

Characterization of Thiol-Functionalised Silica Films Deposited on Electrode Surfaces

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Thiol-functionalised silica films were deposited on various electrode surfaces (gold, platinum, glassy carbon) by spin-coating sol-gel mixtures in the presence of a surfactant template. Film formation occurred by evaporation induced self-assembly (EISA) involving the hydrolysis and (co)condensation of silane and organosilane precursors on the electrode surface. The characterization of such material was performed by IR spectroscopy, thermogravimetry (TG), elemental analysis (EA), atomic force microscopy (AFM), scanning electron microscopy (SEM) and cyclic voltammetry (CV).

Keywords: silica films, 3-mercaptopropyltrimethoxysilane, evaporation induced self-assembly

1. Introduction

Organofunctionalised mesoporous silica materials are of great interest because they combine a high surface area and a narrow pore size distribution with the advantage of owing organic ligand properties. This expands the range of potential applications in catalysis, sensors, separation and opto-electric devices¹⁻⁵. Such materials can be prepared by one-pot co-condensation of organotrialkoxysilane and tetraalkoxysilane. One-pot synthesis of functionalised thin layers requires the Evaporation-Induced-Self-Assembly (EISA) process, which was reported to be particularly suited for the preparation of nicely ordered hybrid mesoporous thin films⁶, even in electrode surfaces⁷, in which a large variety of organic moieties can be incorporated⁸.

Zhao et al. have described how surfactant and non-aqueous cosolvents can be used to define mesophase structure^{9,10}. Interestingly, the templating approach prevents the appearance of cracks into the film, even after surfactant removal. Extraction of the surfactant from ordered mesoporous films led to a large increase of mass transport rates into the materials and imparted high accessibility to the organic moieties of organofunctionalised mesoporous overlayers¹¹.

Silica-based organic-inorganic hybrid materials have become increasingly used in the fields of electroanalytical chemistry¹²⁻¹⁴ and the characterization of these new materials is very important in the understanding of electrodes modification..

In this work a one-step synthesis of organofunctionalised cetyltrimethylammonium bromide (CTAB)-template silica thin films, using 3-mercaptopropyltrimethoxysilane (MPTMS) like an organotrialkoxysilane is presented. The polymeric silica sols were deposited by spin-coating approach on freshly polished gold, platinum and glassy carbon surfaces. The characterization of such material was performed by IR spectroscopy, thermogravimetry (TG) and elemental analysis (EA) to evaluate the organofunctionalisation of the sol-gel film. The surface of the electrodes modified with thiol-functionalised silica film (TFSF) was also characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM) and cyclic voltammetry (CV).

2. Experimental

2.1. Reagents and solutions

The chemicals were of analytical grade and used without further purification. Tetraethoxysilane 95% (TEOS, Acros Organics, USA),

3-mercaptopropyltrimethoxysilane 85% (MPTMS, Acros Organics, USA), cetyltrimethylammonium bromide 98% (CTAB, Vetec, Brazil), ethanol 99.5% (Synth, Brazil) and HCl 37% (Qhemis, Brazil) were used for the preparation of sol solutions.

2.2. Preparation of the electrodes

The polymeric silica sols were typically prepared by heating a mixture of 2.08 g TEOS, including selected equivalent fractions (up to 20%) of MPTMS, 5.5 g EtOH, 0.5 g water and 0.4 g of a 0.1 mol.L⁻¹ HCl solution, at 70 °C for 1 hour, to which 0.78 g of CTAB dissolved in 10 g of EtOH was then added and stirred again for 1 hour at room temperature¹⁵.

The activation of the glassy carbon electrode surface previously to the deposition of the sol-gel film was performed by cycling potentials in a phosphate buffer¹⁶ and helped in improving significantly the mechanical stability of the carbon/silica interface. Thus after activation twenty microliter of sol was deposited on glassy carbon electrode surface and on freshly polished gold, platinum electrodes surface (all 3 mm in diameter), which were rotated at 7000 rpm for 15 seconds. This procedure was repeated five times. The spin-coated films were then kept for 30 minutes at 60 °C in an oven under reduced pressure.

