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Interaction of aqueous Cu(II) with carboxylic acid and alcohol terminated self assembled monolayers: Surface and interfacial characterization



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ABSTRACT

A detailed Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS), X-Ray Photoelectron Spectroscopy (XPS) and electrochemical study of the interaction of copper(II) aqueous solutions with self-assembled monolayers of carboxylic acid and alcohol functionalized thiols of different lengths on gold is reported. Results show that all of these SAMs retain similar amounts of copper, that the interaction takes place mostly with the terminal functional groups, and that for short chain thiols, the copper is electrically connected to the electrode. Furthermore, upon interaction with the copper solution, most of the carboxylic acid moieties deprotonate, forming a complex with the copper cation. This information is relevant for the intelligent design of surfaces with affinity to metal cations that can be used as electrochemical sensors, or in systems for cleaning contaminated water.

1. Introduction

The development of sensitive and specific chemical and biological systems on metallic platforms is of great interest due to their potential applications in sensor, biosensor, electrocatalysis and molecular electronics among others [1–6]. A precise control of the metal-organic interface is needed to design useful devices. Self-assembled organic monolayers (SAMs) using thiols have shown to be one of the most promising systems to modify the surfaces of well-defined, rough, nanoparticle, nanoshell, nanorod or nanocage gold substrates because they provide an organic platform of controllable molecular thickness able to anchor different species by nonspecific interactions [1,3,6,7]. Because of their structural definition and compositional flexibility, thiolate monolayers on gold have been used as models in studies of electron transfer [8–11], wettability [12–15] and metal/organic functional group interaction [16–18].

Self-assembled monolayers of functionalized alkanethiols provide an ideal model surface to study the interactions between organic functional groups and heavy metal ions, using physicochemical surface characterization techniques that can give insights into the processes taking place. This information could be very valuable in the preparation of ionic sensors and/or surfaces that can retain heavy metals.

Numerous toxic heavy metals have been released into the environment, especially in industrial areas. Pollution of water sources by heavy metals represents a serious environmental problem because of their toxicity, persistence and bioaccumulation. These ions can accumulate in the human body and cause many serious diseases even at low concentrations [19]. Different heavy metal ions tend to react selectively with ligands having sulfur, oxygen and / or nitrogen-donor containing groups. Taking advantage of this property, it is possible to prepare surfaces with different affinity to different metals. There is a correlation between behavior and macroscopic, chemical and physical properties of modified surfaces. For a clever design of the surface modification, it is of great importance to perform the physicochemical characterization of the systems and their behavior, so that this will lead to an optimization of the process of modifying the surfaces according to their expected use.

In this work, copper has been used as a model heavy metal. Excess of Cu^{2+} concentration can be highly toxic although it is an essential component of the human body and of the environment [19–20]. Copper is a metal with several industrial and technological applications that make its monitoring in industrial processes and in the environment relevant.

We have functionalized gold surfaces with different organic functional groups with oxygen as donor (-COOH, -OH). We have prepared SAMs with short and disordered alkylic chains, and with long and ordered (crystal-like) alkylic chains. We have tested their affinity with copper ions and have characterized the surface-ion interaction of these different systems via electrochemistry, X-Ray Photoelectron Spectroscopy and Infrared Spectroscopy.

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2. Experimental

2.1. Reagents

The thiolated compounds used 2-Mercaptoethanol (ME, CAS N°60-24-2), 11-Mercapto 1-undecanol (MUD, CAS N°73768-94-2), 3-Mercaptopropionic acid (MPA, CAS N°107-96-0) and 16-Mercaptohexadecanoic acid (MHDA, CAS N°69839-68-5) were purchased from Sigma Aldrich and were used as received. The copper (II) solutions were made from CuSO₄ (Mallinkrodt, CAS N° 7758-99-8). Solutions of potassium chloride used as supporting electrolyte were made from KCl (J.K. Baker, CAS N° 7447-40-7). Absolute ethanol (Sintorgan), and Milli-Q water (high purity water of 18 MΩ) from a Milli-Q purification system (Millipore Products) were used as solvents. All other reagents were of analytical grade.

