



Conformational order of *n*-dodecanethiol and *n*-dodecaneselenol monolayers on polycrystalline copper investigated by PM-IRRAS and SFG spectroscopy

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Abstract – Self-assembled monolayers (SAMs) of *n*-dodecanethiol (C₁₂H₂₅SH) and *n*-dodecaneselenol (C₁₂H₂₅SeH) on polycrystalline copper have been elaborated with the purpose of achieving densely packed and crystalline-like assemblies. By combining the surface sensitivity of polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) and sum-frequency generation spectroscopy (SFG), the effect of the self-assembly time (15min, 30min, 1h, 2h and 24h) on the formation of *n*-dodecanethiol and *n*-dodecaneselenol monolayers on untreated and electrochemically reduced polycrystalline copper has been investigated.

The modification of surfaces with organic molecular assemblies has become a remarkable method to tailor surface properties. It is largely of interest because of its simplicity, adaptability, reproducibility and the possibility of achieving monolayers with a high level of molecular organization. The resulting assemblies are useful in a wide range of technological applications which are based on novel functional materials and surfaces [1-2].

The modification of gold with self-assembled organothiol monolayers, and more recently with their selenol counterparts, has been widely studied. Currently, oxidizable metals (copper [3-5], nickel, zinc, etc.) have become interesting platforms for the adsorption of organothiol and organoselenol molecules. This research opens doors to new interfacial phenomena and to new applications in different fields. It is also motivated by potential applications in microelectronics and connectors where copper can be an advantageous substitute to gold. However copper undergoes a rapid oxidation in contact with air and the resulting oxide layer is undesired in a large number of applications.

In a previous work [3] on electroplated copper, the selenol derivative was shown to lead similar SAMs than its thiol counterpart. The aim of the present research is to form SAMs of *n*-dodecanethiol and *n*-dodecaneselenol on bulk copper where the oxide layer is thicker and more stable. In line with our previous work, we consider the grafting behavior of these molecules on bulk copper, i.e. either directly on the oxide layer or after its electrochemical reduction. In both cases, increasing self-assembly times are considered. SAMs have been prepared on gold substrates for comparison.

n-Dodecanethiol and *n*-dodecaneselenol have been shown to adsorb on bulk copper, even if the copper present an initial oxide layer. Thanks to the surface specific sensitivity of the PM-IRRAS and SFG techniques, the organisation of the different assembly has been evaluated.

On electrochemically reduced copper, both molecules are able to form well organized layers. The PM-IRRAS spectroscopy showed that the vibrational frequencies of the asymmetric CH₂ and the symmetric CH₂ vibrations are very close to those obtained for a densely packed monolayer. In addition, SFG spectroscopy allowed to establish that C₁₂H₂₅SeH molecules are able to form monolayers with only few gauche defects, for immersion time as short as 15 min. The C₁₂H₂₅SeH SAMs film order is even better than the one achieved with C₁₂H₂₅SH.

The same molecules present a different reactivity towards untreated copper, leading to different film organization. The PM-IRRAS spectroscopy indicated that monolayers of C₁₂H₂₅SH, on Cu_{ox} exhibit quality similar to those obtained on Cured. This is confirmed by the SFG spectra which show only a small amount of gauche defects. In contrast, for the C₁₂H₂₅SeH monolayers, the PM-IRRAS spectra show a shift of ~6 cm⁻¹ toward higher frequencies, indicating a more disorganized layer. The SFG spectra confirm the poor organization of these monolayers, as inferred from the presence of gauche defects in the alkane chains.

References

- [1] R.G. Nuzzo, D.L. Allara, J. Am. Chem. Soc. 105 (13) (1983) 4481.
- [2] J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, G.M. Whitesides, Chem. Rev. 105 (2005) 1103.
- [3] Z. Mekhalif, G. Fonder, F. Laffineur, J. Delhalle, J. Electroanal. Chem. 621 (2008) 245.
- [4] Z. Mekhalif, G. Fonder, D. Auguste, F. Laffineur, J. Delhalle, J. Electroanal. Chem 618(1-2) (2008) 24.
- [5] G. Fonder, F. Laffineur, J. Delhalle, Z. Mekhalif, J. Colloid Interface Sci. 326 (2008) 333.