The surfactant extraction was performed in a 1.0 mol.L⁻¹ HCl ethanol solution under hydrodynamic conditions (rotating the electrode at 150 rpm) for 15 minutes¹¹.

2.3. Apparatus

Elemental analysis (EA) was performed in an EAGER-200 apparatus (CE Instruments) and IR spectra were obtained in a Nicolet 55XC spectrometer in the 500-4000 cm⁻¹ range. Films with and without the modifier were prepared in a Petri plate covered with an aluminum foil and dried under an incandescent light, during 3 hours. Then they were transferred to a mortar and powdered. The resulting powders were analyzed by EA. The powder was pressed and IR spectra were taken directly from the resulting thin pellets.

Thermogravimetric curves were recorded in a TGA-951 modulus (TA Instruments) using 7 mg of sample in a platinum crucible at 10 °C/min heating rate under air dynamic atmospheres (flow 100 mL/min).

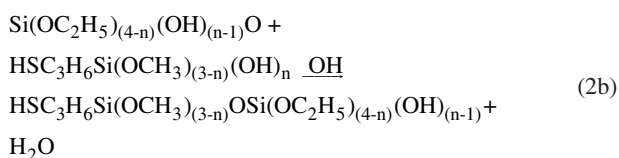
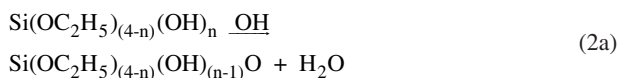
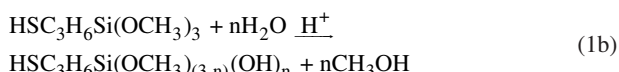
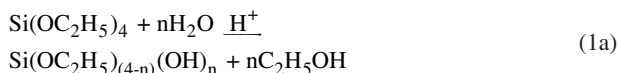
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Scanning electron microscopy (SEM) images were recorded in a LEO-440 (Leica-Zeiss) microscope using 20 kV electronic beam and magnification of 300x and atomic force microscopy (AFM) images were obtained in the contact mode with an Explorer equipment from Topometrix Inc.

Voltammetric experiments were performed using a BAS-CV 50 W potentiostat. A three-electrode cell (20.0 mL full capacity) was used with an Ag/AgCl and a platinum wire ($\varnothing = 1$ mm; $l = 20$ mm) as the reference and auxiliary electrodes, respectively. All the measurements were taken at room temperature without deaeration.

3. Results and Discussion

Thiol-functionalised silica films were synthesized and deposited on the conducting substrates via the sol-gel process. TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$) and MPTMS ($\text{HSC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$) were used for that purpose. The general procedure involves two successive steps: the hydrolysis (Equations 1a and 1b) and (co)condensation (Equations 2a and 2b) of the precursors. Both steps occurring consecutively and sometimes concomitantly.



Elemental analysis, IR spectroscopy and thermogravimetry were employed for evaluating the organofunctionalisation of sol-gel. EA presented an increase in the carbon and hydrogen contents and sulfur appeared after modification. Sols containing 10 and 15% of mercaptopropyl groups, according to the MPTMS/TEOS ratio in the starting sol-gel were synthesized and it is possible to observe an increase in the sulfur contents in the sol-gel containing 15% of mercaptopropyl groups in relation to the 10% MPTMS. The elemental analysis data are presented in Table 1 and revealed the changes in the content of each element after each functionalisation step. The carbon content was used to estimate the number of mols of modifier per 100 g of modified sols (n) in each case. The increase in the carbon and sulfur contents as more MPTMS is used, suggested that the modifier is being incorporated to the sol-gel matrix.

