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Unexpected effect of copper ions on electrochemical impedance behaviour of self-assembled alkylaminethiol monolayer

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A B S T R A C T

Effect of copper ions on the electrochemical behaviour of an alkylaminethiol monolayer has been studied by electrochemical impedance spectroscopy. RAMAN experiment shows the effective adsorption of receptor onto the gold surfaces. The study of Nyquist plot shows that the gold/monolayer/electrolyte interface can be described by a serial combination of two R, CPE electrical circuits. In the presence of increasing amounts of copper, the Nyquist plots at low frequencies were modified showing an increase of the resistance of the second R, CPE electrical circuit. Moreover, this increase of resistance varies linearly with the amounts of copper ions added in solution from $10^{-8} \text{ mol}\cdot\text{L}^{-1}$ to $10^{-5} \text{ mol}\cdot\text{L}^{-1}$.

Keywords:

Equivalent electrical circuit

Self-assembled monolayer

Electrochemical impedance spectroscopy

1. Introduction

The electrochemical impedance spectroscopy (EIS) was a method currently used to study the electrochemical sensing properties of sensors built with self assembled monolayers [1–3]. In the absence of redox probe in solution, EIS was more sensible than cyclic voltammetry to study the change on the electrical interface properties due to the interactions between the guest and the immobilized receptor [4]. Many works have shown that gold/monolayer/electrolyte interface can be described by a simple electrical circuit which associates an electrolyte resistance to a R, CPE parallel electrical circuit [5,6]. Ben Ali et al. have shown that in the presence of copper ions the charge transfer resistance of the sensitive layer decreases linearly with Cu^{2+} concentration when a negative dc potential was applied [7]. On the other hand, some works have shown that an additional R, CPE parallel electrical circuit can be added to describe the gold/short thiol/solution interface [8,9]. This second R, CPE electrical circuit could be related to the monolayer's ability to store a charge [8] or the reorganization of the thiol monolayers on the surface [9], the interpretation of this second electrical circuit was not clear. Bjorefos et al. have shown that in the presence of aluminium ions for positive dc applied potential at low frequencies, the resistance of the second electrical circuit increases from 20% to 30% in the presence of $10^{-4} \text{ mol}\cdot\text{L}^{-1}$ of Al ions [10]. Taking into account these previous works, the electrical circuit to describe the EIS behaviour of a monolayer

was not again clearly defined. Moreover, it seems that the EIS behaviour in the presence of cations depending on the dc potential applied.

In this work, a monolayer formed by the adsorption of a thiol amine compound onto the gold surface was characterized by RAMAN spectroscopy. The electrical parameters corresponding to the gold/SAM/electrolyte interface and the effect of copper ion were studied by EIS.

2. Experimental

2-aminoethanethiol (**1**), potassium nitrate and copper nitrate were purchased from Sigma-Aldrich and were used without purification. The gold surfaces were cleaned with piranha solution for 30 s then were thoroughly rinsed with water and ethanol. A monolayer of 2-aminoethanethiol (**1**) was formed by dipping the gold surfaces (electrodes or gold squares; area: 1 cm^2) for 4 h into an ethanolic solution containing $10^{-3} \text{ mol}\cdot\text{L}^{-1}$ of **1**. The modified surfaces were then rinsed thoroughly with water and ethanol in order to remove the weakly adsorbed **1**. They were dried under vacuum for 6 h. The RAMAN spectra were carried out with a LABRAM HR 800 equipped with a Helium–Neon laser ($\lambda = 638.8 \text{ nm}$).

The gold electrodes, used as working electrode for electrochemical experiments, were fabricated by using microelectronic mass-fabrication processes. Firstly, P-type ($3\text{--}5 \Omega\cdot\text{cm}$) silicon substrates were thermally oxidized to grow an 800 nm thick silicon oxide (SiO_2) layer. The whole metallization process was optimised in order to obtain a good adherence of titanium/gold (Ti/Au – 30 nm/300 nm) layers on the wafer while maintaining good upper interface properties. This optimisation was obtained by suppressing the Ti/Au annealing process and by using low-deposition rates ($\approx 1 \text{ nm/min}$) for both evaporation processes. The gold electrodes were capped by a SiO_2 layer deposited by PECVD

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technique (Plasma Enhanced Chemical Vapour Deposition) to protect the electrical stripes and to define precisely the gold sensitive area (1 mm^2). Photolithography was especially developed to obtain mass fabrication and the precise design for the SiO_2 deposition.