2.2. Preparation of gold surfaces

Silicon (100) substrates were coated with a 20 nm titanium and 20 nm palladium adhesion layer and a 200 nm gold layer, thermally evaporated with an Edwards Auto 306 vacuum coating system at a pressure of 10⁻⁸ bar, and employed as electrodes. Surface contamination of the gold substrates employed as working electrodes was always controlled before its modification. For this purpose, cyclic voltammetry was performed in a solution of H₂SO₄ 2 M, sweeping the potential between 0 and 1.6 V at 0.1 V.s^{-1} . The electrochemically active area of the electrodes was also estimated from the charge of the gold oxide reduction peak. To calculate the effective area of electrode, the charge corresponding to the electrochemical desorption of a monolayer of oxygen (reduction peak of Au) of 450 µC/cm. [21,22] was taken as reference. In general, the factor roughness found by this method for evaporated gold electrodes was 1.2-1.6. A glass electrochemical cell with a Pt counter electrode and an Ag/AgCl, 3 M KCl reference electrode was employed, and potentials herein are reported with respect to this reference.

2.3. Self-Assembly of thiols on gold and incubation with Cu^{2+}

The self-assembled monolayers (SAMs) of thiols on gold were prepared by immersing the gold substrate into a 100 μ M solution of the thiol in absolute ethanol overnight, at room temperature, in the absence of light. Final rinsing was done with ethanol before drying under N₂(g) flow. For clarity, since the abbreviations of the thiols will be used to refer the assembly, Scheme 1 illustrates the assemblies studied.

The samples were then immersed in aqueous solution of Cu^{2+} of concentrations ranging from 0.1 to 0.5 M for 30 min to 2 h times at room temperature. Afterwards, the surfaces were rinsed with ethanol and dried with N₂(g) flow.

2.4. Electrochemistry

Electrochemical measurements were carried out with an Autolab system which was run on a PC using Nova 2.1 software. Immediately after the incubation in copper solution, the thiol-modified gold substrate was used as a working electrode mounted on a three-electrode glass cell with a Pt wire as counter electrode. Typically the voltage was scanned from 0 to -0.8 V at 0.05 V.s⁻¹ and linear voltammetries were performed. All potentials were measured and reported with respect to a Ag/AgCl (3 M KCl) reference electrode and all measurements were made at room temperature, under an atmospheric environment.

2.5. X-Ray photoelectron spectroscopy

XPS measurements were carried out with a Multitecnica Specs with a dual Mg/Al x-ray source, an hemispherical analyzer (PHOIBOS 150) in fixed analyzer transmission mode (FAT), operated at a constant pass energy of 30 eV with Mg anode operated at 200 W. Samples were placed in the instrument holder and evacuated in ultra high vacuum for at least 12 h before measurements. Binding energies (BE) are referenced to the C 1 s of alkyl chains or alkyl contaminants at 284.6 eV. The analysis chamber was always maintained below 1.10^{-9} mbar. Atomic ratios and surface concentrations were calculated from the integrated intensities of core levels after instrumental and photoionization cross-section corrections using Shirley background fits in all cases.

2.6. IR experiment

Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) experiments were performed on a Thermo Nicolet 8700 (Nicolet) spectrometer equipped with a custom-made external table-top optical mount, a MCT-A detector (Nicolet), a photoelastic modulator PEM (PM-90 with II/Zs50 ZnSe 50 kHz optical head, Hinds Instrument) and synchronous sampling demodulator SSD (GWC Instruments). The gold samples were mounted on an adjustable sample holder. The IR signal was maximized adjusting angle, height and position of the gold sample. The IR spectra were acquired with the PEM set for a half wave retardation at 2900 cm⁻¹ for the CH and OH stretching and at 1500 cm⁻¹ for the CH bending and for stretching modes associated with the COOH group. An example of data treatment is shown in supporting information (S1).

The angle of incidence was set at 80° , which gives the maximum of mean square electric field strength for the air/gold interface. The demodulation technique developed by Corn [23,24] was used in this work. The signal was corrected by the PEM response using a method described by Frey et al. [23] Typically 1000 scans were performed and the resolution was set for 4 cm⁻¹.