Table 1. Elemental analysis (%) and number of mol for each element per 100 grams (n) of the sol-gel, sol-gel functionalised with 10% and 15% of MPTMS

Sample	C		H		S	
	%	n	%	n	%	n
Sol-gel	31.18	2.60	6.69	6.64	0	0
Sol-gel/10%MPTMS	34.31	2.86	7.35	7.29	2.56	0.08
Sol-gel/15% MPTMS	35.16	2.93	6.94	6.89	3.86	0.12

Figure 1 presents the IR spectra of sol-gel (curve a) and sol-gel functionalised with 15% of MPTMS (curve b). The band around 3440 cm^{-1} could be attributed to the adsorbed water and to the H-bonded silanol OH groups. IR spectra of surfactant (CTAB) aggregates presented two bands at 2922 and 2854 cm^{-1} due to the CH_2 units asymmetric and symmetric vibrations, respectively¹⁷. Other bands between 1200 and 500 cm^{-1} are associated with Si-O-Si or Si-OH band vibration of the siliceous framework, e.g., 1080 cm^{-1} band with the Si-O-Si asymmetric bond stretching vibration and 960 cm^{-1} band with the Si-OH bond stretching vibration. The methoxy groups of MPTMS are indicated spectrally by a significant decrease in the intensity of the 960 cm^{-1} band¹⁸. The band in 580 cm^{-1} is from thiol group of MPTMS.

Figure 2 presents the thermogravimetric curves of sol-gel (curve a) and sol-gel functionalised with 15% of MPTMS (curve b). The sol-gel and sol-gel/15% MPTMS presented dehydration at the beginning of the TG curves. However the mass losses are not stoichiometric. In order to compare the mass losses in the samples the decomposition steps were normalized by discounting the dehydration process and considering the dried material as the starting mass. The sol-gel presents a second transition from 249 - $320\text{ }^\circ\text{C}$ with a mass loss of 52.7% and a last transition with a mass loss of 5.9% . The sol-gel/15% MPTMS present a second transition from 233 - $432\text{ }^\circ\text{C}$ with a mass loss of 53.0% and a last transition with a mass loss of 7.7% . As expected the mass losses observed for the sol-gel and the modified material did not change markedly. However the decomposition profiles in the region of the organic matter burning, c.a. 200 to $450\text{ }^\circ\text{C}$ are quite different, showing that the modifier promoted changes in the sol-gel.

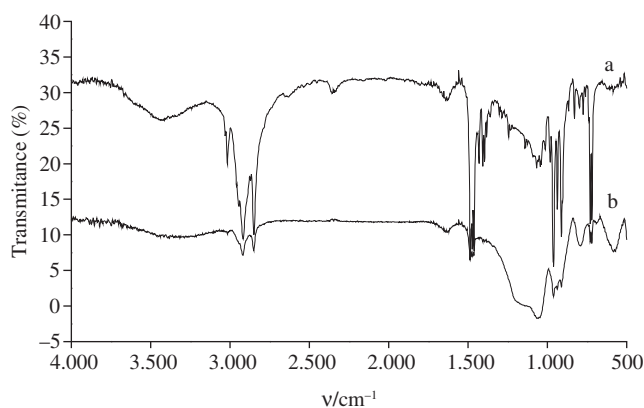


Figure 1. IR spectra: a) sol-gel; and b) sol-gel functionalised with 15% of MPTMS.

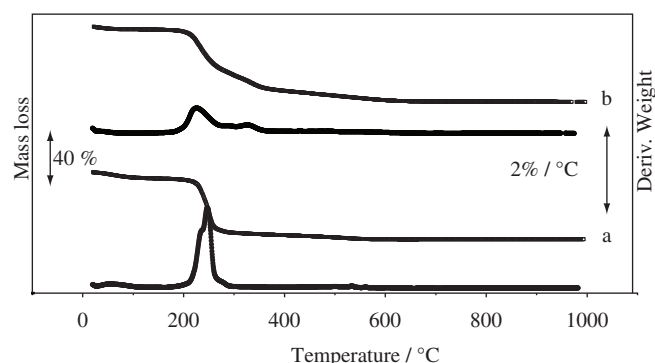


Figure 2. Thermogravimetric curves: a) sol-gel and b) sol-gel functionalised with 15% of MPTMS.

Voltammetric experiments, SEM and AFM images were used to analyse the electrode surface modified with TFSF. AFM images of modified electrodes showed features not present at bare gold, glass carbon and platinum electrodes. The TFSF affect their topography. The image of GC/TFSF reveals that the film grew more uniformly at this surface when compared with Au/TFSF and Pt/TFSF (Figure 3). Rougher films were obtained on the metallic surfaces.

