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UNITATEA EXECUTIVA PENTRU FINANTAREA INVATAMANTULUI SUPERIOR, A CERCETARII DEZVOLTARII SI INOVARII

ROMANIAN ACADEMY - INSTITUTE OF PHISICAL CHEMISTRY ILIE MURGULESCU MCMLXIII

PN-II-RU-PD-2012-3-0086

ELECTOCHEMICAL PROPERTIES OF THE GLUTATHIONE-COVERED Cu(hkl) ELECTRODES

Project no. 3/2013
Duration: 01.05.2013 – 30.10.2015

Project Leader:

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Project Summary:

Functionalization of metallic surfaces with bioorganic molecular assemblies is of great interest, especially in the field of biosensors and biomimetics. In this context, the project is intended to explore the electrochemical response of the glutathione modified Cu(hkl) electrodes and its potential applications in neurotransmitters detection. The study of the self-assembled monolayer of glutathione on Cu(hkl) surfaces requires an analysis of the conformational structure of the adsorbed molecule, which is closely related to the action of an electroactive species in the electrolyte solution. The complexity of the interfacial phenomena requires an interdisciplinary approach. This is intended to be mainly achieved by correlating the information concerning the electrochemical reactivity of the glutathione-covered Cu(hkl) substrates available by cyclic (CV), differential pulse voltammetry (DPV), electrochemical impedance spectroscopy (EIS) and scanning electrochemical microscopy (SECM), the surface chemistry furnished by X-ray photoelectron spectroscopy (XPS) and surface morphology provided by atomic force microscopy (AFM). In addition, density functional theory (DFT) calculations will be made for a better understanding of adsorption process by taking into account different ionic forms of GSH (zwitterions, cations, anions) and possible orientations as well as the interaction between glutathione and neurotransmitters.

Milestones:

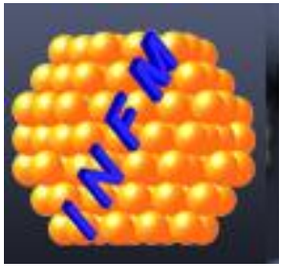
- Finding the most suited conditions to obtaine stable glutathione modified Cu(hkl) electrodes.

- Exploration of the pH effects on the electrochemical behavior of the GSH adsorbed on Cu (hkl) electrodes.

- Examination of the electron transfer (ET) kinetics and the surface reactivity of the film in the presence of redox probes.

- Investigations on the electrochemical interaction of the GSH-modified Cu (hkl) electrodes with neurotransmitters (such as dopamine / serotonin).

Collaboration:



National Institute of Materials Physics

Dr. Mihail F. Lazarescu

Dr. Catalin Negrila

- XPS investigations
- Working electrode preparation

Project Budget (lei):

Budget chapter (expenses)	2013 (lei)	2014 (lei)	2015 (lei)	Total (lei)
Salaries	38.858,89	60376,00	37.330,00	136.564,89
Inventory	54.603,05	32.116,75	24141,13	110.860,93
Mobility	6.538,06	8.157,25	10605,87	25.301,18
Overhead	10.000,00	10.065,00	7.208,00	27.273,00
Total	110.000,00	110.715,00	79.285,00	300.000,00

Project Objectives for 2013

- Chemical modification of Cu and Cu(hkl) electrodes with self-assembled monolayers (SAM) of glutathione.

- XPS investigations on Cu(hkl) substrate chemical composition of the glutathione SAM.

- AFM investigations on Cu(hkl) and GSH/Cu(hkl).

- Electrochemical investigations at Cu and Cu(hkl) bare and glutathione-modified electrodes.

Activity report 2013:

- Spontaneously formed self-assembled layers were prepared by immersion of the previously polished and chemical / electrochemical etched Cu(poly) / Cu(hkl) substrate into 2.5 mM aqueous solutions of glutathione for 20 h.

- XPS investigations showed the protective role of the tripeptide for Cu surfaces and the presence of neutral and zwitterions forms into the adsorbed layers.

- AFM images indicated high roughness due to the presence of oxides for clean surfaces and ordered structures at GSH /Cu(hkl).

- Electrochemical investigations (cyclic voltammetry, dynamic capacity, impedance spectroscopy) pointed out an electro-active adsorbed layer of GSH in sodium perchlorate solutions.

Project Objectives for 2014

- Electrochemical investigations at glutathione-modified Cu(hkl) electrodes at different pH solutions.

- Microstructural (AFM) and/or XPS investigations on the changes in the morphology and chemistry of modified electrodes after the electrochemical measurements.