3. Results and discussion

3.1. Electrochemical characterization

In order to test the affinity of different functionalized surfaces to copper, gold electrodes were modified according to the procedure described above, with short (i.e. two/three carbons) and long (i.e. eleven/sixteen carbons) bifunctional thiols: 2-Mercaptoethanol (ME), 3-Mercaptopropionic acid (MPA), 16-Mercaptohexadecanoic acid (MHDA) and 11-Mercapto 1-undecanol (MUD). These surfaces were incubated for two hours in aqueous solutions of Cu²⁺ 0.05 M at pH = = 4.5. Linear voltammograms with 0.1 M KCl at pH 7 as supporting electrolyte were performed.

Fig. 1 shows representative curves obtained for each kind of electrode incubated for two hours in aqueous solutions of Cu^{2+} 0.05 M. For the ME functionalized electrode a reduction signal at ~ -0.35 V was observed. For MPA modified electrodes the intensity of the signals at -0.1, -0.4 y -0.7 V shown in Fig. 1 are not reproducible. The lack of reproducibility may be related to the disordered structure of the monolayer and/or the nature of the carboxylic acid moiety, that produces the availability of different ways of interaction with the copper cation and subsequent appearance of multiple reduction peaks in the linear voltagramms [25–26]. This issue is addressed and a possible explanation is proposed later.

Gold surfaces modified with MUD and MHDA were studied and no electrochemical signal was observed in the linear sweep after incubation in 0.1 M Cu^{2+} solution, as shown in Fig. 1. This is attributed to the fact that the copper ions interact with the outer functional groups and do not insert into the alkyl chains that remain intact and cause surface electrical blockage.

3.2. XPS characterization

In order to further examine the behavior of these assemblies, XPS measurements were performed. The samples were measured before



Fig. 1. Linear voltammograms from 0 V to -0.8 V vs Ag/AgCl at 0.05 V.s⁻¹ of Au electrodes modified with ME, MUD, MPA and MHDA incubated for two hours in aqueous solutions of Cu²⁺ 0.05 M. Supporting electrolyte: 0.1 M KCl, pH 7.

incubation in copper, after incubation, and, for the short chain thiols, after performing a linear voltammetry from 0 to -0.6 V at 0.05 V.s⁻¹. Survey XPS scans show the presence of C, O, S, and Au with no other elements being observed on the surfaces before incubation in copper solution. All surfaces show the presence of copper after incubation in the Cu(II) solution. Table 1 summarizes the XPS characterization results that are consistent with the expected composition. In all cases, the S 2p XPS spectrum shows a broad signal at around 162 eV which is consistent with organothiols chemically bound to gold surfaces by formation of thiolate [27]. C1s signal consists of two main components: one centered at 284.6 eV due to the C atoms bound to hydrogen, in the alkane chain and a second one at higher binding energies due to the C atoms bound to oxygen, in the alcohol/acid functional group [17].

Table 2 shows the relationship between the corrected areas of the Cu $2p_{3/2}$ and the S 2p signal, used to estimate the coverage of copper on the surface. After copper adsorption on the surface, this ratio was around 0.8 for the short thiol surfaces, indicating a high coverage of copper. For the long alkyl chain thiols this ratio is somehow lower, probably because the ordered alkyl chains (see later) restrict the movement of the outer functional groups, decreasing the number of

Table 1

Table 2	
Atoms ratios obtained by	y XPS data for the Au-SAM-Cu ²⁺ systems.

	Cu:S Ratio
$Au + ME + Cu^{2+}$	0.77
$Au + ME + Cu^{2+} + LV$	0.52
$Au + MPA + Cu^{2+}$	0.85
$Au + MPA + Cu^{2+} + LV$	0.31
$Au + MUD + Cu^{2+}$	0.41
Au + MHDA + Cu^{2+}	0.67

available coordination places for copper. For short chain thiols that showed reduction peaks in the electrochemistry experiments, XP spectra were measured after the linear catodic sweep, and showed that Cu:S relationship lowered to 0.5–0.3, probably because after reduction some copper is not be retained by the surface and pass to the solution.