Impedance measurements were performed using a classical three-electrode cell. The counter and reference electrodes were a platinum wire and a saturated calomel electrode (S.C.E.), respectively. All electrochemical measurements were carried out at room temperature. An aqueous solution KNO_3 $0.1 \text{ mol}\cdot\text{L}^{-1}$ ($\text{pH}=5-6$) was used as supporting electrolyte. Nyquist plots were recorded using a μ autolab Fra II in a frequency range from 10 kHz to 50 mHz at an open circuit voltage ($E = 0.6 \text{ V/SCE}$). The amplitude of alternating voltage was 10 mV. The modified electrodes were dipped into copper ion solution for 20 min before to record the Nyquist plots. The resistances (R) and the constant phase elements (CPE) were estimated, the first time, using the FRA software. These values were then used and adjusted to simulate experimental data, by using the ZSim demo 3.20 freeware, in order to validate the assumed equivalent circuit.

3. Results

Raman spectroscopy experiments were carried out to verify that the compound **1** was adsorbed onto the gold surfaces. After to have dipped the gold square into an ethanolic solution containing $1 \text{ mmol}\cdot\text{L}^{-1}$ of sulphur-amine compound **1**, the modified gold surface was studied by Raman spectroscopy (Fig. 1).

In depict of a low surface coverage (Γ_1 around 10^{-9} – $10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ [11]), the Raman spectrum confirms the presence of receptor **1** adsorbed onto gold surface. Indeed, a peak around 2800 cm^{-1} corresponding to CH_2 groups was observed [12]. Moreover, the presence at 1600 cm^{-1} of an ill defined shoulder shows the presence of amine end group.

The electrochemical behaviours of the gold bare electrodes and the gold electrodes modified by a self-assembled monolayer of **1** were studied in free copper solution by electrochemical impedance spectroscopy (Fig. 2).

For the unmodified gold electrodes (insert Fig. 2), the Nyquist plot in the absence of redox probe exhibits a semi circle at 0.6 V versus S.C.E. This electrochemical behaviour (representing the gold/electrolyte interface) has been interpreted in terms of electrical equivalent circuit by a simple model (Fig. 2) which associated a serial combination of electrolyte resistance (R_e) and a circuit containing the polarization resistance (R_1) in parallel with the Constant Phase Element (CPE_1). At this applied potential the impedance of Warburg is minimised. The polarization resistance R_1 corresponding to the diameter of the semi circle was determined by the cross points between the semi-circle and the Z_r axis at high and low frequencies. The polarization resistance of electrode was estimated to be $3400 \pm 10 \Omega\cdot\text{cm}^{-2}$. The Nyquist plots of gold/SAMs/electrolyte interface exhibit also, in free copper solution, the beginning of a semi-circle with a diameter which is higher than this observed for the gold bare electrode. Similar behaviour has been already reported for gold surfaces modified by a monolayer of mercaptoundecanoic acid in the presence of redox probe [6]. The high value of the charge transfer resistance reported for gold/mercaptoundecanoic acid interface (around $700 \text{ k}\Omega\cdot\text{cm}^{-2}$) was

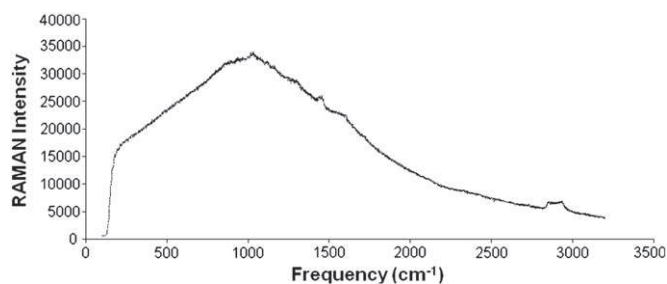


Fig. 1. RAMAN spectrum recorded after functionalization of gold surface by receptor **1**.

