Differentiating Surface and Bulk Interactions using Localized Surface Plasmon Resonances of Gold Nanorods

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Introduction
Localized Surface Plasmon Resonance (LSPR) is the result of the collective oscillation of conduction electrons in a metal nanostructure when illuminated with light, which leads to strong absorption and scattering at plasmon frequency. Metal nanostructures supporting LSPR have found various applications as biochemical sensors. Compared to traditional propagating SPR sensors, it provides greater field enhancement, sensing in dramatically reduced volume solutions and extensive resonance wavelength tunability. Despite the advantages, LSPR sensors suffer from the same problem as propagating SPR sensors – interference from non-specific interactions (bulk and surface). Various groups have investigated propagating SPR sensor that support two modes and can differentiate surface binding interactions from bulk specific interactions (bulk and surface). Various groups [1]-[3] have investigated propagating SPR sensor that support two modes and can differentiate surface binding interactions from bulk specific interactions. To differentiate propagating SPR sensors that support more than two modes to differentiate specific and non-specific interactions. The paper describes the development of a new SPR sensor that is sensitive to surface binding interactions and can be used for sensing applications as biochemical sensors.

Background
The key concept behind this approach is the exploitation of the multiplicity of modes of a metallic nanostructure to distinguish between specific and non-specific interactions. To differentiate between bulk and surface changes we require nanostructures that exhibit multiple plasmonic resonances. Nanorods are the simplest such structure and support at least two LSPRs. Simple calculations using the electromagnetic approximation for coated ellipsoids suggest that the longitudinal and transverse resonances respond differently to surface and bulk effects.

Sample preparation
Gold nanorod arrays are fabricated on an ITO-coated glass substrate using electron beam lithography followed by gold sputtering and lift off. Various steps involved in nanorod fabrication are shown in the schematic below.

Figure 1: Schematic of a gold nanorod array of length 141nm and width 67nm on ITO coated glass substrate.

Optical Characterization
Samples containing gold nanostructures are examined through an inverted microscope using a 20x/0.5NA dark field objective for both illumination and collection. Scattered light is routed through a polarizer to a grating spectrophotograph and thermoelectric coated CCD camera. Schematic of the experimental setup [4] is shown in (a).

Figure 2: Schematic of the experimental setup.

Optical characterization (cont.)

Figure 3: Normalized unpolarized scattering spectra of nanorod arrays of different sizes. The spectrum exhibits a red shift with increasing size of the nanorods.

Biosensing Experiment
Linear model for resonance wavelengths:

\[ \triangle \lambda_S = S_S \Delta n \]
\[ \triangle \lambda_L = S_L \Delta n \]

Directly calculate solution index change (\( \Delta n \)) and surface coverage (\( \Delta \))

\[ \Delta n = \frac{\Delta \lambda_S}{S_S} - \frac{\Delta \lambda_L}{S_L} \]

Figure of merit inversely proportional to the ratio of the sensitivities.

\[ \frac{1}{\mathrm{S}_L} + \frac{1}{\mathrm{S}_S} = \frac{1}{\Delta} \]

Figure of merit, \( \Delta n = 0.2705 \) lower in comparison to the dual mode thin film propagating SPR sensor, \( \Delta n = 1.4 \) [1].

Sensor Characterization
- Sensitivity ratio of change in plasmon resonance to change in index solution (for \( S_L \)) or change in layer thickness (for \( S_S \))

Table 1: Sensitivity of \( S_L \) and \( S_S \).

<table>
<thead>
<tr>
<th></th>
<th>Bulk Sensitivity, ( S_L ) (arb. units)</th>
<th>Surface Sensitivity, ( S_S ) (arb. units)</th>
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</thead>
<tbody>
<tr>
<td>Longitudinal</td>
<td>261.8</td>
<td>3.1762</td>
</tr>
<tr>
<td>Transverse</td>
<td>161.2</td>
<td>2.2462</td>
</tr>
</tbody>
</table>

Conclusion and Future Goals
This work shows that nanostructures supporting dual plasmonic modes can differentiate between surface binding and target analyte and background refractive index changes. The figure of merit for this new array sensor is significantly lower when compared to a thin film SPR sensor. Future goals include:

- Design nanoparticle sensors with modes that better separate surface and bulk effects.
- Design nanoparticle sensors that support more than two modes to differentiate specific and non-specific binding.