Fig. 2 shows the XP spectra of the Cu 2p region corresponding to A) a mercaptoethanol SAM, B) a mercaptopropionic acid SAM, C) a 11-Mercapto 1-undecanol SAM and D) a 16-mercaptohexadecanoic acid SAM, before and after immersion of the Au covered substrate in the Cu (II) solution. In the case of short chain thiols (i.e. ME and MPA) XP spectra after performing the linear voltammetry were taken. Signals corresponding to the bare Au substrate are shown for comparison. These spectra were used to qualitatively study the oxidation state of copper on the surface. Quantitative studies were not possible since copper can be reduced by the electron beam during the XPS experiment [28]. The Cu $2p_{3/2}$ binding energy position reflects the oxidation state of the Cu ion on the surface. It is well established that Cu^{2+} has a Cu $2p_{3/2}$ peak around 934 eV, a Cu $2p_{1/2}$ peak around 952 eV and two characteristic Cu(II) satellite structures at 938-945 eV and 963 eV; whereas the Cu $2p_{3/2}$ and the Cu $2p_{1/2}$ peaks corresponding to Cu and/ or Cu⁺ are located at BEs around 932 and 952 eV [17,29-30]. No significant differences in the peak positions were observed between copper interacting with monolayers functionalized with -COOH or -OH groups. All the spectra of the surfaces incubated in copper show the presence of Cu(I) or Cu⁰, even the ones only in contact with the Cu (II) solution and no electrochemical treatment. This observation is attributed to the effect of the electron beam on the surface, since partial reduction from Cu(II) to Cu(I) on surfaces containing a carbonaceous layer by the electron beam in XPS experiments has been observed previously [28]. In fact, we observed this phenomenon in our samples after repeated irradiaton (not shown). The spectra of the short chain thiols obtained after the linear voltammetry showed the peaks

		Binding energy (eV)						
	S 2p	C 1s	0 1s	Cu 2p _{3/2}	Cu(II) satellite	Cu 2p _{1/2}	Cu(II) satellite	
Au + ME	162	284.7	532.1	-	-	-	-	
		285.4						
$Au + ME + Cu^{2+}$	162.4	284.9	531.6	931.9 934.2	938–946	951.8	958-965	
		286.8						
$Au + ME + Cu^{2++} + LV$	162.5	284.7	531.9	932.1	-	951.7	-	
		285.9						
Au + MPA	161.8	284.6	531.2	-	-	-	-	
		287.7						
$Au + MPA + Cu^{2+}$	162.4	284.6	531.7	932.2 934.4	938–947	954.5	959-965	
		287.9						
$Au + MPA + Cu^{2+} + LV$	162.6	284.6	531.4	932.1	-	951.9	-	
		287.2						
Au + MUD	162.1	284.6	532.3	-	-	-	-	
		286.3						
$Au + MUD + Cu^{2+}$	162.4	284.6	531.6	932.3	938–945	952.3	960-964	
		286.3						
Au + MHDA	162.7	284.6	531.8	_	-	-	_	
		287.4						
$Au + MHDA + Cu^{2+}$	162.1	284.6	531.7	932.6	939–947	952.6	960-964	
		287.2						



Fig. 2. XP Cu 2p Spectra of (A) a mercaptoethanol SAM, (B) a mercaptopropionic acid SAM, (C) a 11-Mercapto 1-undecanol SAM, (D) a mercaptohexadecanoic acid SAM, before and after immersion of the Au covered substrate in the Cu(II) solution.

corresponding to the reduced copper (Cu^0 or Cu(I)), implying that during the cathodic linear sweep the reduction was carried out massively.

the monolayer.

3.3. Infrared characterization

To further characterize the interaction of the copper and the SAMs, PMIRRA spectroscopic measurements were made. Fig. 3 shows the spectra for ME, MPA, MUD and MHDA monolayers before and after the incubation in copper (II) solutions. Peak positions and band assignments are given in Table 3.

The bands at $\sim 2923 \text{ cm}^{-1}$ and $\sim 2855 \text{ cm}^{-1}$ can be assigned to the CH₂ asymmetric and symmetric stretching modes respectively [15,31–32]. As expected for short chain thiols, the peaks for ME and MPA appear at around 2929 and 2860 cm⁻¹, indicating disordered monolayers. For MUD and MHDA these peaks appear at ~ 2921 and $\sim 2852 \text{ cm}^{-1}$, indicating a more ordered, almost crystal like monolayer [15,31–33].