Electronic micrographies revealed significant changes in the morphology of TFSF before and after the extraction of the surfactant, exemplified in Figure 4 for the glassy carbon electrode modified with the film. In agreement with AFM images, the micrography of GC/TFSF showed a more uniform film in this case, mainly after the extraction of the surfactant when a smooth surface was reached.

Typical cyclic voltammograms recorded in hexacyanoferrate solutions are depicted in Figure 5 to compare the response obtained prior

to film deposition (curve a), after templated film deposition (curve b), after surfactant extraction from the film (curve c), and TFSF (curve d). After deposition of the sol-gel film before surfactant removal on gold electrode, the voltammetric signals were suppressed, indicating that the surfactant templated mesoporous film acts as a barrier for the $\text{Fe}(\text{CN})_6^{3-}$ redox probes. This suggests the existence of a crack-free film preventing the external solution to reach the electrode surface, even after prolonged immersion times because of the hydrophobic character of the surfactant template located in the mesopores of the silica material.

After template removal by treating the electrode in an ethanol/HCl solution, a remarked increase in the $\text{Fe}(\text{CN})_6^{3-}$ current was observed, indicating significant permeation properties. The redox probes are now able to cross the mesoporous film to be detected on the electrode surface. Etienne and Walcarius¹¹ described that when preparing a thin silica film in the absence of surfactant template,

