SUPPORTING INFO

Calculation of actual percentage of the PC and CH₃ terminated thiols on the mixed SAMS based on the XPS C1s high resolution data

Defining the actual percentage of the PC terminated thiol on the surface to be a and the percentage of the CH₃ terminated thiol in the mixed PC/CH₃ monolayer to be b, and since the CH₃ terminated thiol contains 11 carbon atoms and the PC thiol contains 16 carbon atoms, the percentage of the aliphatic carbons over the total amount of carbons can be described as equation 3 and set equal to the experimental value of 72% found by XPS measurement:

$$\frac{10 \times a + 11 \times b}{16 \times a + 11 \times b} = 0.72$$

since

$$a + b = 100,$$

it can be calculated that b equals 33%.

It is a general rule that the ratio of the two components in the monolayer is not the same as their respective ratio in solution. Bain et al. studied four two-component systems each composed of a methyl-terminated thiol and a thiol with a polar or a polarizable group and found that the adsorption of the polar thiol is disfavored. It is also known that the type of the functional group affects the solubility of the thiols in solution. For example, it was found that in mixed SAMs formed from methyl and hydroxyl-terminated thiol solutions, hydrogen bonding between the hydroxyl-terminated thiols and the ethanol solvent results in the preferential adsorption of the nonpolar methyl-terminated component. Longer chain alkanethiols adsorb more readily than short-chain alkanethiols because of the lower solubility of the longer thiol. To investigate this further, mixed SAMs created from 50% PC and 50% OH and CH₃ solutions were prepared and studied. Based on the C1s high resolution analysis by XPS of the surfaces, the percentages of the CH₃ and OH thiols on the surface were 82.2% and 49.7% respectively. These percentages of CH₃ and OH on the surface explain the measured water sessile contact angles of 70° for the CH₃-mixed SAM and 25° for the OH-mixed
SAM. It is possible that in the case of the CH$_3$-mixed SAMs the adsorption of the phosphorylcholine thiol is hindered due to hydrogen bonding between the PC and the ethanol solvent allowing the CH$_3$ thiol to reach the surface faster and occupy more area. In contrast, in the case of the PC/OH mixed SAMs, both PC and OH thiol can hydrogen bond with the ethanol’s hydroxyl groups so that the adsorption of neither molecule is favored.

**Angle-resolved C1d peak fits**

Table A presents the angle resolved C1s peak fits for each of the three PC based SAMs for the three different depths of XPS analysis. Differences at take-off angles of 55° and 80° are not significant. However, if we compare the 0° and 80° take-off angle results, it can be seen that as the surface is approached, the ratio of the C-O and C-N carbons over the total carbon present increases. This is an indication that these bonds are situated closer to the SAM-air interface as expected.

### Table A. Angle-dependent XPS C1s analysis of single and two component PC SAMs on gold.

<table>
<thead>
<tr>
<th>Sampling Depth</th>
<th>C-C</th>
<th>C-O &amp; C-N*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PC</td>
<td>PC/CH$_3$</td>
</tr>
<tr>
<td>100</td>
<td>70</td>
<td>76</td>
</tr>
<tr>
<td>57</td>
<td>65</td>
<td>72</td>
</tr>
<tr>
<td>17</td>
<td>66</td>
<td>72</td>
</tr>
<tr>
<td>Theory</td>
<td>63</td>
<td>65</td>
</tr>
</tbody>
</table>

* It was assumed that the C-O and C-N carbons are at approximately the same energetic states.
SAMs Fingerprint area by FTIR-GA

Figure B presents the fingerprint area for the three PC containing monolayers and for a HS(CH$_2$)$_{17}$CH$_3$ monolayer that was used as a control. No peaks are detected for the HS(CH$_2$)$_{17}$CH$_3$ monolayer while many peaks are present for the phosphorylcholine containing SAMs. Contamination appeared to be higher on the PC and the PC/CH$_3$ samples than on the reference spectra and thus, after subtracting the reference spectrum, a new peak appeared around 1700 cm$^{-1}$. In the case of the PC/OH spectra contamination was lower and after the subtraction of the deuterated octadecylthiol reference spectrum, it appeared as an inverse peak.

Figure B. Grazing angle FTIR spectra showing the fingerprint region of thiols adsorbed on gold: (a) HS(CH$_2$)$_{17}$CH$_3$, (b) PC, (c) PC/CH$_3$ and (d) PC/OH SAM.
References


