Adsorption of 3-Mercaptopropionic acid (3-MPA) and 16-Mercaptohexadecanoic acid (16-MHDA) at Platinum Surfaces

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Gold surfaces can anchor sulfur organic groups, such as thiols (RSH) and disulfides (RSSR), where R is an alkyl chain. This is the prototype of supramolecular system using self-assembled monolayers (SAMs)[1]. It is used for the functionalization of extended surfaces and for the preparation of monolayer protected clusters [(2,3)]. SAMs give a the wealth of potential technological applications, including corrosion inhibition, lithography, lubrication, catalysis, and molecular recognition. The chemical processes accompanying the formation of the adsorbed species are largely unknown, the final interface and the nature of the head groups have not been characterized to satisfaction, and the existence of dimers versus thiolates in the full-coverage regime of Au surfaces is still under debate[(4,5)].

This research studies how mercapto terminated alkyl chains can modify the surface of platinum electrodes and create nanometer size holes. The amount of molecules on the surface is controlled electrochemically on the metallic surface. Surfaces analysis techniques such as X-ray photoelectron spectroscopy (XPS), quartz crystal microbalance (QCM), and electrochemistry were used to study the composition and structure of the self- assembly of 3-MPA and 16-MHDA on platinum surfaces in ethanol solution. By Cyclic Voltammetry (CV) it is found that the modification of platinum electrodes surfaces with 16-MHDA decreases the wave corresponding to Pt oxide formation. Also, hydrogen adsorption is notably suppressed. On the other hand, the CV of $Fe(CN)_6^{3-}$ at a 16-MHDA changed from an electrochemically reversible shape to a capacitive shape (Figure 1). The 16-MHDA system on platinum is free of mass transfer effect and the redox couple cannot contact the platinum surface. Also it was proved by CV that the adsorption of the 3-MPA and 16-MHDA on platinum is affected by the initial applied potential creating partial coverage of the thiol molecule on the surface. The QCM was used in this work to study the deposition of 3-MPA and 16-MHDA from ethanol solution onto MAXTEK® platinum electrodes. XPS has been widely used to study the composition of self-assembled thiols. We performed XPS measurements to study the composition and structural orientation of self-assembled 3-MPA and self-assembled 16-MHDA onto platinum surface.

Also, high-resolution XPS studies showed the presence of S-Pt bonds, indicating that 3-MPA and 16-MHDA films are adsorbed to the platinum through the sulfur functionality. Curve-fitted high-resolution XPS spectra, of the C (1s) region, of the 3-MPA/Pt system and 16-MHDA system were made in order to be able to differentiate the carbon species present at the platinum surface.

We are grateful to National Science Foundation (NSF)-EPSCoR, grant number (OSR-9452893) and to the Consejo Nacional de Investigación Científica y Tecnológica, CONICIT from Venezuela.

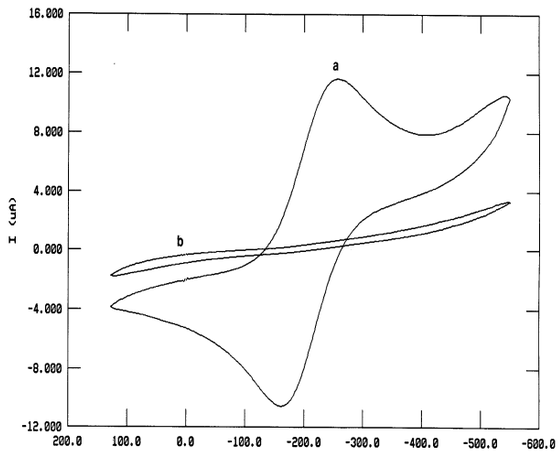

Figure 1. Cyclic Voltammograms of (a) platinum disk electrode in 2.5 mM $K_3Fe(CN)_6$, and (b) 16-MHDA/Pt in 2.5 mM $K_3Fe(CN)_6$. Scan rate 100mV/s.

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