Application Note # 140

Self-assembly of Gold Nanoparticles Measured with MP-SPR

Gold nanoparticles were immobilized on a monolayer self-assembled on gold. Functional groups on the chain ends of the monolayer facilitated an anchoring of gold nanoparticles to the layer. Multi-Parametric Surface Plasmon Resonance (MP-SPR) enabled a real-time measurement of the binding of the gold nanoparticles to the surface layer.

Introduction

Gold nanoparticles (AuNPs) exhibits interesting optical and electronic properties that find application in sensors, catalysis, electronics, photonics, solar cells, cancer diagnosis and therapy. Controlled attachment of Au nanoparticles at a solid interface is required for many of these applications. Although many methods have been developed to fabricate Au nanoparticle assemblies, developing simple and effective routes is still very attractive. Usually, the immobilization can be performed using a covalent or an electrostatic interaction between the nanoparticles and the substrate. In this study functional molecules are used for linking gold nanoparticles to a solid surface. Molecules possessing functional groups can be attached to the solid surface in a controlled manner and permits nanoparticle immobilization (Fig.1).

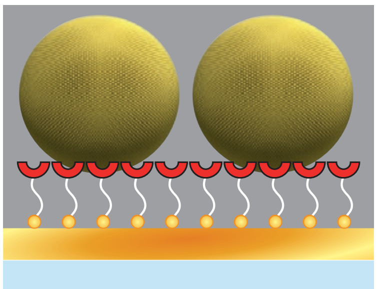

Figure 1. Cartoon showing the anchoring of AuNPs on a monolayer self-assembled on gold.

The SPR phenomenon is based on free electrons resonating at a metal surface, which are excited with visible or near infrared light. There is an absorption maximum as a function of the angle of the incident light, and the SPR phenomenon is highly dependent on the dielectric constant near the metal surface. Any changes near the surface, such as nanoparticles binding, change the angle of the absorption maximum. Using the SPR phenomenon, the Multi-Parametric Surface Plasmon Resonance (MP-SPR) is a sensitive tool for measuring real-time surface interactions and layer properties. MP-SPR measures in a wide angular range and the whole SPR curve is monitored which enables observing not only the SPR peak minimum position, but also other parameters as peak minimum intensity enabling measurements with light absorbing samples as metal nanoparticles.

Materials and methods

AuNPs with an average diameter of 50 nm were prepared according to a method by Turkevich and modified by Frens´. The particles were washed with water and the pH of the solution was adjusted to a pH of 6.5. Bi-functional molecules bearing groups for anchoring to gold were self-assembled on gold sensor slides to facilitate SPR measurements. The sensor slides were cleaned in a hot hydrogen peroxide/ammonium hydroxide/water solution (1/1/5) and rinsed with water before assembling of the monolayer.

BioNavis SPR Navi™ 210A-L instrument was used to determine the binding of AuNPs to the surface monolayer at two wavelengths, 670 and 785nm. The monolayer surface was washed with water, the baseline was measured and the AuNPs were injected over the surface with a speed of 10 µL/min for about 10 minutes. AuNPs were injected three times and rinsed with water in between every injection.

Results and discussion

A minimum in the reflectivity corresponding to the surface plasmon resonance effect for the two wavelengths (670 and 785 nm), but at different internal incident angle can be seen in Figure 2a and b (1st curve to the left). The resonance curve at 670 nm was broader than that at 785 nm. When AuNPs were injected over the surface there was shift in the angular position of the curves, but also a shift in minimum intensity of the curves (Fig. 2 and 3). This can be ascribed to a change in the actual refractive index of the gold layer when gold nanoparticles are deposited on the surface, but also to the surface plasmon effect of the nanoparticles.

MP-SPR enables a detection of even large shift in the resonance angle due to the wide angular range measured. The whole SPR curve can be monitored which enables observing not only the SPR peak minimum position during binding of the nanoparticles to the surface layer, but also the shift in peak minimum intensity and total internal reflection (TIR). TIR region is sensitive to the optical properties of the media outside the evanescent field (bulk), whereas the SPR peak intensity is giving information on light absorption and the homogeneity of the layer. A shift in the resonance curve towards larger incident angles can be observed. The resonance curves become wider, but also the intensity of the resonance minima shifts upwards.