For the alcohols (ME and MUD) the peaks around 3400 cm^{-1} can be attributed to OH stretching [34]. A broad peak (from around 3500 to 3100 cm^{-1}) is observed in ME and MUD functionalized gold samples. The frequency of the stretching of OH is very sensitive to the environment and depends strongly on the degree of H-bonding. "Free" non-hydrogen bonded OH in lineal alcohols usually show absorption peaks at higher wavenumbers (i.e. 3650 cm^{-1}) [35] while the linear dimer is expected to absorb at 3485 cm^{-1} and H-bonded OH absorbs at even lower wavenumbers, i.e. 3350 cm^{-1} . The broad peaks shown in our samples imply that OH is forming H-bonds to a different extent on

For MPA a small and broad peak at $3500-3200 \text{ cm}^{-1}$ appears and can be attributed to the carboxylic acid OH stretching, while the peaks at 1734 and 1690 cm^{-1} are attributed to the carboxylic acid C==O antisymmetric stretch. The position of the carbonyl stretching bands is very sensitive to the environment of the carbonyl group. In general, carboxylic acids in the condensed phase are hydrogen bonded, forming head-to-head dimers or linear polymeric structures. The hydrogenbonded carbonyl groups forming dimers typically have absorption bands that appear at 1700–1715 cm⁻¹, the hydrogen-bonded carbonyl forming polymeric structures usually groups absorb at 1650–1700 cm⁻¹, while non-hydrogen bonded carbonyl groups generally absorb at 1730–1760 cm⁻¹ [17,34]. In our sample, the peaks at 1734 and 1695 cm⁻¹ reveal the presence of both non-hydrogen bonded and polymeric carbonyls of the surface.

In the case of MHDA a small and broad peak at $3500-3200 \text{ cm}^{-1}$ appears and similarly to MPA can be attributed to the carboxylic acid OH stretching. Nonetheless, in this case, only a peak appears in the carboxylic acid C==0 antisymmetric stretch at 1722 cm^{-1} , and can be attributed to non-hydrogen bonded or dimer-forming carbonyl groups. Probably, because the alkyl chains are ordered, the carboxylic groups have not freedom of movement to accommodate into polymeric forms.

3.4. Surface affinity with copper

PMIRRA spectra of the surfaces after incubation with copper were taken. In the case of short chain thiols (ME, MPA), that showed



Fig. 3. PMIRRA Spectra of the gold sample modified with: (A) ME, (B) MPA, (C) MUD and (D) MHDA. Before incubation in Cu^{2+} , after incubation in Cu^{2+} and after LV in case of ME and MPA. Resolution was set to 4 cm⁻¹ and 1000 scans were performed.

reduction signals in the electrochemical experiments, spectra after the linear sweeps were also measured.

After incubation with the Cu(II) solution, there were no significant changes in the position of the CH_2 stretching peaks for any sample. On the other hand, significant changes are observed in the absorption peaks corresponding to the functional group of the thiols.

For the alcohols, ME and MUD, the broad OH stretching peak at \sim 3400 cm⁻¹ changes its position and shape, indicating interaction of the copper ions with the –OH alcohol group. In the case of ME, the peak shifts to lower wavelengths and increases its area. In the case of MUD, a shift to lower wavelengths is also observed and the shape and area of the peak change. The changes in the –OH stretching peaks can be attributed to the interaction between copper and the surface –OH. It is

well known that the frequency of the -OH stretching depends mostly on the O–O distance in the hydrogen bond: the shorter the O–O distance, the longer the O–H distance, the lower the OH stretching frequency [36]. The changes in these peaks can be explained by the appearance of different surroundings for the -OH as a consequence of the presence of copper (not homogeneously distributed on the surface) so that some of the -OH moieties interact closely to the Cu cations.

The change in the outer functional group, and the lack of change in the alky chain IR absorption peaks suggests that the copper interacts only with the outer —OH functional group and does not intercalate into the alkyl chain. This idea is reinforced by the results observed in the electrochemical experiments, that is, the electrochemical blockage observed for the long chain thiol, MUD (see before).



Scheme 1. Schematic representation of the assemblies studied: SAMs of bifunctional thiols on Gold.

Table 3

Spectral mode assignment of PMIRRAS spectra of self-assembled monolayers of ME, MUD, MPA and MHDA adsorbed at Gold(111). The wavenumber values are informed in $\rm cm^{-1}$.