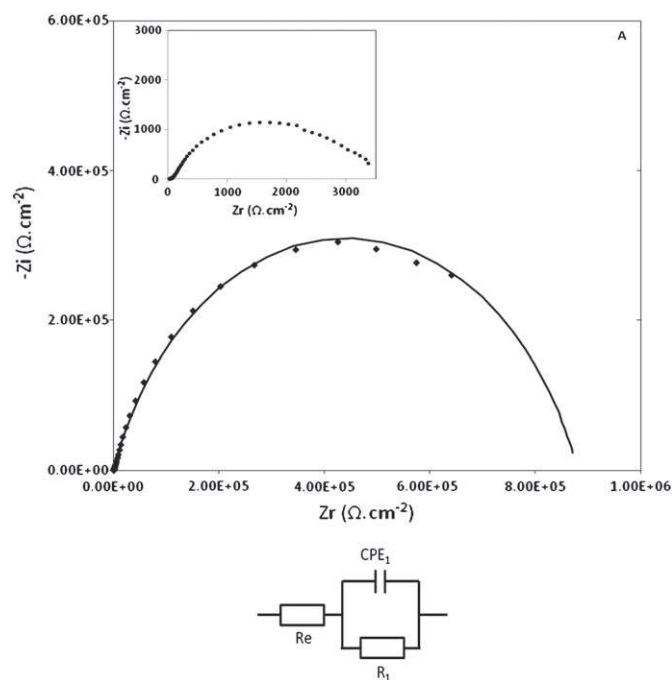


Fig. 2. In insert: Nyquist plots for the gold bare electrode ($\bullet$). Nyquist plots for the gold electrode modified by a monolayer of **1** ($\blacklozenge$). Fitting curve obtained by using the electrical circuit represented here (—).

explained by the high insulating properties of thiol adsorbed on gold. In this work, the polarization resistance (R_1) of gold/thiol interface was estimated (taking into account the simple model described above) to be $880 \pm 10 \text{ k}\Omega\cdot\text{cm}^{-2}$ (Fig. 2). This increase of resistance at the SAM's/electrolyte interface shows an increase of the insulating properties of the monolayer of **1** due to the formation of a more compact organic layer. Indeed, adsorption of thiol with a weak length chain increases the coverage surface (less area defects) compared to sulphur compounds with a long carbonated skeleton.

However, in a frequency range from 10 kHz to 35.8 Hz, the simulated Nyquist plots did not fit with the experimental data showing that the simple model used for the gold/thiol/electrolyte interface was not adapted (Fig. 3).

Taking into account the previous works [8,9] an additional R_2 , CPE_2 parallel electrical circuit can be added to the simple equivalent circuit (insert Fig. 2) to describe the gold/short thiol/solution interface. The resulting equivalent electrical circuit (insert Fig. 3) contains then the

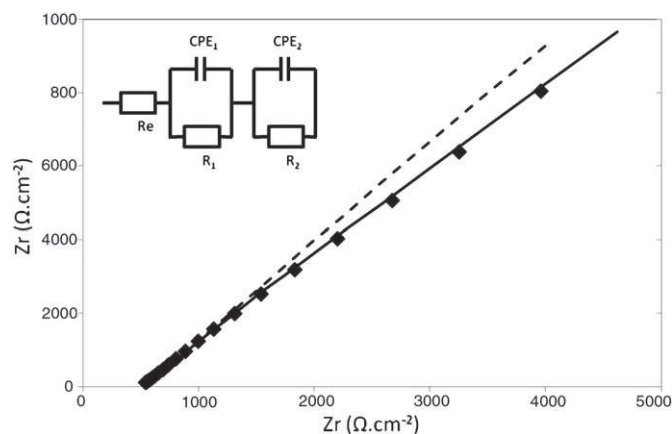


Fig. 3. Nyquist plots for the gold electrode modified by a monolayer of **1** recorded in the frequency range from 10 kHz to 35.8 Hz ($\blacklozenge$). Fitting curve obtained by using the simple electrical circuit describes Fig. 2 (— — —). Fitting curve obtained using the electrical circuit added in inset (—).