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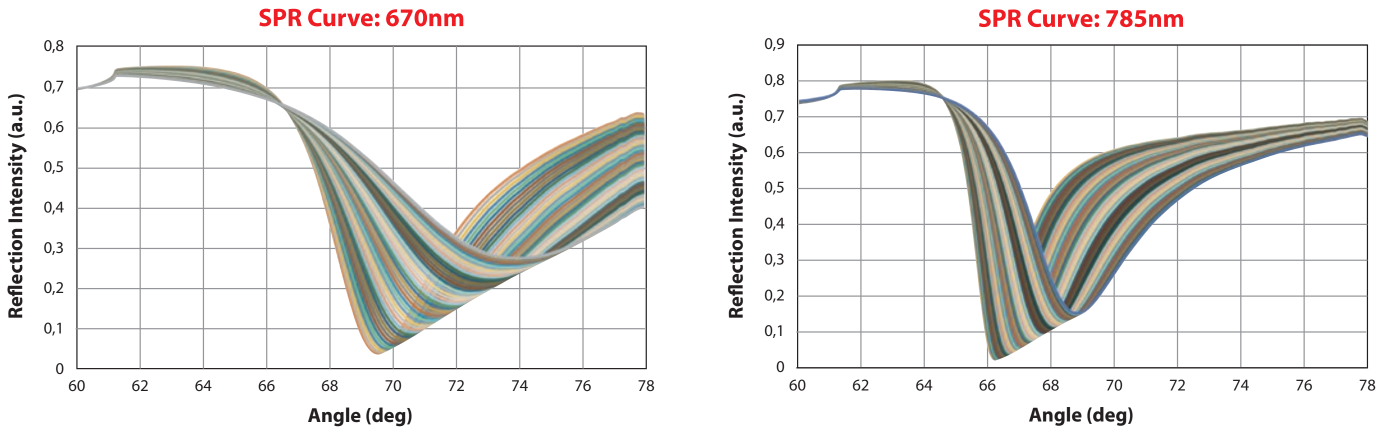

Figure 2. SPR resonance curves at 670nm (left side curve) and 785nm (right side curve) for binding of AuNPs to monolayers assembled on a gold surface. Curves were obtained from left to right as gold nanoparticles interacts with the surface layer.

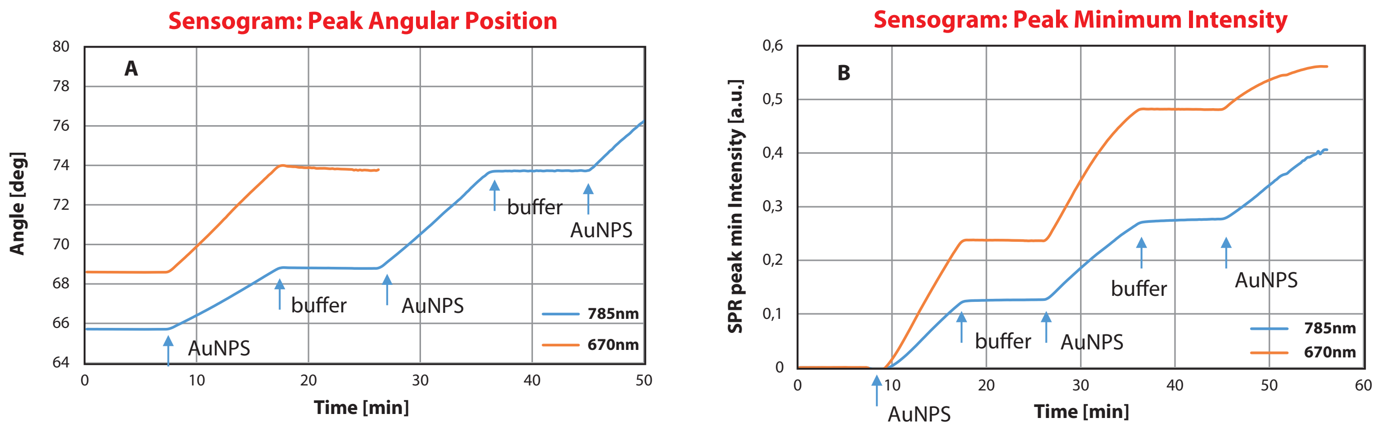

Figure 3. Shift in a) SPR peak angular position and b) peak minimum intensity during binding of AuNPs to monolayers assembled on a gold surface. AuNPs were injected three times over the surface and the surface was rinsed with buffer in between.

Conclusions

Monolayers with functional groups assembled on a gold surface can be used for coupling of gold nanoparticles. In this study MP-SPR turned out to be a unique method for determining the deposition of metal nanoparticles to the surface layer in real-time. AuNPs exhibit strong surface plasmon resonances and even a large response could be observed by MP-SPR when nanoparticles were interacting with the surface layer. Functional groups on the chains ends enable an anchoring of gold nanoparticles or even embedding into the chains. MP-SPR is a unique tool for studying metal nanoparticles for applications in sensors, electronics, photonics, solar cells or cancer diagnosis and therapy.

References:

[1] M. S. Khan, G. D. Vishakante, S. H,. Advances in Colloid and Interface Science, 199–200, 44-58, 2013.

[2] M. Notarianni, K. Vernon, A. Chou, M. Aljada, J. Liu, N. Motta Solar Energy 106, 23-37, 2014.

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Recommended instrumentation for reference assay experiments
SPR Navi™ 200, 210A or 220A with additional wavelength (-L)
Sensor surfaces: Gold, other metal or inorganic coating
Software: SPR Navi™ Control, SPR Navi™ DataViewer, SPR Navi™ LayerSolver

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