	ν(OH)	$\nu_{as}(CH_2)$	$\nu_{\rm s}({\rm CH_2})$	$\nu_{as}(C==0, COOH)$	$\nu_{as}(COO^{-})$	ν _s (COO ⁻)
ME	3400-3200	2927.5	2858	-	-	-
$ME + Cu^{2+}$	3350-3130	2927.4	2860	-	-	-
$ME + Cu^{2+} + LV$	3500-3150	2927.5	2873.5	-	-	-
MUD	3500-3200	2921.7	2850.3	-	-	-
$MUD + Cu^{2+}$	3500-3180	2921.7	2854.2	-	-	-
MPA	3500-3270	2929.4	2858.0	1733.7	-	1421.3
				1695.2		1400.1
						1373.1
MPA + KCl		2929.4	2858.0	1739.0	-	-
MPA + Cu^{2+}	3300-3130	2929.4	2858.0	1631.5	1573.7	1442.5
						1357.7
$MPA + Cu^{2+} + LV$	3400-3200	2925.5	2858.0	1726.0	1571.7	1438.7
				1637.7		1357.7
MHDA	3309-3141	2919.7	2854.2	1722.1		
MHDA + Cu^{2+}	3382-2970	2917.8	2850.3	1720.2	1544.7	1448.3
				1646.9		

Other studies such as Kolb and coworkers [37-38] report a Cu monolayer formed at the interface of Au(111) electrodes modified with ethanethiol. In these studies, authors performed cyclic voltametry in 0.1 M H₂SO₄ + 1 mM CuSO₄ solutions, and observed that holding the potential in the underpotential range close to the Nernst potential for more than 1 h results in the formation of a complete Cu monolayer. Our system is somehow different: the organic layer modifying the gold surface is incubated in copper solution without applying potential and afterwards a cathodic linear sweep is performed in supporting electrolyte (free of copper ion). Our experimental evidence (see before), including electrochemical, infrared and XPS results, indicates that copper does not intercalate into the alkyl chains for our systems.

Fig. 3 shows that for MPA and MHDA, after incubation with the Cu (II) solution, the peaks corresponding to the CH_2 stretching peaks of the alkyl chain do not change appreciably while the peaks corresponding to the carbonyl group change drastically. Once more, there is evidence that the copper interacts with the outer functional group of the SAM, strengthened, again, by the electrochemical blockage observed for MHDA, the long chain thiol, in the electrochemical experiments.

Fig. 3 shows for MPA that the C = =O stretching peak at 1734 cm⁻¹ diminishes while a peak at 1631 cm⁻¹, another at 1573 cm⁻¹ and a peak at 1443 cm⁻¹ appear. Fig. 3 also shows the spectrum of a MPA modified surface that was incubated in a KCl solution of the same pH as the copper incubation solution. In this case only a peak at 1739 cm⁻¹, attributed to the C==O stretching, appears.

In a similar way to MPA, for MHDA, the spectrum after Cu²⁺ incubation shows the appearance of a peak a 1647 cm^{-1} , a peak at 1545 cm^{-1} and a peak at 1448 cm^{-1} . The changes in the spectra of the mercaptoalcanoic acids indicate interaction of the copper ions with the carboxylic acid moieties. The peaks at ~1550 and ~1440 cm⁻¹ can be attributed to antisymmetric and symmetric stretching of carboxylate anion respectively, and reveal that upon interaction with the copper ion, the carboxylic acid groups deprotonate. This deprotonation is not observed in the solution incubated in KCl at the same adjusted pH, that is, the copper cation is responsible for the deprotonation. In fact, deprotonation of the carboxylic acid groups to form a coordinatively bonded carboxylate with metals has been observed previously by others [17,39–41]. The presence of the peaks at \sim 1730 and \sim 1650 cm⁻ indicate that some of the carboxylic acid moieties are still protonated and non-hydrogen bonded and/or polymerically connected, and probably have not reacted with the copper.

Scheme 2 shows some possible ways of interaction of the carboxylic acid moiety and copper [26]. It is well known that the reduction potential of metals is very sensitive to the coordination of the metal [42–43]. The different ways of coordination may be the cause for the many peaks and lack of reproducibility observed in the electrochemical

experiments for MPA (see before).