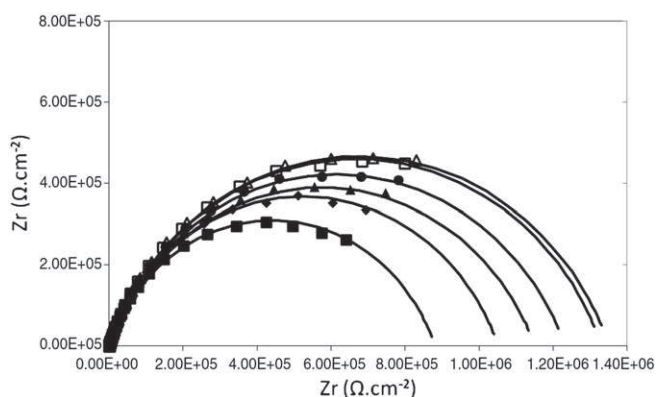


Fig. 4. Nyquist plots recorded for a gold electrode modified by a monolayer of **1** in KNO_3 $0.1 \text{ mol}\cdot\text{L}^{-1}$ at an applied potential to 0.6 V versus S.C.E in the presence of copper ions. (■: $0 \text{ mol}\cdot\text{L}^{-1}$; ◆: $10^{-8} \text{ mol}\cdot\text{L}^{-1}$; ▲: $10^{-7} \text{ mol}\cdot\text{L}^{-1}$; ●: $10^{-6} \text{ mol}\cdot\text{L}^{-1}$; ▽: $10^{-5} \text{ mol}\cdot\text{L}^{-1}$; □: $10^{-4} \text{ mol}\cdot\text{L}^{-1}$). Fitting curve obtained using the electrical circuit added in insert Fig. 3 (—).

electrolyte resistance (R_e) associated to a serial combination of two R , CPE parallel electrical circuit. The first R_1 , CPE₁ electrical circuit could be related to the ion permeation inside the monolayer and was observed at high frequency range. The second R_2 , CPE₂ parallel electrical circuit which was observed at low frequency corresponds to the SAM end group/electrolyte interface. This extra R , CPE circuit was related to either the ability of the monolayer to store a charge at the SAM/electrolyte interface and the ease to move an ion from the interface to the SAM [8] or a change of structure of the SAM [9]. This point is not clear and is subject to discussion. Whatever it was, the simulated curves fit better with the experimental data at high and low frequencies (Fig. 3 and Fig. 4).

Addition of copper ions to KNO_3 $0.1 \text{ mol}\cdot\text{L}^{-1}$ solution modified the Nyquist plots of the functionalized gold electrodes (Fig. 4).

In the presence of increasing amounts of copper cations in solution, an increase of the diameter of the semi circle was observed until $10^{-5} \text{ mol}\cdot\text{L}^{-1}$ of Cu^{2+} added. A similar behaviour has been reported for electrodes modified by SAM of phosphorylated tyrosine-terminated propanethiol [10]. Indeed, when a positive dc potential was applied, an increase of the resistance at low frequency was observed in the presence of $100 \mu\text{M}$ of aluminium ions. Taking into account the equivalent electrical circuit (insert Fig. 3), this is the resistance of the second R_2 , CPE₂ parallel circuit which increases in the presence of copper ions. This increase of resistance could be explained by the formation of a more compact monolayer due to a reorganization of the amine end group of the monolayer. Indeed, the binding of copper ions needs two amine groups per Cu^{2+} ion which induces a change of the structure of the monolayer at the interface SAM/electrolyte. In this case, the area defects were reduced and the layer becomes more insulating. This kind of behaviour has been already reported by Echegoyen et al. [13]. In the presence of potassium cations, a change of the structure of the SAM was observed. After removing the ions, the

Table 1
Simulated values of electrical elements in the equivalent circuit (Fig. 3) obtained by fitting the experimental data.

