Effect of cavitation intensity control on self-assembling of alkanethiols on gold in room temperature ionic liquids

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ARTICLE INFO

Keywords:
Ultrasound
RTIL's
Cavitation
SAM
Electrochemistry
XPS

ABSTRACT

This study investigates the effect of cavitation intensity on self-assembling of alkanethiol molecules on gold in room temperature ionic liquids (RTILs) under low frequency ultrasound irradiation (20 kHz). The use of RTILs, with low vapor pressure, enabled cavitation activity to be controlled up to quenching through pressure decrease within an argon-saturated atmosphere. This control possibility was used to acquire deeper insights into the role of cavitation on self-assembling processes. It was shown by electrochemical, contact angles and Polarization Modulation - Infrared Reflection Absorption Spectroscopy (PM-IRRAS) measurements that cavitation activates orientation and organization of self-assembled monolayers (SAM). X-ray Photoelectron Spectroscopy (XPS) revealed that, even if chemical adsorption of molecules is highly activated under ultrasound irradiation, it is not dependent on acoustic cavitation intensity.

1. Introduction

Over the past 30 years, self-assembled monolayers (SAMs) have been extensively studied. SAMs are grafted by substrate immersion in a solution of active molecules, which will spontaneously be adsorbed onto the surface. The possibility to tune some of the properties such as thickness, compactness, and chemical reactivity makes them useful in many applications e.g. corrosion [1–3], lubrication [4] and adhesion [5]. The affinity between the reactive group and the substrate is of prime importance for ensuring efficient chemisorption on the surface. Many types of SAMs exhibiting various reactive headgroups (thiols [6], phosphonic [7,8], carboxylic [9,10]) have been grafted on gold [11], titanium [12], copper [13] or stainless steel [14] to name just a few.

Organothiol SAM grafted on gold is certainly the most studied system. Thiol groups exhibit very strong reactivity towards gold, while the SAMs obtained are very compact and organized. The mechanism of thiol grafting on gold consists in exothermic homolytic cleavage of S-H bond [15,16] with H2 formation [17]. Nevertheless, to carry out grafting of well-organized and compact monolayers, long modification times are needed i.e. between 16 and 24 h, which renders industrial applications very difficult. In an attempt to solve this problem, some studies on the use of ultrasound to accelerate SAM grafting process have been carried out [11,14,18–20]. The studies by Atobe et al. showed that the adsorption rate and saturated amount of self-assembled adsorption of aliphatic thiolate species on gold surface were increased under ultrasonic irradiation (20 kHz), as well as the adsorption rate of aliphatic thiolate [18]. Dai et al. showed that formation of very compact dodecanethiol monolayers within 15 min was possible under low frequency ultrasound irradiation (40 kHz) [20]. Recently, studies at high frequencies have been carried out by our group. Roy et al. showed that high quality undecanethiol SAM can be grafted on gold after 1 h of modification under high frequency ultrasonic irradiation (575 kHz) compared with 19 h in silent conditions [11]. They also studied self-assembling of alkylphosphonic acids on stainless steel under high frequency ultrasonication. They reported an increase in layer formation process under sonication: 1 h under irradiation to obtain a coating of good quality compared with 8 h in silent conditions [14]. In all these studies, cavitation activity was claimed to be the main cause for these kinetics in comparison to ionic liquids (RTILs) has shed light on new possibilities. The low volatility of these solvents associated with control of dissolved gases have
The aim of this work is to better understand the role of cavitation intensity during SAM grafting under ultrasound irradiation. Alkanethiol SAMs have been grafted on gold in RTILs as solvent under sonication at different pressures to observe the effects of cavitation intensity. A variety of characterization methods have been used: electrochemistry, contact angle measurements, X-ray photoelectron spectroscopy (XPS), and phase modulation - infrared reflection absorption spectroscopy (PM-IRRAS). As detailed in our previous work [21], cavitation activity is quantified through 2 indicators, both extracted from electrochemical measurements (polarization curves): Sherwood number (Sh) and average of current density variation (|Δj|average). Sh is a dimensionless number that is extracted from the steady-state component of polarization curves and permits characterization of mass transfer efficiency independently from parameters inherent to electrochemical system. |Δj|average is extracted from the time-dependent component of polarization curves i.e. current fluctuations. It is an important indicator of cavitation activity as it is only caused by cavitation bubble activity (oscillations and implosions on the surface). According to these indicators, for the lowest absolute pressure (P = 26 kPa), cavitation intensity was reduced by about 50% for a transmitted power of 0.7 W.m\(^{-2}\). Indeed, the Sherwood number was reduced from 280 to 145, and |Δj|average from 0.385 to 0.19 A.m\(^{-2}\). Therefore, three working conditions have been chosen for this study: silent conditions (no ultrasound irradiation), ultrasound irradiation at atmospheric pressure 100 kPa (cavitation intensity: 100%), and ultrasound irradiation at 26 kPa (cavitation intensity: 50%).