Another interesting change in the spectra, occurring for MPA exclusively, is the relative decrease of intensity of the CH₂ stretching peaks after incubation in copper. According to the surface selection rules [44] the diminishing of peak intensity indicates that the dipole moment of that particular vibration is moving to a more parallel position respect to the surface. Fig. 3 shows that the intensity of the bands corresponding to the CH₂ symmetric and antisymmetric bands diminishes after incubation in copper. It is well-known that CH₂ stretching is perpendicular to the backbone of the alkyl chain, so that this diminishing can be attributed to the alkyl chains standing up as a consequence of the interaction with copper. This effect was not observed in the case of the long mercaptoacid (MHDA), probably because in that case the interaction among the alkyl chains is greater, prevailing against the carboxylate-Cu(II) interaction. A hint of this behavior was observed for ME, but it is not a marked effect. Again, it was not observed in the long chain thiol MUD.

3.5. Final remarks

We have performed a detailed and combined PMIRRAS, XPS and electrochemical study on the interaction of Cu(II) with self-assembled monolayers of carboxylic acid and alcohol functionalized alkane thiols on Au. XPS experiments show that copper binds both to alcohol and carboxylic acid terminated SAMs, and in similar concentration. Changes in the absorption peaks corresponding to the –OH and –COOH functional groups in PMIRRA spectra, before and after incubation of the surfaces in the copper solution, show that, in both, cases the cation interacts with the terminal functional group, while the lack of changes in the peaks corresponding to the stretching of the methylene groups indicates that copper does not intercalate into the alkyl chain. This finding is reinforced by electrochemical results that show that for long chain thiols, no electrochemical reduction is possible because of blockage of the electron transfer by the alkyl chain, confirming the expected closed packed, crystal-like structure of these SAMs.

In the case of carboxylic acid functionalized SAMs, PMIRRAS showed that, interaction with copper causes the deprotonation of the acid and consequent formation of the salt. Different ways of coordination of the copper with the carboxylic acid moieties are possible so that in the electrochemistry analysis, three signals at different reduction potentials with no reproducible intensity are observed. In the case of alcohol functional group, the reduction potential is well defined.

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Scheme 2. Scheme of the possible ways of interaction of Cu(II) with MPA.

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Declaration of Competing Interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.susc.2019.121529.

References

- C. Vericat, M.E. Vela, G. Benitez, P. Carro, R.C. Salvarezza, Chem. Soc. Rev. 39 (2010) 1805.
- [2] M. Li, H. Gou, I. Al-Ogaidi, N. Wu, ACS Sustain. Chem. Eng. 1 (2013) 713.
- [3] J.C. Love, L.A. Estroff, J.K. Kriebel, R.G. Nuzzo, G.M. Whitesides, Chem. Rev. 105 (2005) 1103.
- [4] P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson, J.-M. Savéant, J. Am. Chem. Soc. 119 (1997) 201.
- [5] J. Pinson, F. Podvorica, Chem. Soc. Rev 34 (2005) 429.
- [6] S. Ko, G. Han, J.K. Lee, Tetrahedron Lett. 56 (2015) 3721.
- [7] A. Ulman, Chem. Rev. 96 (1996) 1533.
- [8] T. Kitagawa, T. Kawano, T. Hase, I. Hayakawa, K. Hirai, T. Okazaki, Molecules 23 (2018) 2893.
- [9] T. Wächter, A. Tröster, S. Hock, A. Terfort, M. Zharnikov, J. Phys. Chem. C 122 (2018) 4105.
- [10] A. Ricci, C. Rolli, S. Rothacher, L. Baraldo, C. Bonazzola, E.J. Calvo, N. Tognalli, A. Fainstein, J. Solid State Electrochem. 11 (2007) 1511.
- [11] A.M. Ricci, N. Tognalli, E. De La Llave, C. Vericat, L.P. Méndez De Leo, F.J. Williams, D. Scherlis, R. Salvarezza, E.J. Calvo, Phys. Chem. Chem. Phys. 13

(2011) 5336.

