Increasing the limit of detection of LSPR sensors by use of anisotropic array of Au nanoparticles

Yves Borensztein*, William L. Watkins and Antonio Assaf
Institute for NanoSciences in Paris, CNRS and Sorbonne University, Paris, France
Email address: yves.borensztein@insp.jussieu.fr

Direction of deposition

Transmission anisotropy due to the dichroic plasmons of the NPs

Measurement for change of the refractive index of water down to $10^{-4}$

$\Delta T / T$ vs. wavelength (nm) for in air and in water.

Water + ethanol: $n=1.3340$

Pure water: $n=1.3330$

$n=1.3330$

$n=1.3336$

$n=1.3332$

$n=1.3331$

100 nm
1. Principle of a localized surface plasmon resonance (LSPR) sensor

The localized surface plasmon resonance (LSPR) is red-shifted by $\delta \lambda$ because of the adsorption of chemical entities.

**Two methods for measuring the shift:**

1. Directly on the position of the LSPR by use of a high-resolution monochromator.
2. By measuring the change of the signal $\delta I$ at a fixed wavelength.

- Needs excellent stability of the signal
- Solutions: e.g. self-referenced systems, perfect absorbers

2. Motivation

- Following previous results with plasmonic sensors based on anisotropic metal nanoparticles for investigating gas adsorption [1-2], we undertook studies in aqueous environment.

The use of anisotropic LSPR permits us to develop a highly stable system working at a single wavelength, with enhanced theoretical Factor of Merit $\text{FoM}^{*}$ larger than 10 000.

→ Bulk sensitivity is checked with variable refractive index solutions
→ Surface sensitivity to bio-molecule sensing is calculated for the avidin/biotin couple.

*Single molecule sensitivity is reached*

Increasing the limit of detection of LSPR sensors by use of anisotropic array of metal nanoparticles (3/6)

3. Sample elaboration: grazing angle deposition; plasmonic dichroism

Grazing incidence deposition leads to anisotropic nanoparticles, due to the shadowing effect

Anisotropic localized surface plasmon resonance (LSPR) in gold ellipsoids

Two different LSPR, parallel and perpendicular to the deposition direction, due to the elongated shape of the Au NPs, which yields a measurable dichroism of the sample.
4. Transmission anisotropy (TA) for a high sensitive sensor

We use a home-made transmission anisotropy spectrometer (TAS) which delivers the signal:

\[ \frac{\Delta T}{T} = \frac{T_\perp - T_\parallel}{1/2 (T_\perp + T_\parallel)} \]

The TA spectrum has a derivative shape, the positive and negative maxima are related to the \( \perp \) and \( \parallel \) LSPR.

When introduced in water, there is an overall redshift of the spectrum

At wavelength \( \lambda_o = 665 \text{ nm} \), the signal is fixed at zero.

Rather than measuring the shift \( \delta \lambda \), we measure the change of signal \( \delta I \), when the refractive index \( n \) of the ambient medium changes from 1.3330 to 1.3344

Here, \( \delta \lambda = 0.5 \text{ nm} \)

\[ \delta I = 10^{-3} \] , 100 time larger than the sensitivity of the apparatus
5. Bulk sensitivity to refractive index change: enhanced FOM*

Signal \( I = T A \) at the wavelength 665.5 nm, monitored during successive changes of the refractive index \( n \) of the water/ethanol mixing, as a function of time. The reached sensitivity is \( \delta n = 10^{-4} \).

**Fig (a)** shows that the bulk sensitivity to the variations of the refractive index of the ambient medium reaches \( \delta n = 10^{-4} \).

The sensitivity and stability is here \( 3 \times 10^{-5} \), and can reach less than \( 10^{-5} \).

The Factor of Merit FOM* for an intensity-based LSPR sensor is given by:

\[
FOM^* = \frac{\delta I(\lambda)/\delta n}{I(\lambda)}
\]

Here, the signal \( I(\lambda) \) is fixed at \( 0 \pm \varepsilon \) where \( \varepsilon \) is about \( 4 \times 10^{-5} \), and \( \delta I(\lambda)/\delta n \) is equal to 0.7 RIU⁻¹.

It gives an enhanced value \( F_{oM}^* = 18\,000 \).

This is 20 times larger than previously obtained FoM* by use or perfect absorbers [1,2].

1. Wang et al, Nanoscale 2017, 9, 11085
2. Zhou et al, Nanotechnology 2020, 31, 285501
6. Surface sensitivity to bio-molecule adsorption: theoretical investigation

The TAS spectrum is reproduced by taking into account the average shape of the Au NPs on the glass substrate and their interaction.

We calculate the change of signal when the bare Au NPs, are recovered by a full layer of biotin, and when one avidin molecule per NP is adsorbed

The signal calculated for 1 adsorbed avidin molecule per NP, \(2.5 \times 10^{-3}\), is 100 larger than the sensitivity:

it should be possible to detect one avidin molecule for 100 NPs, covering an area of \(0.5 \mu m^2\) of the sample

7. Conclusion

The use of anisotropic gold NPs simply elaborated by vacuum deposition at grazing incidence, combined with the measurement of their transmission anisotropy, yields a high-sensitive plasmonic sensor, without using a monochromator.

We demonstrate a limit of detection down to a change of the refractive index equal to \(10^{-4}\).

Theoretical calculation shows that one avidin molecule adsorbed upon a sample area of \(0.5 \mu m^2\) can be detected.

This opens the way for single-molecule detection by use of simple and low-cost optical system which could be miniaturized.