



Propagating and localized surface plasmon resonance sensing – A critical comparison based on measurements and theory



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ABSTRACT

With its potential for ultrasensitive, label-free detection of molecular interactions, sensing methods based on the surface plasmon resonance (SPR) effect fully meet the requirements for modern analytical techniques. Already established by using propagating SPR in thin gold layers, the last years witnessed the emergence of another related technique utilizing extremely miniaturized noble metal sensor structures, based on a localized SPR.

This paper provides a critical comparison of these kinds of SPR sensing, reviews the foundation of both general approaches, presents experimental data on exactly the same molecular model system using both techniques, as well as theoretical considerations in order to allow reasonable comparison. It highlights the specific features and effects, in order to provide guidance in choosing the right technique for given bioanalytical tasks.

The study demonstrated the capabilities of LSPR for sensing of molecular layers even in the lower nanometer dimension. For the detection of small (bio)molecules, smaller particle diameters are favored regarding highest sensitivity. It also presents an approach to obtain refractive index and the thickness of a molecular film by analyzing the signal response of plasmonic sensors with metal nanoparticles. Moreover, an additional method for the improvement of the parameters' determination is introduced.

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1. Introduction

Detection of biomolecular binding, the adsorption of thin bio-films or conformational changes of macromolecules is of high interest in various branches of biology, medicine and pharmacy [1]. One possible detection method is based on the optical spectroscopy of metallic structures exhibiting surface plasmon resonances [2]. It represents a label-free approach, with rather high sensitivity in comparison to other label-free techniques. In this detection scheme, the molecular binding occurs near the surface of the metallic structures, in which the light is captured in the form of surface plasmon polaritons. The excitation of the surface plasmon polaritons requires specific illumination conditions such as illumination wavelengths and incident angles. These excitations are also strongly sensitive on the presence of the molecules on the surface, and therefore, the changes in the plasmon excitation indicate molecular adsorption events. The established method of such sensing (a wide range of commercial products is available on the market [3,4]) is by using thin smooth metallic layers [5,6] (propagating surface plasmon resonance – pSPR), which achieve remarkably low limits of detection. However, this basic geometry of the metallic structure does not reach its maximal sensitivity for very small molecules (few nanometers), because the spatial confinement of the plasmon modes (~several

hundred nm) is still much larger than these molecules (~few nm) and complex immobilization strategies using thick hydrogels are used to compensate the spatial mismatch. Avoiding the critical surface chemistry, this could be also overcome by either structuring the smooth layers or by using more spatially confined nanostructures (exhibiting localized surface plasmon resonances – LSPR) instead of metallic layers [7–12].

The first objective of our work was to compare the signal responses from plasmonic sensors with different geometries (implicating different spatial confinement of the generated plasmons). The second objective was to compare signal responses from sensors with different numbers of nanostructures (ensemble versus single nanostructure). In order to make the comparison, for both measurements the same model system is used, namely the sequential adsorption of thin polymer layers of defined thickness and number (also known as layer-by-layer technique). Additionally, we were interested if both thickness and refractive index of the adsorbed layer can be obtained by adjusting the volume of the plasmon.

The results of these direct comparisons reveal the advantages and disadvantages of each plasmonic transducer and their best applicability. The information about thickness and refractive index of the adsorbed layer would be quite useful, because it can be used to determine the density of the adsorbed layers. Thereby, for example, conformational changes of molecules in the layer could be monitored. Unfortunately, the established plasmonic sensing using gold films yields only the average mass adsorbed on the surface. However, as shown by Hull

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[13], the conformational changes of proteins can be deduced if there is enough spatial confinement of the plasmon.

In the article we compare plasmonic transducers with different spatial confinement: a planar gold layer, and spherical gold nanoparticles of different sizes. We analyzed the responses of these systems and experimentally measured their responses to the subsequent adsorption of molecular layers. We showed that the nanoparticles with a short plasmon confinement yield a non-linear dependence of the signal on the number of deposited layers. By analyzing the non-linear response of the signal, the refractive index and the thickness layer can be obtained in principle. We experimentally demonstrate that adsorption of individual layers can be detected even on a single nanoparticle and discuss the method of obtaining refractive index and thickness of the layer adsorbed on single nanoparticle (NP) level.

Briefly, we present the reader experimental data demonstrating the effect of spatial confinement of the plasmon on the signal response with identical adsorption layers and show the determination of the layer thickness and refractive index of these layers by analyzing the non-linear signal response.

