

Electrochemical, surface enhanced Raman scattering and surface plasmon resonance investigations on the coordination of cyanopyridine to ruthenium on surface



Dieric dos Santos Abreu^a, Tércio de F. Paulo^{a,b},
Márcia L.A. Temperini^{b,*}, Izaura C.N. Diógenes^{a,*}

^a Departamento de Química Orgânica e Inorgânica, Universidade Federal do Ceará, Cx. Postal 6021, Fortaleza, CE 60455-970, Brazil

^b Instituto de Química Orgânica, Universidade de São Paulo, Cx. Postal 26077, São Paulo, SP 05508-000, Brazil

ARTICLE INFO

Article history:

Received 28 June 2013

Received in revised form 15 October 2013

Accepted 18 October 2013

Available online 1 November 2013

Keywords:

Electrochemistry

SERS

SPR

Ruthenium complex

ABSTRACT

Electrochemical, SERS and SPR results indicated that the SAM of $[\text{Ru}(\text{NH}_3)_4(\text{CNpy})(\text{pyS})]^{2+}$ complex was successfully formed on gold. At first, the modification procedure was achieved by the self-assembling of the sulphate starting complex, $[\text{Ru}(\text{SO}_4)(\text{NH}_3)_4(\text{pyS})]^+$. Then, a potential of -0.4 V vs. Ag/AgCl was applied in order to reduce the metal center and induce the substitution reaction of $(\text{SO}_4)^{2-}$ by H_2O which, in turn, was replaced by CNpy. The surface pK_a of the SAM formed with $[\text{Ru}(\text{NH}_3)_4(\text{CNpy})(\text{pyS})]^{2+}$ was calculated as 3.05 indicating an increasing in the π -back-bonding interaction upon adsorption since a value of 2.66 is observed for the complex in solution. This behavior was reinforced by the observation of the shift of the $\nu(\text{C}\equiv\text{N})$ mode to lower frequency (2190 cm^{-1}) in the SERS spectrum in comparison to the spectrum in the solid state (2201 cm^{-1}). The enhancement of the back-bonding interaction upon adsorption is consistent with the existence of gold adatoms in 1+ oxidation state that is assumed to act as a withdrawing group attached to the pyS moiety. The mass of the adsorbed complexes per unit area, calculated by SPR, indicated an excess of CNpy which is consistent with the SERS results where it was observed the frequency assigned to the $\text{C}\equiv\text{N}$ mode of CNpy free of coordination.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Self-assembled monolayers (SAMs) provide a convenient and simple system to design the interfacial properties of metals. The use of SAMs as platform is very attractive since terminal functional groups can be attached to a given surface thus forming modified substrates that can be used in a wide range of applications. Hypothetically, through the use of different immobilization approaches one can produce modified surfaces which can be used as biosensors, electronic devices, surface science, drug delivery, electrocatalyst and so on [1–9]. In the field of molecular electronics, it is critical the knowledge of the kinetics of electron transfer to setup the transport of electrons between the electrodes through molecular bridges. Therefore, in a fundamental context, electrochemical techniques are particularly useful for the study of electron transfer reactions, which is facilitated on SAMs since the parameters such as the Gibbs free energy (ΔG), reorganization energy (λ) and electronic coupling between the donor and the acceptor (H_{AB}) can be

experimentally controlled. One of the most studied classes of SAMs is that formed by sulfur containing molecules on gold electrodes. The strong affinity between the sulfur and gold atoms induces a spontaneously adsorption process as a result of a simple immersion of the electrode into the solution of the modifier [10–12]. SAMs of ferrocenes containing sulfur atoms and SAMs of pentaammine and tetraammine ruthenate complexes on gold have been widely used in the study of electron transfer kinetics [13–19]. However, the electronic structure of the interface formed between the sulfur containing molecules and the gold surface is still not complete. This lack of information has been assigning to the initial works in which the modification of the electrode was believed to be due to a passivation process. With the evolution of the studies and the emergence of new techniques, particularly those based on microscopy, some ideas were raised with the covalent interaction at the gold–sulfur interface being the most accepted one [11,12,20]. More recently, density functional theory computations together with experimental data on scanning tunneling microscopy, low-energy electron diffraction and surface-sensitive X-ray spectroscopic techniques have shown that the gold–sulfur interface involves the formation of a polymeric complex with $\text{RS} - \text{Au(I)} - \text{SR}$ units and the existence of two oxidation states of gold (Au(0) and Au(I)) [5,21,22]. While more experiments are needed in order to confirm the model, it

* Corresponding author. Tel.: +55 11 3091 3890; fax: +55 11 3091 3890.