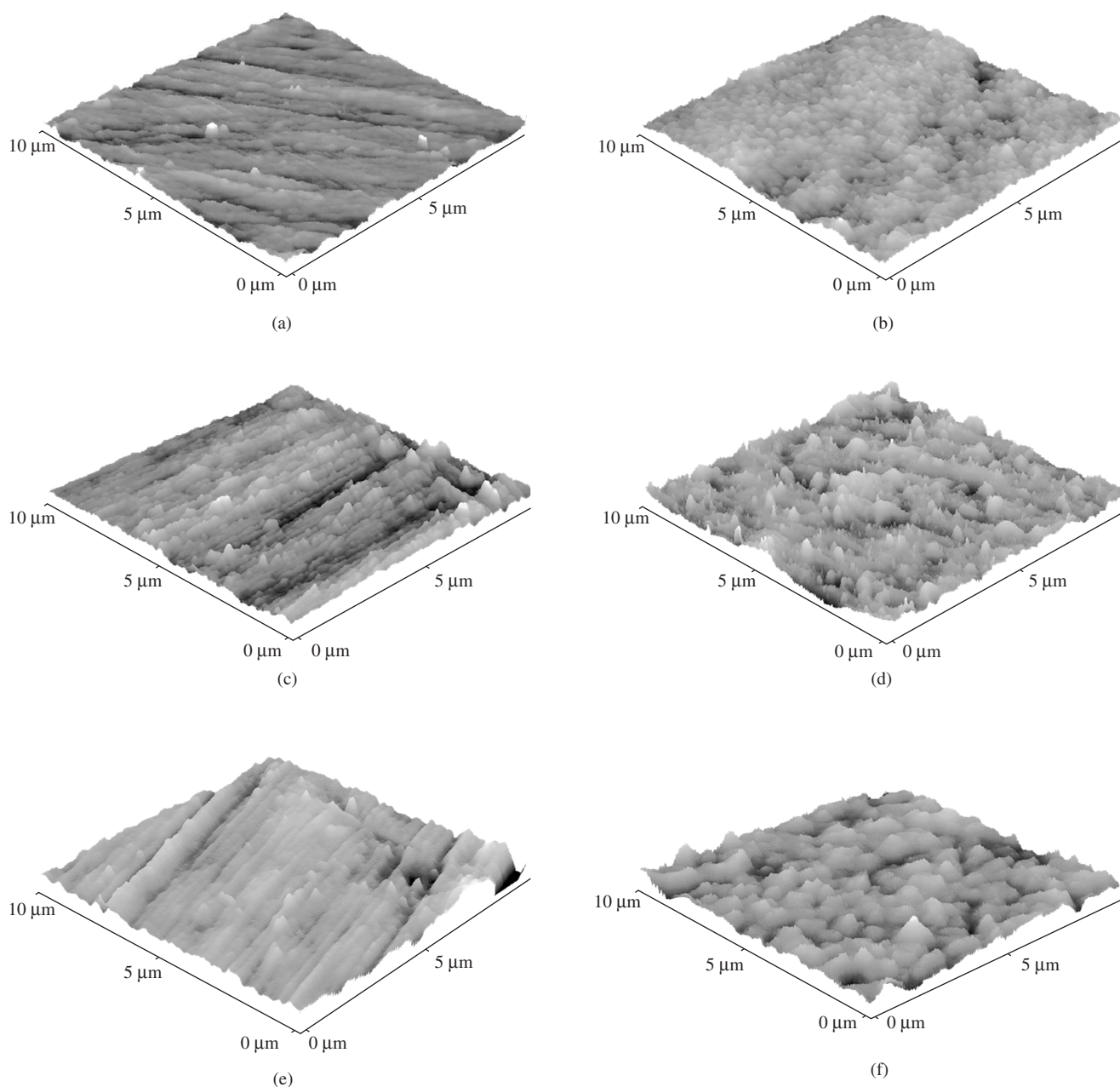
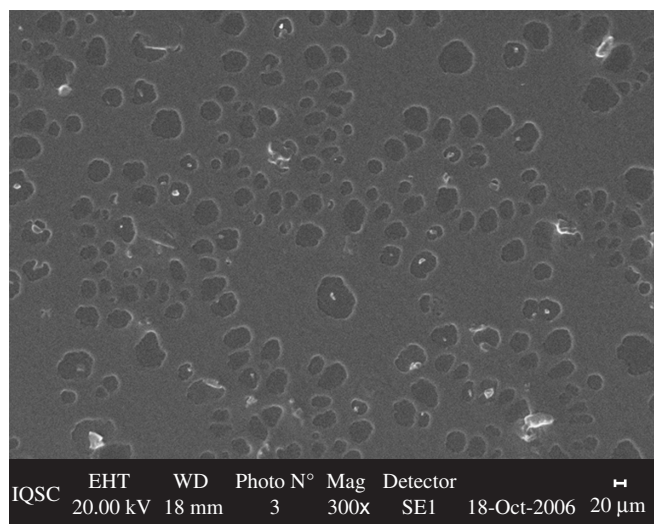
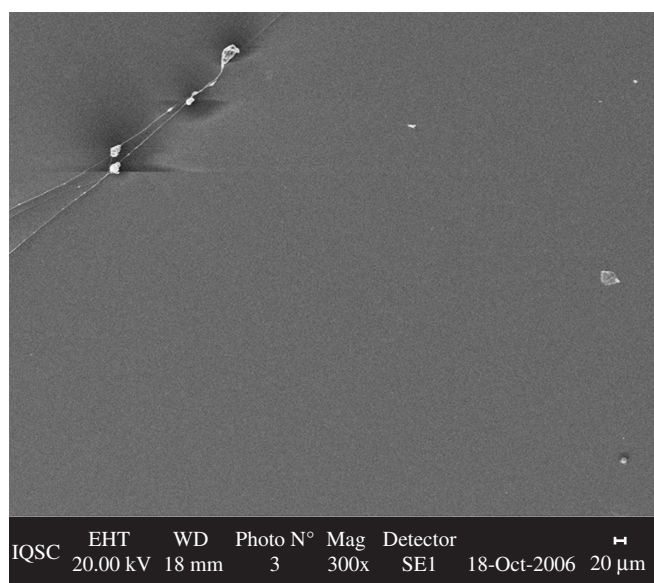


Figure 3. AFM images a) bare GC, b) GC/TFSF, c) bare Au, d) Au/TFSF e) bare Pt and f) Pt/TFSF.



(a)



(b)

Figure 4. GC/TFSF micrographies before and a) and after b) the extraction of the surfactant.