2. Experimental

All chemicals were purchased from SIGMA ALDRICH except for ionic liquid: 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide (Bmim)(Tf\(_2\)N) which was purchased from SOLVIONIC (purity > 99.9% - water content < 200 ppm). The gold substrate was mechanically polished (grain size 10, 1 and 0.25 µm) and rinsed twice with water and ethanol. Potential cycling was then carried out from 0 to 1.7 V (vs SCE) at 100 mV.s\(^{-1}\) for 50 cycles in 0.5 M H\(_2\)SO\(_4\) solution to reduce surface oxides. Finally, the substrate was dried and rapidly immersed in the modification solution (1 mM alkanethiol in the ionic liquid).

The experimental set-up has been described in our previous paper [21] and is reported in Fig. 1. The transducer (20 kHz, 25 mm horn diameter) was separated from the electrolyte by a cooling fluid to protect the solution from external pollution [22]. Moreover, this cooling jacket was over-pressurized to optimize energy transmission. The ultrasonic horn and the inner cell bottom were distanced by 30 mm. All tests are carried out with a transmitted intensity of 0.7 W/cm\(^2\).

For characterization purposes, samples were rinsed with 96% ethanol and dried under argon flow. Electrochemical experiments were carried out using an AUTOLAB PGSTAT302N from Metrohm. A three-electrode setup was used with a saturated calomel electrode (SCE) reference, platinum wire as counter electrode (length = 5 cm and diameter = 0.5 mm), and the functionalized gold substrate (disk Φ3mm) as working electrode. Cyclic voltammetry experiments were carried out in acetonitrile with 10 mM ferrocene and 0.2 M of lithium perchlorate (supporting salt) at 100 mV/s. X-Ray Photoelectrons Spectroscopy (XPS) and Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) apparatuses were described in previous work [11].
3. Results and discussion

3.1. Electrochemical measurements

Fig. 2 shows cyclic voltammetry experiments for gold substrates modified with dodecanethiol (C12SH) SAM for 15 min in silent condition and under ultrasound irradiation at 26 kPa and 100 kPa (atmospheric) pressure. Indeed, Dai et al. showed that C12SH SAM can be formed in RTILs within short periods of time [23].

As expected, the electrochemical signal of ferrocene is clearly visible, and reversible on bare gold. The oxidation and reduction peaks are visible at about 400 mV/SCE and 250 mV/SCE, respectively. After SAM grafting, the electrochemical system slows down with a shift in redox potentials, and the signal becomes sluggish. This shows that an adsorbed layer is present on the surface. The electrochemical blocking rate is 10%. Electrochemical blocking rates (τ) are calculated from charge quantity values (Q) using the following equation:

$$
\tau = \frac{Q_{\text{before grafting}} - Q_{\text{after grafting}}}{Q_{\text{before grafting}}} \times 100
$$

When ultrasound with intermediate cavitation intensity (26 kPa) is used during SAM grafting, the ferrocene system is much slower, and the reduction peak is no longer visible. SAM blocking diminished drastically reduction kinetics, and as a consequence, reduction peak intensity is not high enough to be observed on the cyclic voltammogram which presents only a sluggish and flat reduction signal. This trend is even more pronounced when the SAM is grafted under strong cavitation activity (P atm).