- DFT calculations of different ionic forms of glutathione (neutral, anion, dianion) on the Cu(hkl) surfaces, for a better understanding of the orientation of adsorbed molecules.

- Electrochemical investigations on the changes caused by redox probes at glutathione modified Cu(hkl) electrodes.

- Microstructural (AFM) and/or XPS investigations on the changes in the morphology and chemistry of modified electrodes after the electrochemical measurements in presence of redox probe.

Activity report 2014:

- Electrochemical investigations at Cu(hkl)/GSH electrodes revealed a pH dependent behavior. At lower pH the charge transfer is favored at both limits of the potential range and the protonated forms of the amine and carboxyl moieties result in an increase of the double layer capacity. At higher pH an adsorption process coupled with a partial charge transfer was observed.

- XPS investigations of the modified electrodes after the EIS measurements showed that the electrochemical bias brings about the formation of Cu^{2+} species and the disappearance of NH_3^+ species regardless the solution pH value.

- DFT calculations pointed out that the neutral and anion forms of GSH have a 'Y' shape and the dianion a 'T' shape, that is more closer to the surface. The adsorption site most favorable energetically is the bridge site and the ordering of binding energy is dianion > anion > neutral.

- Electrochemical investigations showed that the GSH adsorption shifted the potential of the redox probe to more negative values with respect to the Cu(hkl) bare electrode.

- AFM and XPS investigations indicated that the presence of the redox probe induced changes in the morphology and chemistry of the adsorbed layers both before and after the electrochemical bias.

Project Objectives for 2015:

- Electrochemical investigations on the changes do to the presence of dopamine / serotonin neurotransmitters at glutathione modified Cu(hkl) electrodes.

- Microstructural (AFM) and/or XPS investigations on the changes in the morphology and chemistry of modified electrodes after the electrochemical measurements in the presence of dopamine / serotonin neurotransmitters .

- DFT calculations of the interactions between the glutathione and dopamine / serotonin neurotransmitters molecules.

Activity report 2015:

- The presence of neurotransmitters in the solution brings chances in the electrochemical behavior. A new redox couple appears at more negative potential with adsorption - controlled electron transfer and only the presence of dopamine shifts to positive values of the potential the redox couple of glutathione. The variation of phase angle with the potential bias indicated reversible (in presence of dopamine) / irreversible (in presence of serotonin) changes in the ionic properties of the adsorbed layers.

- XPS investigations indicated that the presence of dopamine/serotonin is leaded to appears of –N-Cu species and after the potential bias to the disappearance of NH_3^+ species and the formation of Cu^{2+} species in the dopamine presence / the increases of the peak at 530.3 eV from the O-1s spectra in the serotonin presence.

- AFM investigations indicated that the presence of the neurotransmitters induced changes in the morphology of the glutathione layers both before and after the electrochemical bias.

- DFT calculations of the interactions between the glutathione and dopamine / serotonin molecules pointed out the formation of an association complex. The most stable systems have a compact arrangement.

Results Dissemination:

- Journees d'Electrochimie 2013, Paris, France, July 8-11th, 2013

Studies of metal electrodes (Au, Cu) covered with glutathione by cyclic voltammetry and impedance spectroscopy electrochimicque
A. M. Toader, A. Latus, E. Volanschi, V. Lazarescu

- 15th International Conference on Physical Chemistry, ROMPHYSCHEM 15, September 11-13, 2013, Bucharest

pH Effects on the electrochemical behavior of glutathione modified Cu electrodes
A. M. Toader, C. Negrila, M. Anastasescu and V. Lazarescu

- XVIth Iberic Meeting of Electrochemistry, 30th June – 2nd July, 2014, Aveiro, Portugal

Electrochemical behavior of the glutathione self-assembled monolayer on Cu(100) in the presence of a redox probe
A. M. Toader and V. Lazarescu

Results Dissemination:

- Journees d'Electrochimie 2015, Rome, Italy, July 6-10th, 2015

Effects of the potential applied on the self-assembled monolayer of glutathione on the electrode structure of the Cu(100)
A. M. Toader, V. Lazarescu

- 10th International Frumkin Symposium on Electrochemistry, Moscow, Russia, October 20-23th, 2015

Electrochemical behavior of the glutathione self-assembled monolayer on Cu(100) in the presence of neurotransmitters
A. M. Toader, C. Negrila, V. Lazarescu

Training of the Project Director:

- Impedance Course, 29th June – 2nd July, 2014, Aveiro, Portugal

- 1st - 14th June 2014, Institute of Theoretical Chemistry, Ulm University, Germany, working stage - theoretical calculations