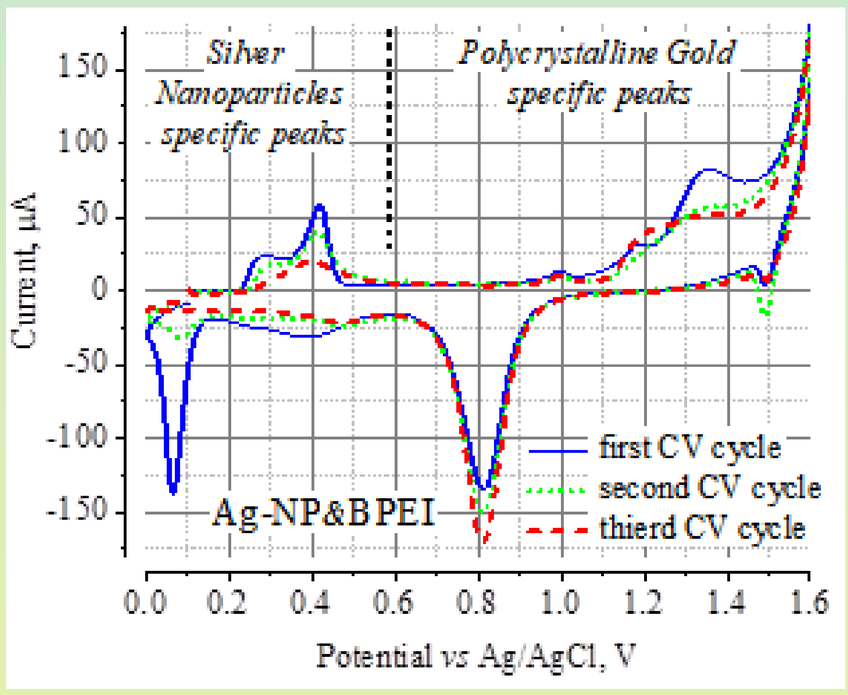
ELECTROSTATIC SURFACE FUNCTIONALIZATION OF PHYSICAL TRANSDUCERS OF (BIO)CHEMICAL SENSORS: THIOCYANATE-MODIFIED GOLD INTERFACE

Borys A. Snopok[1,2,*]
Arwa Laroussi[1]
Tetyana V. Snopok[2]
Shavkat Nizamov[1]

Surface charging has been widely used in various functionalization technologies to create (bio)chemical sensing layers. This is due to the unique ability of electrostatic interactions not only to immobilize the desired receptors, but also to cause their uniform distribution over the surface owing to in-plane electrostatic repulsion. Self-assembling protocols based on self-limiting aggregation of electrostatic arrays are widely used in sensor science from classical layer-by-layer deposition to electrostatic levitation of proteins over the surface of thiocyanate-modified gold. Thiocyanates are extremely promising compounds for creating an ultrathin buffer layer on the surface of SPR, QCM, etc. transducers, due to their small size and ability to self-organize into a monolayer on the surface of gold.

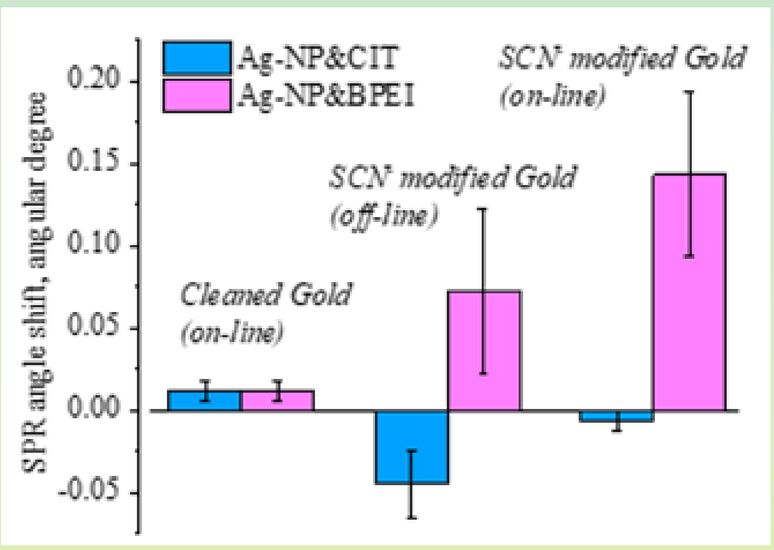
Despite the apparent simplicity of thiocyanate structure (complex compounds with the $^{-}S{-}C{\equiv}N$ or $S{=}C{=}N^{-}$ anion), they continue to be the subject of active scientific debate: an important issue is the experimental confirmation of the presence of the supposed effective negative charge of their self-organizing monolayer

To determine the sign of the surface charge of gold modified by thiocyanate monolayer, we used 60 nm organic stabilized silver nanoparticles as an electrostatic probe with various surface functionality, namely, branched PolyEthylenImine (AgNP&BPEI, ζ-potential is c.a. +60 mV at pH 6), PolyVinyl-Pyrrolidone polymer (AgNP&PVP, c.a. -40 mV), Poly(Ethylene Glycol) (AgNP&PEG, c.a. -30 mV), and classical citrate coating (AgNP&Cit, c.a. -50 mV).



Cyclic voltammograms recorded for a polycrystalline gold electrode with previously adsorbed AgNP&BPEI in 0.05 M H_2S0_4 at 25◦C in a conventional three-electrode cell setup

The processes of adsorption of silver nanoparticles were studied using surface plasmon resonance and UV-VIS spectroscopy, cyclic voltammetry; adsorbed silver particles were visualized using wide-field Surface Plasmon Resonance Microscopy (wf-SPRM)



Typical SPR responses achieved after 15 min of AgNP adsorption on the various surfaces. The "off-line" samples were prepared in advance, unlike the "on-line" samples, the purification and modification of which was carried out in a single experiment with the adsorption reaction

… The findings obtained are consistent with the hypothesis that the Gold surface modified with thiocyanate behaves as a negatively charged object in processes drive by electrostatic interactions. The nature and mechanism of formation of such a charge still remain unclear. Possible explanations include the higher electronegativity of nitrogen and the stabilization of the $S{=}C{=}N^{-}$ tautomer upon formation of the sulfur bond with gold as well as potential participation of other ions in the formation of a thermodynamically stable surface structure. These issues still require detailed theoretical consideration

Thiocionate modified Gold surface (a) | After injection of Ag-NP&CIT suspension (b) | After injection of Ag-NP&BPEI suspension (c)

Differential wf-SPRM images of SCN-modified gold surface in water (a), the same after addition of 60 nm citrate stabilized AgNP&CIT (b) or AgNP&BPEI suspension (c). Image size: 1900 × 1900 pixels (field of view is c.a. 0.9×0.9 mm^2). The inset shows the optical image of nanoparticles caused by the processes of interference of surface waves of plasmon-polariton excitations

This work has received funding through the MSCA4Ukraine project (Grant ID 1119494), which is funded by the European Union

[1]Nanobiotechnology - Institute of Biotechnology, Brandenburg Technical University Cottbus-Senftenberg, Universitätsplatz 1, Senftenberg, 01968, Germany

[2]Optoelectronics - V.E. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 pr. Nauki, Kyiv, 03028, Ukraine

[*]Prof. Borys Snopok
snopok@b-tu.de
snopok@isp.kiev.ua
b_snopok@yahoo.com