The increase in cavitation activity leads to a more insulating and blocking layer. It is possible that high localized releases of energy induced by cavitation lead to more favorable orientation of SAM through some kind of energetic activation. Indeed, previous works showed that reorientation of self-assembled monolayers into an energetically more favorable structure can occur at temperatures high enough to reversibly break sulfur–gold interaction [24]. Such cavitation reorientation has been suggested by Atobe et al. [18] and seems to be experimentally confirmed by our works. On the contrary, agitation generated by acoustic activity is noxious for the SAM grafting process, as showed in previous studies [11].

The influence of active molecule concentration was also studied for the different grafting conditions. Fig. 3 shows the electrochemical blocking rate of C12SH SAM grafted for 15 min on gold for modification solution concentrations ranging between 0.5 and 3 mM. For the same concentration, the electrochemical blocking rate is always highest when cavitation activity is strongest, confirming the beneficial effects of cavitation for the SAM grafting process. In all cases, blocking rate saturation is reached. For grafting in silent conditions and in intermediate cavitation intensity (26 kPa), this saturation is reached as from 1.5 mM. In high cavitation intensity (P atm), saturation is reached from lower concentrations (around 1 mM).

The influence of carbon chain length was investigated by using four different alkanethiols: propanethiol C3SH, butanethiol C4SH, dodecanethiol C12SH, and hexadecanethiol C16SH. Fig. 4 shows electrochemical blocking rates as a function of carbon chain length for the different grafting conditions. Obviously, the electrochemical blocking rate increases with the number of carbons, as the SAM insulating effect is due to the carbon chain, and the shorter the chain, the more electron transfer can occur through tunneling effect. Moreover, a threshold effect is observed. For grafting in silent conditions, this effect occurs between 12 and 16 carbons, as the blocking rate is between 5% and 10% for C3SH, C4SH and C12SH, before increasing sharply to 26% for C16SH. In silent conditions, important defects are present within the adsorbed layer (e.g. inhomogeneity, holes…) for chain lengths up to 12 carbons which leads to facilitated electron transfers and to the observed low electrochemical blocking rates. This issue gets less predominant for 16 carbons grafting, probably due to the increase in Van der Waals interactions between active molecules, leading to the fast increase in blocking rates. For modifications under sonication, this threshold effect occurs between 4 and 12 carbons, with no consideration of cavitation activity. The important role of cavitation intensity regarding SAM grafting under ultrasound irradiation is, once again, highlighted by these results, as the most blocking layers are those generated in high cavitation conditions for all chain lengths. Within intermediate cavitation intensity, results are also intermediate between silent conditions and high cavitation.

![Graph showing the evolution of electrochemical blocking rate as a function of the number of carbons for alkanethiol SAMs grafted on gold for 15 min in (Bmim)(Tf2N) in silent conditions, under low cavitation ultrasound irradiation (26 kPa) and under high cavitation ultrasound irradiation (100 kPa).](image)

**Fig. 4.** Evolution of electrochemical blocking rate as a function of the number of carbons for alkanethiol SAMs grafted on gold for 15 min in (Bmim)(Tf2N) in silent conditions, under low cavitation ultrasound irradiation (26 kPa) and under high cavitation ultrasound irradiation (100 kPa).

| Number of carbons | Contact angles (°) |
|-------------------|-------------------|
|                   | Silent conditions | US at 26 kPa | US at 100 kPa |
| 3                 | 91                | 95           | 100           |
| 4                 | 94                | 98           | 103           |
| 12                | 99                | 101          | 105           |
| 16                | 100               | 105          | 107           |