E-mail addresses: mlatampe@iq.usp.br (M.L.A. Temperini), izaura@dqoi.ufc.br (I.C.N. Diógenes).

seems reasonable to consider the formation of a complex involving a gold adatom in the state +1 to explain the thermodynamic stability of modified surfaces with sulfur containing compounds.

Throughout the discussions based on electrochemistry, SERS and SPR results, we believe that the reader will follow the formation of the SAM of $[\text{Ru}(\text{NH}_3)_4(\text{CNpy})(\text{pyS})]^{2+}$ on surface through the coordination of 4-cyanopyridine ligand to the SAM of $[\text{Ru}(\text{NH}_3)_4(\text{OH}_2)(\text{pyS})]^{2+}$ on gold, where pyS = 4-mercaptopyridine. In addition, some of the presented results may suggest the involvement of gold adatoms (Au^1) in the formation of the ruthenium complex on surface.

2. Experimental

2.1. Apparatus

Electronic spectra in the Ultraviolet and Visible (UV–Vis) regions were acquired with a UV–VIS Hewlett Packard, photo-diode-array, model 8453 spectrophotometer. The infrared spectra of the compounds dispersed in KBr were obtained by using a ABB Bomen FTLA 2000-102 spectrometer. SERS and normal Raman spectra were acquired with a Renishaw Raman InVia spectrometer equipped with a CCD (charge-coupled device) detector and an Olympus (BTH2) microscope with a $50\times$ objective to focus the laser beam on the sample in a backscattering configuration. The 632.8 nm line from a He–Ne (Spectra-Physics) laser was used as exciting radiation (λ_0). For the acquisition of the spectra of gold colloidal suspensions containing the complex, a $63\times$ water-immersion lens (Leica, 0.9 NA) was used. The electrochemical measurements were performed with a conventional glass cell with gold and Pt as working and auxiliary electrodes, respectively, using an EPSILON potentiostat (Bioanalytical Systems Inc., BAS, West Lafayette, IN) at $25 \pm 0.2^\circ\text{C}$. All electrochemical data, unless otherwise specified, are cited against the Ag/AgCl electrode (3.5 mol L^{-1} KCl, BAS). The supporting electrolyte was purged with nitrogen or argon for 20 min prior to experiments, and an inert atmosphere was maintained during all the experiments. Surface plasmon resonance measurements were acquired using a double channel Autolab ESPRIT instrument. The Scanning Electron Microscope (SEM) micrographs were recorded on a Jeol JSM–7401 F–Field Emission Scanning Electron Microscope at the Central Analítica of the Instituto de Química of the Universidade de São Paulo.

Polycrystalline gold substrates used for SERS acquisition were polished with 600 mesh and subsequently with 1200 and 2000 mesh sandpapers and thoroughly rinsed with deionized water. Briefly, the working electrode was submitted to 25 cycles of oxidation and reduction in 0.1 mol L^{-1} KCl in the potential range from -0.3 to $+1.3 \text{ V}$ vs. Ag/AgCl at a scan rate of 0.1 V s^{-1} . Gold surfaces for electrochemistry experiments were mechanically polished with alumina paste of different grades to a mirror finish, rinsed and sonicated (10 min) in Milli-Q water. They were then immersed in a freshly prepared “piranha solution” (3:1 concentrated $\text{H}_2\text{SO}_4/30\% \text{ H}_2\text{O}_2$; **CAUTION:** Piranha solution is a highly oxidant mixture that reacts violently with organic compounds), rinsed exhaustively with water, and sonicated again. The cleanliness was evaluated by comparison of the i – E curve obtained in a 0.5 mol L^{-1} H_2SO_4 solution with the well-established curve for a clean gold surface [23]. The gold disks for SPR measurements were used as received from Eco Chemie BV.

2.2. Chemicals

The water used throughout was purified from a Milli-Q water system (Millipore Co.). Organic solvents (Merck and Aldrich) of spectroscopic grade were used as received. 4-mercaptopyridine

