Optimization of Localized Surface Plasmon Resonance (LSPR) Transducers

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Abstract
Nanogenstructured metal (e.g., gold, silver) surfaces exhibit an optical extinction band in the UV-vis-NIR range, attributed to collective charge-density oscillations (localized surface plasmon resonance, LSPR). The resonance band is sensitive to the refractive index near the nanostructures, changing upon analyte binding. LSPR transducer performance is commonly quantified using the refractive index sensitivity (RIS), i.e., change in the resonance wavelength associated with unit change of the refractive index of the bulk medium. Numerous studies have focused on maximizing the RIS. The response to layer adsorption decreases exponentially with the distance of the adsorbed layer from the nanostructure, as a result of the exponential decay of the plasmon evanescent field into the dielectric medium. Here we measure the decay length ($\Delta l$) and RIS ($m$) of a series of gold nanoparticle arrays evaporated on glass slides and annealed, to evaluate the transducers’ realistic performance.

Introduction
The response of LSPR transducers to analyte layer adsorption onto a recognition interface is modeled by Equation 1:

$$ R = m \Delta n \eta e^{-\frac{\Delta l}{l}} \left(1 - e^{-\frac{d_1}{l}}\right) $$

where $R$ is the response (resonance peak shift), $\Delta n$ is the difference of refractive index between layer and medium, and $d_1$ and $d_2$ are the recognition and analyte layer thicknesses.

Sensing Model

For maximal response to analyte adsorption we need to maximize $m$, and optimize $\Delta l$ to the sizes of the analyte and recognition layer.

Transducers

By evaporating different thicknesses of gold on glass, followed by thermal annealing (580 °C, 10 hr), we form films of different average nanoparticle size.

Results

$m$ and $\Delta l$ for various particle sizes

The decay length ($\Delta l$) and RIS ($m$) are strongly correlated. Large nanoparticle transducers, with high RIS, have large decay lengths, and hence produce only a weak response for thin adsorbate layers (occupying only a small fraction of their large sensing volume).

Response to thin adsorbate layers

We examined the response to adsorption of a thin analyte layer (2.1 nm thick), at different distances from the nanoparticle, simulating recognition interfaces of different thicknesses. Small nanoparticles produced the strongest response for thin adlayers (few nm), despite their lower RIS, owing to better matching between the adlayer thickness and the small decay length ($l = 3.9 \pm 0.3$ nm). For maximum sensitivity the transducer should be optimized to the recognition and analyte layer dimensions, taking into account both the RIS and decay length.

Reflection

Simple setup, stronger response

Both transmission and reflection modes can be used to monitor the plasmon peak. In reflection, the peak shifts for layer adsorption are larger, for a wide range of adsorbate thicknesses, and the RIS for bulk RI change (e.g., different solvents) is 42-105% higher.

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