**Table 1**

Contact angle values for gold samples modified with CnSH for 15 min in (Bmim)(Tf2N) in silent conditions, under low cavitation ultrasound irradiation (26 kPa) and under high cavitation ultrasound irradiation (100 kPa).
3.2. Water contact angle measurements

Contact angle measurements were carried out to assess surface hydrophobicity. A more pronounced hydrophobic behavior is expected after grafting of C\textsubscript{n}SH SAM due to the presence of alkyl chains. The contact angle values give information on SAM organization, as the more compact the monolayer, the more methyl groups are exposed to the surface and the more the layer will exhibit hydrophobic behavior. Table 1 shows results for water contact angle measurements on gold samples modified with C\textsubscript{n}SH under the various conditions. As observed, contact angles increase with the use of ultrasound and are highest for samples produced under high cavitation activity. These results tend to prove that cavitation has beneficial effects for SAM organization, thus confirming the results and conclusions of electrochemical experiments.

3.3. PM-IRRAS analyses

This technique allows infrared analysis of very thin layers. Alkanethiol SAMs were extensively studied by PM-IRRAS. By analyzing positions of CH\textsubscript{2} and CH\textsubscript{3} stretching bands, it is possible to obtain information on molecular orientation and organization of carbon chains. Organized monolayers lead to known values of carbon chain elongations: symmetrical (\nu\textsubscript{s}) and asymmetrical (\nu\textsubscript{a}) bands for CH\textsubscript{2} groups at 2850 and 2917 cm\textsuperscript{-1}, respectively, and symmetrical and asymmetrical bands for CH\textsubscript{3} groups at 2871 and 2955 cm\textsuperscript{-1}, respectively [25-27].

Table 2 displays peak values for C12SH SAMs obtained in the various conditions (spectra not shown). It seems that, under high cavitation intensity, the SAM is the most organized, as CH\textsubscript{2} and CH\textsubscript{3} vibration frequencies are the closest to the values of the perfectly organized SAM.

3.4. XPS analyses

XPS analyses were conducted on C12SH samples produced in the various conditions. Fig. 5 shows spectra from Au4f, S2p and C1s regions obtained for the sample produced under ultrasound irradiation at atmospheric pressure (100 kPa).

The C1s region mainly displays a signal at 285.1 eV, characteristic of C12SH aliphatic chain. The other components are due to traces of solvent. Indeed, as grafting has only been carried out for 15 min, the SAM is still in the organization process and, therefore, the presence of such residue is not surprising. For the cationic part of the solvent (1-butyl-3-methylimidazolium), three components are present at 286.6, 287.1 and 287.8 eV as evidenced in the literature [28]. For the anionic part (bis(trifluoromethanesulfonyl)imide), a peak at 293.1 eV is present corresponding to CF\textsubscript{3} groups [28].

The S2p region is more interesting as it reveals the nature of interactions between the SAM and the gold substrate. Two components are present [29,30]:

- The first at 162 eV attributed to thiol groups chemisorbed on the metal (-S-Au).

![Fig. 5. Au4f, C1s and S2p regions from XPS analysis for gold samples modified with C12SH under ultrasound irradiation at atmospheric pressure.](image-url)
- The second at 163.5 eV corresponding to free thiol groups physisorbed on the surface (-S-H).

The ratio \( \text{Chemisorbed} / \text{Total} \) allows information to be obtained on relative amounts of C12SH molecules chemisorbed on the surface. Thus, in silent conditions only 30% of grafted molecules are chemically adsorbed on gold. This ratio increases to 50% when modification occurs in low cavitation medium (26 kPa) and up to 56% in high cavitation medium (100 kPa). Therefore, it would appear that the chemisorption process is sensitive to cavitation presence but less so to cavitation intensity, as the difference in chemisorbed species ratio between low and high cavitation conditions is not significant. This can be explained by the fact that, as the chemisorption mechanism is radical in nature, the radical species produced by cavitation activity interact strongly during this process, even for lower cavitation intensities.

