Electrochemical impedance spectroscopy study of carbohydrate-terminated alkanethiol monolayers on nanoporous gold: Implications for pore wetting

Abeera Sharma, Jay K. Bhattarai, Swati S. Nigudkar, Salvatore G. Pistorio, Alexei V. Demchenko, Keith J. Stine

PII: S1572-6657(16)30533-1
DOI: doi: 10.1016/j.jelechem.2016.10.013
Reference: JEAC 2880

To appear in: *Journal of Electroanalytical Chemistry*

Received date: 6 July 2016
Revised date: 6 October 2016
Accepted date: 7 October 2016

Please cite this article as: Abeera Sharma, Jay K. Bhattarai, Swati S. Nigudkar, Salvatore G. Pistorio, Alexei V. Demchenko, Keith J. Stine, Electrochemical impedance spectroscopy study of carbohydrate-terminated alkanethiol monolayers on nanoporous gold: Implications for pore wetting, *Journal of Electroanalytical Chemistry* (2016), doi: 10.1016/j.jelechem.2016.10.013

Electrochemical impedance spectroscopy study of carbohydrate-terminated alkanethiol monolayers on nanoporous gold: Implications for pore wetting

Abeera Sharma, Jay K. Bhattarai, Swati S. Nigudkar, Salvatore G. Pistorio, Alexei V. Demchenko, and Keith J. Stine

Department of Chemistry and Biochemistry, University of Missouri–Saint Louis, Saint Louis, MO 63121

Abstract

Electrochemical impedance spectroscopy (EIS) is used to compare the apparent electron transfer rate constant (k_{app}) for a series of alkanethiol and of carbohydrate-terminated alkanethiol self-assembled monolayers (SAMs) on both flat gold and on nanoporous gold (np-Au). Using the surface area for np-Au determined by oxide stripping, the values of k_{app} for the alkanethiol modified np-Au are initially over two orders of magnitude smaller than the values found on flat Au. This result provides evidence that the diffusing redox probe $Fe(CN)_6^{3-/4-}$ only accesses a fraction of the np-Au surface after alkanethiol modification suggesting very limited wetting of the internal pores due to the hydrophobic nature of these surfaces. In contrast, for np-Au modified by carbohydrate-terminated (mannose or galactose) alkanethiols the values of k_{app} are about 10–40 fold smaller than on flat gold, suggesting more extensive access of the diffusing redox probe within the pores and better but still incomplete wetting, a result also found for modification of np-Au with mercaptododecanoic acid. A short chain PEG thiol derivative is found to result in a comparison of k_{app} values that suggests nearly complete wetting of the internal pores for this highly hydrophilic derivative. These results are of significance for the potential applications of SAM modified np-Au in electrochemical sensors, especially for those based on carbohydrate–protein recognition, or those of np-Au modified by SAMs with polar terminal groups.