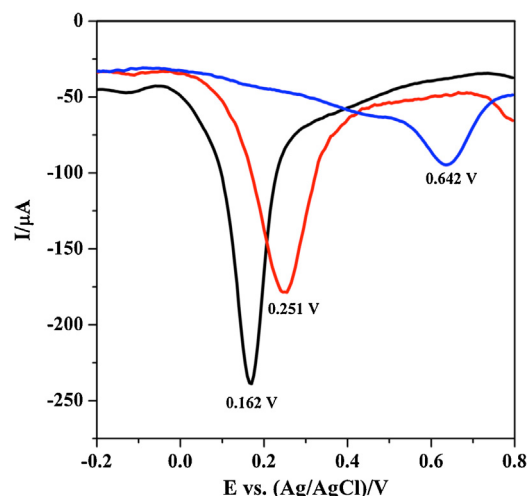


Fig. 1. Differential pulse voltammograms (DPV) at 20 mV s^{-1} in 0.10 mol L^{-1} Na_2SO_4 ($\text{pH} = 3.0$) of the gold electrode modified with $[\text{Ru}(\text{SO}_4)(\text{NH}_3)_4(\text{pyS})]^+$ (—), $[\text{Ru}(\text{NH}_3)_4(\text{OH}_2)(\text{pyS})]^{2+}$ (—) and $[\text{Ru}(\text{NH}_3)_4(\text{pyS})(\text{CNpy})]^{2+}$ (—). Pulse amplitude = 50 mV and pulse period = 200 ms .

(pyS), 4-cyanopyridine (CNpy), KCl, KOH, H_2SO_4 , CF_3COOH , NaOH and Na_2SO_4 were purchased from Aldrich and used as received. NaOH, CF_3COOH or H_2SO_4 were used to adjust the pH values of electrolyte solutions.

Citrate-stabilized gold nanoparticles (AuNPs) of $45 \pm 5 \text{ nm}$ in diameter as determined by scanning electron microscopy (not shown) were synthesized according to Frens’s method [24] with a few modifications proposed by Rodrigues [25]. For SERS measurements, $100 \mu\text{L}$ of a 1.0 mmol L^{-1} aqueous solution of the isolated complex was added to 1.0 mL of the suspension of AuNPs. And the spectra were acquired 5 minutes after the mixing.

The starting complex $[\text{Ru}(\text{SO}_4)(\text{NH}_3)_4(\text{pyS})]\text{Cl}$ was synthesized according to the literature [26,27]. The synthesis of $[\text{Ru}(\text{NH}_3)_4(\text{CNpy})(\text{pyS})(\text{PF}_6)_2]$ was performed as described in the literature [28]. Vibrational and electronic spectroscopic data as well as electrochemical were coincident with those reported [28] indicating, therefore, the isolation of the desired compound. $\lambda(\text{MLCT}, \text{NaCH}_3\text{COO}, \text{pH} 3.0)$: 382 and 510 nm; $E_{1/2}(\text{V vs. Ag/AgCl}, \text{NaCH}_3\text{COO}, \text{pH} 3.0)$: 0.654 V; IR (KBr): $\nu(\text{C}\equiv\text{N})$ 2201 cm^{-1} , $\nu(\text{C}=\text{C}+\text{C}=\text{N})$ 1594 and 1624 cm^{-1} , $\nu(\text{C}=\text{S})$ 1110 cm^{-1} . Figs. S1 to S6 of the Supporting Information show the cyclic voltammogram, electronic spectrum and IR and Raman vibrational spectra.

3. Results and discussion

The SAM of the $[\text{Ru}(\text{NH}_3)_4(\text{CNpy})(\text{pyS})]^{2+}$ ion complex was formed stepwise starting with the spontaneous adsorption of the sulphate complex, $[\text{Ru}(\text{SO}_4)(\text{NH}_3)_4(\text{pyS})]^+$, on gold. In addition, the $[\text{Ru}(\text{NH}_3)_4(\text{CNpy})(\text{pyS})]^{2+}$ ion complex was synthesized in homogeneous medium following the procedure described in the literature [28] in order to be used as reference for the analysis of its SAM on gold, which was characterized by electrochemistry and SERS techniques.

3.1. Electrochemical studies and surface pKa

The electrochemical monitoring of the formation of the SAM of $[\text{Ru}(\text{NH}_3)_4(\text{pyS})(\text{CNpy})]^{2+}$ on gold is shown in Fig. 1.

The SAM of the starting complex, $[\text{Ru}(\text{SO}_4)(\text{NH}_3)_4(\text{pyS})]^+$, was formed by the addition of a drop of 10 mmol L^{-1} aqueous solution of the compound on gold electrode for 1 h. The gold modified surface was washed and transferred to an electrochemical cell containing Na_2SO_4 solution and the DPV curve showed a wave at 0.162 V

Download English Version:

<https://daneshyari.com/en/article/186311>

Download Persian Version:

<https://daneshyari.com/article/186311>

[Daneshyari.com](https://daneshyari.com)