Cu^{2+} concentration ($\text{mol}\cdot\text{L}^{-1}$)	CPE ₁ 10^{-5} ($\text{F}\cdot\text{cm}^{-2}$)	R_1 ($\text{k}\Omega\cdot\text{cm}^{-2}$)	CPE ₂ (Q) 10^{-4} ($\text{F}\cdot\text{cm}^{-2}$)	R_2 ($\text{k}\Omega\cdot\text{cm}^{-2}$)
0	1.26 ± 0.6	100 ± 50	2.19 ± 0.1	880 ± 10
10^{-8}	^a	^a	2.87 ± 0.1	950 ± 10
10^{-7}	^a	^a	3.75 ± 0.15	1050 ± 20
10^{-6}	^a	^a	3.07 ± 0.15	1130 ± 20
10^{-5}	^a	^a	3.07 ± 0.15	1230 ± 20
10^{-4}	^a	^a	3.05 ± 0.15	1250 ± 20

^a Not indicated due to too large uncertainties.

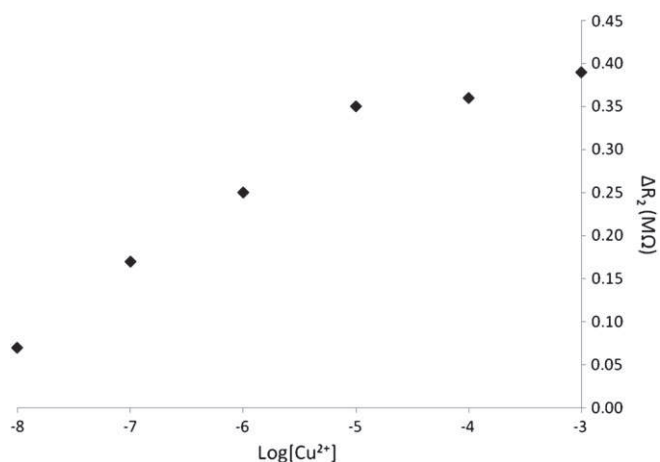


Fig. 5. Calibration plot of ΔR_2 versus pCu^{2+} .

resistance of charge transfer was increased showing that the SAM became more compact.

Using the assumed electrical circuit (Fig. 3), the analysis of Nyquist plots shows that R_2 increases until $1230 \pm 10 \text{ k}\Omega\cdot\text{cm}^{-2}$ in the presence of $10^{-5} \text{ mol}\cdot\text{L}^{-1}$ of Cu^{2+} (Table 1). The uncertainties associated to R_1 and CPE₁ were too large probably due to the strong influence of the second electrical circuit which masks them.

The evolution of ΔR_2 ($\Delta R_2 = R_2$ in the presence of copper – R_2 in free copper solution) was followed in function of copper concentrations added in solution (Fig. 5).

Between $10^{-8} \text{ mol}\cdot\text{L}^{-1}$ and $10^{-5} \text{ mol}\cdot\text{L}^{-1}$, ΔR_2 increases linearly with the copper ion concentration. Above $10^{-5} \text{ mol}\cdot\text{L}^{-1}$ of copper ions, the ΔR_2 was unchanged showing the saturation of sensitive monolayers adsorbed on gold surface.

4. Conclusion

RAMAN spectroscopy shows the effective adsorption of thiol amine compound onto the gold surface. Analysis of Nyquist plots of the modified electrode shows that the equivalent electrical circuit which transduces the electrical properties of the gold/monolayer/interface contains two R , CPE parallel circuit. In the presence of Cu^{2+} , the resistance R_2 increases linearly with the copper concentrations from $10^{-8} \text{ mol}\cdot\text{L}^{-1}$ to $10^{-5} \text{ mol}\cdot\text{L}^{-1}$ of copper ions. The unexpected increase of R_2 was probably due to a reorganization of the thiol monolayers which form a more compact layer with an increase of its insulating properties.

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