- [12] Z. Besharat, D. Wakeham, C.M. Johnson, G.S. Luengo, A. Greaves, I. Odnevall
- Wallinder, M. Göthelid, M.W. Rutland, J. Colloid. Interface Sci. 484 (2016) 279.[13] P. Chinwangso, H.J. Lee, A.C. Jamison, M.D. Marquez, C.S. Park, T.R. Lee,
- Langmuir 33 (2017) 1751.
- [14] R.G. Nuzzo, D.L. Allara, J. Am. Chem. Soc. 105 (1983) 4481.
- [15] R.G. Nuzzo, L.H. Dubois, D.L. Allara, J. Am. Chem. Soc. 112 (1990) 558.
- [16] A.W. Czanderna, D.E. King, D. Spaulding, J. Vac. Sci. Technol. A 9 (1991) 2607.
 [17] E.L. Smith, C.A. Alves, J.W. Anderegg, M.D. Porter, L.M. Siperko, Langmuir 8 (1992) 2707.
- [18] C.M. Whelan, J. Ghijsen, J.-J. Pireaux, K. Maex, Thin. Solid Films 464–465 (2004) 388.
- [19] P.B. Tchounwou, C.G. Yedjou, A.K. Patlolla, D.J. Sutton, Exp. Suppl. 101 (2012) 133.
- [20] Z.L. He, X.E. Yang, P.J. Stoffella, J. Trace Elem. Med. Biol. 19 (2005) 125.
- [21] D.A.J. Rand, R. Woods, J. Electroanal. Chem. 35 (1972) 209.
- [22] H.O. Finklea, D.A. Snider, J. Fedyk, Langmuir 6 (1990) 371.
- [23] B.L. Frey, R.M. Corn, S.C. Weibel, Polarization-modulation Approaches to
- Reflection-Absorption Spectroscopy 2 John Wiley & Sons, 2002, p. 1042.
- [24] B.J. Barner, M.J. Green, E.I. Saez, R.M. Corn, Anal. Chem. 63 (1991) 55.
- [25] L.-S. Long, Cryst. Eng. Comm. 12 (2010) 1354.
- [26] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry, Wiley, 2009.
- [27] C.D. Bain, H.A. Biebuyck, G.M. Whitesides, Langmuir 5 (1989) 723.
- [28] A. Losev, K. Rostov, G. Tyuliev, Surf. Sci. 213 (1989) 564.
- [29] M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.S.C. Smart, Appl. Surf. Sci. 257 (2010) 887.
- [30] L.S. Dake, D.E. King, A.W. Czanderna, Solid State Sci. 2 (2000) 781.
- [31] M.D. Porter, T.B. Bright, D.L. Allara, C.E.D. Chidsey, J. Am. Chem. Soc. 109 (1987) 3559.
- [32] D. Grumelli, L.P. Méndez De Leo, C. Bonazzola, V. Zamlynny, E.J. Calvo, R.C. Salvarezza, Langmuir 26 (2010) 8226.
- [33] D.L. Allara, R.G. Nuzzo, Langmuir 1 (1985) 52.
- [34] D. Lin-Vein, N.B. Colthup, W.B. Fateley, J.G. Grasselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press Inc, San Diego, CA, 1991.
- [35] L. Wilson, R.B. d. Alencastro, C. Sandorfy, Can. J. Chem. 63 (1985) 40.
- [36] P. Tarte, Spectrochim. Acta 13 (1958) 107.
- [37] H. Hagenström, M.A. Schneeweiss, D.M. Kolb, Electrochim. Acta 45 (1999) 1141.
- [38] H. Hagenström, M.A. Schneeweiss, D.M. Kolb, Langmuir 15 (1999) 7802.
- [39] H. Hu, J. Saniger, J. Garcia-Alejandre, V.M. Castaño, Mater. Lett. 12 (1991) 281.
- [40] J. van den Brand, O. Blajiev, P.C.J. Beentjes, H. Terryn, J.H.W. de Wit, Langmuir 20 (2004) 6308.
- [41] O. Seitz, M. Dai, F.S. Aguirre-Tostado, R.M. Wallace, Y.J. Chabal, J. Am. Chem. Soc. 131 (2009) 18159.
- [42] G. Tabbì, A. Giuffrida, R.P. Bonomo, J. Inorg. Biochem. 128 (2013) 137.
- [43] H. Nagao, N. Komeda, M. Mukaida, M. Suzuki, K. Tanaka, Inorg. Chem. 35 (1996) 6809.
- [44] V. Zamlynny, J. Lipkowski, Quantitative SNIFTIRS and PM IRRAS of organic molecules at electrode surfaces, in: R.C. Alkire, D.M. Kolb, J. Lipkowski, P.N. Ross (Eds.), Advances in Electrochemical Science and Engineering, 9 WILEY, Weinheim, 2006.