhaps the most significant difference between Au and Pt w. r. t. TPP-2M calculations is the much higher electron density near the Fermi level in Pt, which will increase inelastic

scattering in Pt due to a mechanism not explicitly included in the TPP-2M model.

Inelastically scattered photoelectrons do account for a larger fraction of the total intensity of Pt core level peaks compared to Au (most notable for the 4f peaks). Therefore, there is a larger uncertainty associated with properly accounting for the inelastic background intensities in fitting Pt peaks. This uncertainty could affect the measured intensity ratios of Au and Pt peaks; however, a comparison of Pt peak intensity values obtained from a range of fitting models and parameters suggests that this uncertainty is ≤30%.

An empirical check of the Pt reference is a comparison between the clean reference Au and Pt signals. If the formal parameters used in eqs. 1 and 2 for Au and Pt are correct, the fully-normalized Au/Pt ratio should be strictly unity (eq 3).

$$\left[\frac{I_{\mathrm{Au}}}{\sigma_{\mathrm{Au}} T_{\mathrm{Au}} L^{Q}_{\mathrm{Au}} N_{\mathrm{Au}}}\right] \Big/ \left[\frac{I_{\mathrm{Pt}}}{\sigma_{\mathrm{Pt}} T_{\mathrm{Pt}} L^{Q}_{\mathrm{Pt}} N_{\mathrm{Pt}}}\right] \equiv 1 \qquad (3)$$

In our experiments this normalized ratio is 1.51±0.06, thus clearly the quantitative description that works well for Au substrates, fails for Pt. Moreover, the ratio is identical for p-Pt and TS-Pt substrates, thus surface structure and roughness are largely ruled out as a factor, as these two types of substrates are dramatically different in terms of roughness (see Materials and Methods).

The above represents only a summary of our attempts to find a fundamental solution or explanation to this discrepancy—an extensive list of factors that we have considered is too long to be presented here, but we could not find a satisfactory solution. However, in practical terms the stability of the empirical Au/Pt reference intensity ratio suggested a very simple solution to the quantification problem—the factor of 1.5 can be used to correct the "Pt reference" values, effectively converting them to the "Au reference" validated by us and others (Tables 3, SI3). As already indicated, in formal terms this corresponds to introducing an empirical Au/Pt sensitivity factor—a procedure typically used when no internal standards or *a priori* parameter values are available.

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(44) The oxygen-free deposition on TS-Pt substrates resulted in the lowest overall O 1s signals in our study. For C6SH/TS-Pt the Scofield-adjusted intensity ratios (same units as in Table SI2) are 227 for C2+C3 components, 220 for O 1s, and 101 for S2. The total intensity of the oxidized C components is equal to the total O signal, thus the data are consistent with essentially no PtO_x on the surface, while S2 is still present.
(45) Each of the alkanethiol molecules contains two chemically distinct carbon atoms: one bound to the sulfur head group and one in the methyl group. The former is likely to have BE higher than the alkyl carbons of the main C1 peak. The C2/C1 intensity ratios in fits to our data (Figure 6), however, are about half of what would be expected for ideal SAMs of respective thicknesses. An additional component of the appropriate intensity and BE shift < 1 eV can be added without sacrificing the quality of the fits to account for the head group bound carbons. C2 and C3 components then must be interpreted as due to adventitious and/or solvent molecules. In the literature, assignment of C 1s components with BE shifts of 1.2-1.6 eV (C2) and 2.7-3.6 eV (C3) varies, e.g., refs 6,27.
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