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

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## 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  $\text{Fe}(\text{CN})_6^{3-/4-}$  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.

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