The decrease in intensity of the Au 4f signal after SAM grafting is proportional to the distance X-rays have to cross through the coating. Therefore, monolayer thickness can be calculated using the following equation [31],

\[
(Au) = (Au_{0})e^{-\frac{d}{\lambda sin(\gamma)}}
\]

\((Au)\) is the photoelectron intensity of gold attenuated by a layer of thickness \( d \) (Å), \((Au_{0})\) is the photoelectron intensity of bare gold, \( \lambda \) is the average free path of photoelectrons (42 Å in our case), \( \gamma \) is the angle between the parallel to the surface and the detector (45°). Bain et al. have shown that, for a monolayer of thiols oriented perpendicularly to the gold surface, thickness can be calculated by considering a value of 1.27 Å per CH2 and 4 Å for the sulfur group [31]. For C12SH, this leads to a thickness of 19.2 Å. The angle of the monolayer inclination can be calculated from the difference between this theoretical value and that observed experimentally. By hypothesizing that a double layer is formed under silent conditions, the thickness found is 14 Å per layer. In this case, the angle is close to 43°, while it decreases for experiments under ultrasound with a value of 33° (\( d = 16 \) Å) for low cavitation and of 30° (\( d = 16.5 \) Å) for high cavitation. The smaller the angle of inclination, the denser the layer. As described in the literature, optimum compactness is obtained when the angle of inclination is 30° [32]. These results also prove that cavitation improves SAM orientation and organization, as already suggested by electrochemistry, contact angles, and PM-IRRAS experiments.

4. Conclusion

This work investigates the effect of cavitation intensity on SAM self-assembling on gold under ultrasound irradiation. The use of RTILs was necessary for selective cavitation quenching through pressure modulation within controlled reactor atmosphere. It was experimentally shown that cavitation activates orientation and organization of SAMs as deduced from electrochemistry, contact angles, and PM-IRRAS analyses. Interestingly, XPS experiments pointed out that cavitation intensity has little impact on the chemical adsorption process. Overall, even if ultrasound irradiation is beneficial for SAM self-assembling, both in terms of organization and chemical adsorption, only the first process is truly dependent on cavitation intensity. The chemical adsorption process only relies on the presence of cavitation, independently from its intensity.

Controlling cavitation intensity in such media emerges as an interesting tool for mechanism elucidation, and further work will be undertaken on chemical and electrochemical deposits (e.g. metallic coatings) using the same low pressure conditions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge the region Bourgogne Franche-Comté for its financial support with the doctoral scholarship for Bouzid Naidji and the technical platforms PCU UTINAM and ARCEN-ICB for the analyses.

