

Distance-Dependent Electron Transfer at Passivated Electrodes Decorated by Gold Nanoparticles

Abbas Barfidokht, Simone Ciampi, Erwann Luais, Nadim Darwish and J. Justin Gooding*
School of Chemistry, The University of New South Wales, Sydney NSW 2052, Australia

The phenomenon of nanoparticles attached to an electrode passivated by an organic layer allowing efficient electron transfer between redox species in solution and the underlying electrode to be restored has resulted in Chazalviel and Allongue proposing a theory [Chazalviel, J.-N.; Allongue, P. *J. Am. Chem. Soc.* 2011, 133, 762–764] to explain this phenomenon. The theory suggests that with electrode-organic layer-nanoparticle constructs, high exchange current densities, compared with when the nanoparticles are absent, results in the rate of electron transfer being independent of the thickness of the organic layer until a threshold thickness is exceeded. Thereafter, the thicker the organic layer, the slower the rate of electron transfer. Herein we provide the first experimental data to support this theory using a single experimental system that can show the transition from thickness independent electron transfer kinetics to distant dependent kinetics. This was achieved using ethylenediamine electrodeposited on a glassy carbon electrode. Different numbers of deposition cycles were applied in order to fabricate different thicknesses of the organic film. The deposited films showed progressively greater blocking abilities toward ruthenium hexamine, as a redox active probe in solution, as the films got thicker. Electron transfer kinetics of nanoparticle decorated surfaces showed a change from thickness independent to thickness dependent as the organic layer exceeded an average thickness of 20 Å [1]. Moreover, the effect of the homogeneity of the organic film on the efficient electron transfer reaction at these NP-assemblies was also assessed in a comparative study, applying poly(phenylenediamine), which revealed that the polymer system must be able to form uniformly continuous films even at thicknesses below 20 Å to fully exploit the potential of electrode/organic layer/NP constructs [2]. These results provide important insights into designing analytical devices based on these nanoparticle-assemblies.

References:

- [1] A. Barfidokht, S. Ciampi, E. Luais, N. Darwish, J. J. Gooding, *Anal. Chem.* 2013, 85, 1073–1080.
[2] A. Barfidokht, S. Ciampi, E. Luais, N. Darwish, J. J. Gooding, *ChemPhysChem*, DOI: 10.1002/cphc.201300047.