2. Background

2.1. Geometry of pSPR and ISPR detection

In the following section the detection principles on thin metallic layers and metallic spherical nanoparticles are recalled and an effective refractive index is defined in order to compare the signals from the pSPR and ISPR systems. Standardly, the plasmon waves in a thin metallic layer are excited by the illumination of the metallic films on its back side attached to a prism with a high refractive index (Kretschmann configuration see Fig. 1). If the condition of momentum conservation for the illumination light and the plasmon (angle of incidence) and the condition of the energy conservation (wavelength of the incident light) are fulfilled, the light is coupled to the plasmon waves (with evanescent field on the top side of the films), and the coupling leads to an intensity drop in the reflected light [14]. The pSPR instrument used in the experiments utilized a monochromatic light with a range of incident angles. Therefore, the plasmon excitation corresponds to the minimum in the graph of the reflectivity on the incident angle (see Fig. 1). Upon

the change of refractive index in the vicinity of the layer, the coupling condition changes and the peak's minimum shifts. On the other hand, the localized plasmons in metal nanoparticles are excited by direct illumination independently of the angle. If the condition on energy (wavelength of the incident light) is fulfilled than the light is coupled to the plasmon (with an evanescent field around the NP) and leads to intensity drop in the transmitted light [15]. Therefore, the plasmon excitation corresponds to the maximum observed in absorbance (see Fig. 1 – right side down). Upon changes of the refractive index in the vicinity of the NPs, the coupling condition changes and leads to a shift of the peak maximum.

2.2. Signal analysis from SPR and LSPR system

The electric field of plasmons excited on a thin metallic layer (pSPR) is analytically described by an exponential function [14] (Table 1, Eq. (1a)). The associated E-field is maximal at the interface and it decays exponentially into the dielectric bulk material. The rate of the decay is given by the parameter penetration depth (L_{pd}), which depends only on optical properties of both metal and bulk at a given wavelength. Although the E-field can be theoretically compressed to volumes much smaller below the diffraction limit, in real metals the compression is still much larger than sizes of typical biomolecules (~few nanometers). In our setup the theoretical value of L_{pd} was 318 nm. Also in case of a plasmon generated on a spherical nanoparticle (ISPR), the associated E-field is maximal at the surface of the particles and then steeply decays into the dielectric bulk. In the electrostatic approximation, the profile can be described by a simple analytical expression, where the decay depends on the order of the mode and the radius of the particle [16] (Table 1, Eq. (1b)). For 20 nm diameter gold nanoparticles for example, the E-field of dipole modes ($p = 1$) drops at approx. 3 nm down to the half. Therefore, the localized plasmon can be much stronger spatially confined than propagating plasmons, and this confinement is determined by the nanoparticle size. The electric fields' profiles (calculated with full electromagnetic theory) of propagating and localized plasmon on nanoparticles with different radius are displayed in Fig. 2 (right).

In order to compare the performances, the same signal has to be defined for both systems, what can be done in the following way: The

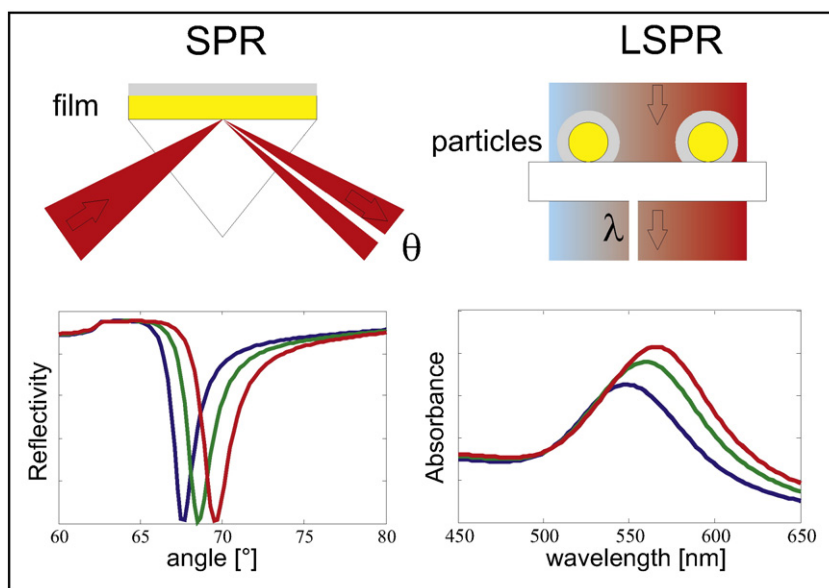


Fig. 1. Schematics of the sensing principle for the studied pSPR (left) and ISPR (right) systems. The graphs below show the calculated shift of dip/peak upon adsorption of 10 nm (green line) and 20 nm (red line) thick molecular film with an refractive index of 1.48 in water ($n = 1.33$), which mimics the properties of biomolecules.

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