

**THE BIOCATALYTIC CHARGING OF AU NANOPARTICLES ASSOCIATED WITH SELF-ASSEMBLED MONOLAYERS. A SURFACE PLASMON RESONANCE SPECTROSCOPY STUDY.**

Vladimir Chegel<sup>1</sup>, Yuriy Shirshov<sup>1</sup>, Oleg Lioubashevsky<sup>2</sup>, Fernando Patolsky<sup>2</sup>, Eugenij Katz<sup>2</sup>, Itamar Willner<sup>2</sup>

1) Institute of Physics of Semiconductors, National Academy of Science of Ukraine  
Prospect Nauki, 41, Kiev, Ukraine

2) Institute of Chemistry, The Farkas Center for Light-induced Processes, The Hebrew University of Jerusalem, Jerusalem 91904, Israel  
E-mail: [vche111@yahoo.com](mailto:vche111@yahoo.com) [che@isp.kiev.ua](mailto:che@isp.kiev.ua)

The quantum charging of Au nanoparticles by electrochemical means is a subject of extensive research[1]. The interactions of localized surface plasmon of Au-nanoparticles and, specifically, of charged Au-nanoparticles, with the surface plasmon excited on the surface of the bulk gold is of special interest and could be studied by surface plasmon resonance (SPR) technique. Surface plasmon resonance spectroscopy is a versatile method to probe and characterize physico-chemical changes on thin films such as Au-surfaces [2]. The ability to probe chemical modifiers on surfaces by means of SPR turned the method into a useful analytical tool, and different biorecognition processes, such as protein binding or DNA hybridization were followed by SPR measurements[3]. In most of these studies, the chemical modification alters the refractive index and film thickness, and these changes affect the resulting SPR spectra.

In presented work the enzyme glucose oxidase (GOx) is reconstituted on a flavin adenin dinucleotide, cofactor-functionalized Au-nanoparticle (Au-NP), 1.4 nm, and the GOx/Au-NP hybrid is linked to a bulk Au-electrode by a short dithiol, 1,4- benzenedithiol or a long dithiol, 1,9-nonanedithiol monolayers. The reconstituted GOx/Au-NP hybrid system exhibits electrical communication between the enzyme redox-cofactor and the Au-NP core. Since the monolayers linking the Au-NPs to the bulk Au-electrode provide an electron tunnelling barrier, the electron transfer from the enzyme redox center to the Au-NPs occurring upon the biocatalytic oxidation of glucose results in the Au-NPs charging. The charging of the Au-NPs alters the plasma frequency and the dielectric function of the Au-NPs leading to the changes of the dielectric function of the whole interface. These are reflected in the pronounced shifts of the surface plasmon angle,  $\theta_{sp}$ , in the SPR spectra. As the biocatalytic charging phenomenon is controlled by the concentration of glucose, the changes in the  $\theta_{sp}$  values correlate with the concentration of glucose.

The tunnelling barrier generated by the short dithiol is lower than that generated by the long dithiol and consequently the steady-state biocatalytic charging of the Au-NPs is higher with long dithiol monolayer used as a molecular bridge. The biocatalytic charging process is characterized by following the capacitance of the GOx/Au-NP interface, and by monitoring the potential generated on the bulk Au-electrode. The biocatalytic charging of the Au-NPs linked to the Au-electrode by the short or long dithiols increases the capacitance of the interface by 22% or 80%, respectively.

The charging of the GOx/Au-NPs is also accomplished in the absence of glucose by the application of an external potential on the electrode. The analysis of the results enable us to estimate the number of electrons per Au-NP at variable concentrations of glucose and with the different GOx/Au-NP architectures assembled on the electrode.

## References:

- [1] J.F Hicks; D.T Miles; R.W. Murray, *J. Am. Chem. Soc.* **124** (2002) 13322.  
 [2] W.Knoll, *Annu. Rev. Phys. Chem.* **49** (1998) 569.  
 [3] J.Rao; L.Yan; B.Xu; G.M.Whitesides, *J. Am. Chem. Soc.* **121** (1999) 2629.

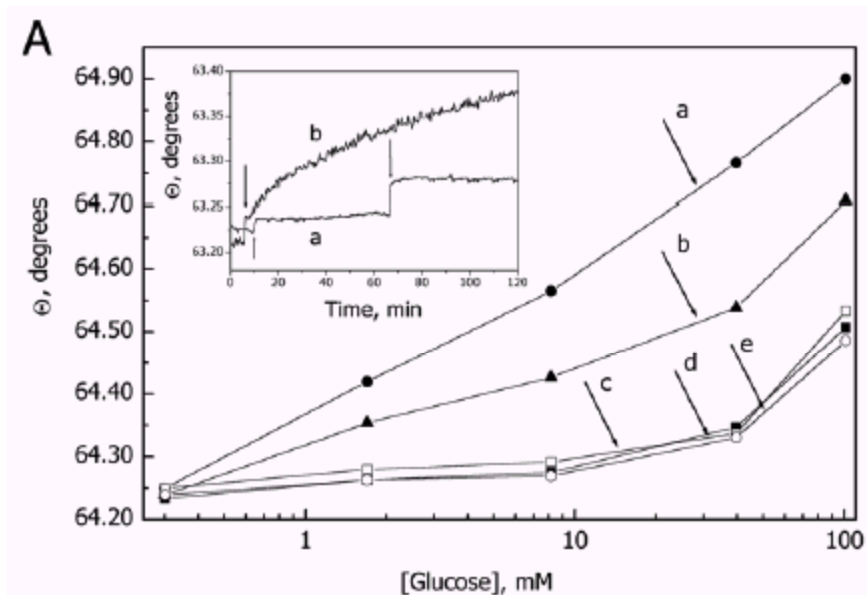


Figure 1. Shifts of the plasmon angles induced upon addition of different concentrations of glucose to: (a) The aligned GOx-reconstituted Au-NPs bridged to the Au-electrode with the long dithiol. (b) The aligned GOx-reconstituted Au-NPs bridged to the Au-electrode with the short dithiol. (c) The non-aligned GOx randomly covalently bound to the Au-NPs bridged to the Au-electrode with the long dithiol. (d) The NP-array bridged to the Au-electrode with the long dithiol. (e) The Au-electrode surface modified with the long dithiol monolayer. Inset: (a) Time-dependent changes of the plasmon angle of the non-aligned GOx/Au-NP system bridged with the long dithiol monolayer upon the addition of 0.3 mM and 1.6 mM glucose (injection times are shown by the arrows). (b) Time-dependent changes of the plasmon angle of the aligned GOx/Au-NP system bridged with the long dithiol monolayer upon the addition of 1.6 mM glucose (injection time is shown by the arrow).