References

[1] F. Sinapi, S. Julien, D. Auguste, L. Hevesi, J. Delhalle, Z. Mekhalif, Monolayers and mixed-layers on copper towards corrosion protection, Electrochim. Acta 53 (12) (2008) 4228–4238.
[2] F. Berger, J. Delhalle, Z. Mekhalif, Self-assembled bilayers based on organothiol and organoamine dibromomethyl on polycarbonate overlayer, Electrochim. Acta 63 (2012) 260–276.
[3] J. Denayer, C. Volcke, J. Delhalle, Z. Mekhalif, Formation on copper of perfluoroetheralkyl-thiol and dithiol self-assembled monolayers with a perfluoropolyether overlayer, Electrochim. Acta 68 (2012) 116–123.
[4] T. Patosi, A. E. Taouil, F. Lallemand, L. Carpenter, X. Roizard, J.-Y. Hihn, V. Bondeau-Patissier, Z. Mekhalif, Microbiotribological and corrosion behaviors of 1H,1H,2H,2H-perfluorodecanethiol self-assembled films on copper surfaces, Surf. Coat. Technol. 205 (7) (2011) 2511–2517.
[5] M. Mrkisch, C.S. Chen, Y. Xia, L.E. Dike, D.E. Ingber, G.M. Whitesides, Controlling cell attachment on contoured surfaces with self-assembled monolayers of alkanethiolates on gold, Proc. Natl. Acad. Sci. 93 (20) (1996) 10775–10779.
[6] A. Ulman, Formation and Structure of Self-Assembled Monolayers, Chem. Rev. 96 (4) (1996) 1533–1554.
[7] E.S. Gawalt, G. Lu, S.L. Bernaekte, J. Schwartz, Enhanced Bonding of Alkanephosphonic Acids to Oxidized Titanium Using Surface-Bound Alkoxyceriziron Complax Interfaces, Langmuir 15 (25) (1999) 8929–8933.
[8] N. Adden, L.J. Gamble, D.G. Castner, A. Hofmann, G. Gross, H. Menzel, Phosphonic Acid Monolayers for Binding of Bioactive Molecules to Titanium Surfaces, Langmuir 22 (19) (2006) 8197–8204.
[9] A. Raman, M. Dubey, I. Gouroum, E.S. Gawalt, Formation of self-assembled monolayers of aliphosphonic acid on the native oxide surface of SS316L, Langmuir 22 (15) (2006) 6469–6472.
[10] G. Shurik, A.J. Domb, Mandler, Preparation and Characterization of n-Alkanolic Acid Self-Assembled Monolayers Adsorbed on 316L Stainless Steel, Langmuir 20 (18) (2004) 7499–7505.
[11] F. Roy, A. E. Taouil, F. Lallemand, O. Heintz, V. Moutarlier, J.-Y. Hihn, Alkanethiol self-assembling on gold: Influence of high frequency ultrasound on adsorption kinetics and electrochemical blocking, Ultrason. Sonochem. 40 (2018) 9–16.
[12] E.S. Gawalt, M.J. Avatroni, N. Koch, J. Schwartz, Self-Assembly and Bonding of Alkanephosphonic Acids on the Native Oxide Surface of Titanium, Langmuir 17 (19) (2001) 5736–5738.
[13] M.M. Meine, X. Roizard, J.-M. Melot, L. Carpenter, P.-H. Cornusaut, F. Lallemand, J.-M. Rauch, O. Heintz, S. Lallemand, Grafting and characterization of dodecaphosphonic acid on copper: Macro-tribological behavior and surface properties, Surf. Coat. Technol. 232 (2013) 567–574.
[14] F. Roy, A. E. Taouil, F. Lallemand, J.-M. Melot, X. Roizard, O. Heintz, V. Moutarlier, J.-Y. Hihn, Influence of modification time and high frequency ultrasound irradiation on self-assembling of alkanophosphonic acids on stainless steel: Electrochemical and spectroscopic studies, Ultrason. Sonochem. 28 (2016) 269–275.
[15] J.B. Schlenoff, M. Li, H. Ly, Stability and Self-Exchange in Alkanethiol Monolayers, J. Am. Chem. Soc. 117 (50) (1995) 12528–12536.
[16] M. Jacob, G. Rajaraman, F. Totti, On the kinetics and thermodynamics of S-X – H, CH3, S(3)H, COCH3, and CN cleavage in the formation of self-assembled monolayers of alkylthiols on Au(111), Theor. Chem. Acc. 131 (2012) 1150.
[17] L. Kankate, A. Turchanin, A. Giltshauer, On the Release of Hydrogen from the S–H groups in the Formation of Self-Assembled Monolayers of Thiols, Langmuir 25 (18) (2009) 10435–10438.
[18] M. Atobe, N. Yamada, T. Fuchigami, T. Nonaka, Ultrasonic effects on electroorganic processes Part 24. Rate and saturated amount of the self-assembled adsorption of thiophenol species on a gold surface, Electrochim. Acta 48 (12) (2003) 1759–1766.
[19] M. Atobe, N. Yamada, T. Nonaka, Ultrasonic effects on electroorganic processes Part 15. Self-assembled adsorption of pyridinethiolate species on a gold surface, Electrochim. Commun. 1 (1999) 532–535.
[20] J. Dai, J. Cheng, Z. Li, J. Jin, S. Bi, Rapid formation of high-quality self-assembled monolayers of dodecanethiol on polycrystalline gold under ultrasonic irradiation, Electrochim. Acta 53 (9) (2008) 3479–3483.
[21] B. Naidji, L. Haller, A.E. Taouil, M. Rebetz, J.-Y. Hihn, Influence of pressure on ultrasonic cavitation activity in room temperature ionic liquids: An electrochemical study, Ultrason. Sonochem. 54 (2019) 129–134.
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[22] C. Costa, J.-Y. Hihn, M. Rebetez, M.-L. Doche, I. Bisel, P. Moisy, Transport-limited current and microsonoreactor characterization at 3 low frequencies in the presence of water, acetonitrile and imidazolium-based ionic liquids, PCCP 10 (16) (2008) 2149, https://doi.org/10.1039/b716032a.