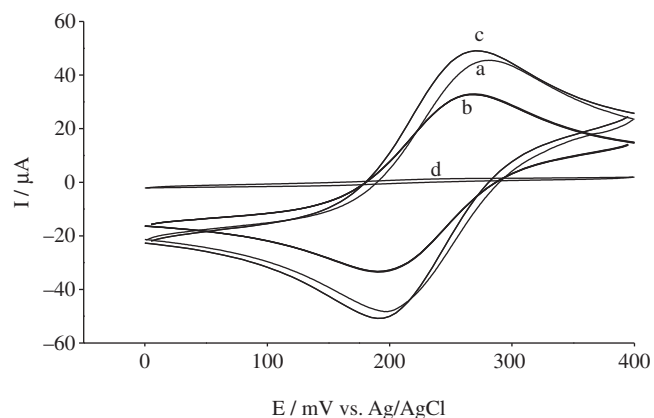


Figure 5. Cyclic voltammetric curves recorded in 5 mM $\text{Fe}(\text{CN})_6^{3-}$ using gold electrodes: a) bare Au; b) after deposition of film, c) after surfactant removal and d) Au/TFSF. Voltammograms obtained 50 mV/s scan rate.

the resulting deposit was microporous and nonordered, and was practically non-permeable to the redox probe (current response less than 1 μA). Our results agreed with these findings, illustrating the importance of the template approach to produce highly permeable films.

The behavior of the film electrode containing 15% of MPTMS reflects the strong interactions existing between the organic groups of the film with the electrode surface, which would induce a control of the electrochemical response by the particular nature of the electrode/film interface rather than by the mass transfer processes through the mesoporous layer.

The GC/TFSF containing 15% of mercaptopropyl groups has been tested for accumulation and detection of Hg^{2+} ions. A sample solution was made of 20 $\mu\text{mol.L}^{-1}$ Hg^{2+} in 0.1 mol.L $^{-1}$ HNO_3 . Under these conditions, Hg^{2+} species can only be adsorbed via a complexation reaction with thiol groups. This preconcentration experiment is a satisfactory way to evaluate the accessibility to the binding sites in the functionalised film.

A typical measurement involves two successive steps: the GC/TFSF was first immersed into the accumulation medium for 1 minute, then removed, and finally transferred into a detection solution containing HCl 3.0 mol.L $^{-1}$ where detection was performed by anodic stripping voltammetry. In this medium, the previously accumulated Hg^{2+} species complexed by the thiol groups in the open circuit pre-concentration step are then directly reduced at -0.5 V during 60 seconds prior to be quantified by a differential pulse anodic scan from -0.5 to 0.3 V (vs. Ag/AgCl).

A stripping peak appeared at about -0.06 V (Figure 6), which is directly proportional to the quantity of analyte previously accumulated into the film. These results are promising in using the GC electrode modified with TFSF can be a useful tool in determining Hg^{2+} in waters or other, natural samples, in which this metal is a potential pollutant.

4. Conclusion

The results showed that the functionalisation of sol-gel with 3-mercaptopropyltrimethoxysilane can be performed and the bare electrodes were modified with thiol-functionalised silica films. The electrochemical properties of the modified electrode are strongly related to the presence of the surfactant and interactions between the modifier and the electrode surface.

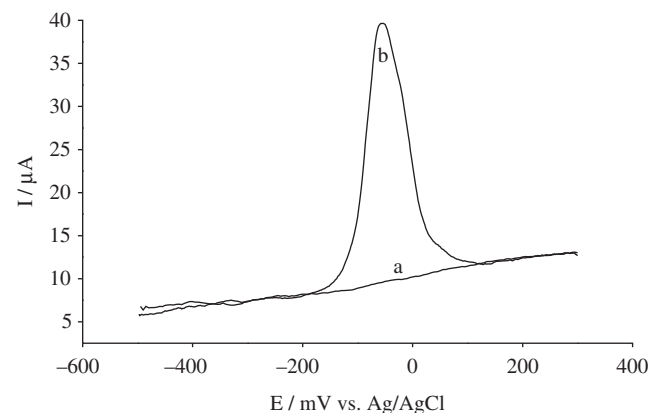


Figure 6. Electrochemical response of GC/TFSF: a) before and b) after 1 minute accumulation of Hg^{2+} ions in an open-circuit. Scan rate of 10 mV/s and pulse amplitude of 100 mV.

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