[23] J. Dai, J. Cheng, J. Jin, Z. Li, J. Kong, S. Bi, Room-temperature ionic liquid as a new solvent to prepare high-quality dodecanethiol self-assembled monolayers on polycrystalline gold, Electrochem. Commun. 10 (4) (2008) 587–591.

[24] E.U. Thoden van Velzen, J.F.J. Engbersen, D.N. Reinhoudt, Self-Assembled Monolayers of Receptor Adsorbates on Gold: Preparation and Characterization, J. Am. Chem. Soc. 116 (8) (1994) 3597–3598.

[25] P.E. Laibinis, G.M. Whitesides, D.L. Allara, Y.T. Tao, A.N. Parikh, R.G. Nuzzo, Comparison of the structures and wetting properties of self-assembled monolayers of normal alkanethiols on the coinage metal-surfeces, Cu, Ag, Au, J. Am. Chem. Soc. 113 (1991) 7152–7167.

[26] H. Ron, H. Cohen, S. Matlis, M. Rappaport, I. Rubinstein, Self-assembled monolayers on oxidized metals. 4. Superior n-alkanethiol monolayers on copper, J. Phys. Chem. B 102 (49) (1998) 9861–9869.

[27] M.D. Porter, T.B. Bright, D.L. Allara, C.E.D. Chidsey, Spontaneously organized molecular assemblies. 4. Structural characterization of normal alkyd thiol monolayers on gold by optical ellipsometry, infrared spectroscopy and electrochemistry, J. Am. Chem. Soc. 109 (1987) 3559–3568.

[28] E.J. Dick, A.E.A. Fouda, N.A. Besley, P. Licence, Probing the electronic structure of ether functionalised ionic liquids using X-ray photoelectron spectroscopy, PCCP 22 (3) (2020) 1624–1631.

[29] D.G. Castner, K. Hinds, D.W. Grainger, X-ray Photoelectron Spectroscopy Sulfur 2p Study of Organic Thiol and Disulfide Binding Interactions with Gold Surfaces, Langmuir 12 (21) (1996) 5083–5086.

[30] S. Kumar, S. Soni, W. Danowski, C.L.F. van Beek, B.L. Feringa, P. Rudolf, R. C. Chiechi, Correlating the Influence of Disulfides in Monolayers across Photoelectron Spectroscopy Wettability and Tunneling Charge-Transport, J. Am. Chem. Soc. 142 (35) (2020) 15075–15083.

[31] C.D. Bain, G.M. Whitesides, Attenuation lengths of photoelectrons in hydrocarbon films, J. Phys. Chem. 93 (4) (1989) 1670–1673.

[32] H.S. Hansen, S. Tougaard, H. Biebuyck, The adsorption of alkanethiols on gold studied quantitatively by XPS inelastic background analysis, J. Electron Spectrosc. Relat. Phenom. 58 (1-2) (1992) 141–158.