Size and aspect ratio dependency of sensitivity of ellipsoidal metal nanoparticle based liquid sensor

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Abstract. Detection of bio chemical species in a liquid is very important for research and technical purposes. In the last decade, metallic nanoparticles have been shown to be potential for such measurement. Resonance wavelength (or frequency) of free electron oscillation on metallic nanoparticle surface is very sensitive to tiny changes of its surrounding environment. Change in surrounding medium shifts the resonance wavelength with a slope determined mainly by the size and geometry of nanoparticle. We numerically optimized size and aspect ratio of silver and gold nanoparticles to obtain the highest sensing sensitivity. Here, sensitivity is defined as the slope of resonance wavelength on refractive index of liquid. We found that size, aspect ratio, and material of metal affect sensing sensitivity of metal nanoparticle based sensor significantly.

1. Introduction
Detection of biological and chemical substances is a routine and an important step in scientific research, environmental hazard monitoring, and food and process control [1]. Surface plasmon resonance (SPR) sensing is now widely investigated to detect biological and chemical species dissolved in liquids or gasses [2,3]. SPR sensing offers high sensitivity and measurement accuracy due to strong dependency of plasmonic resonance on local change. Surface plasmons occur when free electrons on metal oscillate coherently upon illumination by electromagnetic wave having appropriate wavelength. There are two types of SPR, namely propagating surface pasm on polaritons (SPP) and non-propagating localized SPR (LSPR) [4]. SPP occurs at the interface of planar (thin film) metal and has been intensively investigated to realize nanoscale optical devices and to study interactions and binding mechanism of proteins and other biological structures. LSPR, on the other hand, occurs at the surface of metallic nanoparticles.

Compared to SPP, LSPR based sensing is often chosen as it can be easily excited without a complex optical set up using prism, grating, or scatterer. Furthermore, the wavelength at which coherent oscillation occurs (resonance wavelength) depends dielectric constants of metal and surrounding medium, the size, and the geometry of metal nanoparticles [5,6]. Dependency of the resonance intensity and wavelength on local dielectric environment has been used to develop label-free optical sensing. Adsorption of biological or chemical species on the surface of metal nanoparticles changes refractive index of surrounding locally. The changes can even be monitored in a real time [7,8].
Significant progress of SPR based sensing is mainly facilitated by the availability of many chemical synthesis recipes to obtain gold and silver nanoparticles. Gold and silver nanoparticles have been synthesized in forms of sphere [9], cube [10], rod [11], bar [12], rice [12], pyramid [9], and triangle [13]. Gold and silver nanoparticles are vastly used because of their high free electron density and low loss.

We report numerical study on dependency of sensing sensitivity of ellipsoidal metal nanoparticles on its size and aspect ratio. Ellipsoidal particles are promising for biochemical sensing because their resonance exhibits polarization dependent spectra due to anisotropy in particle dimension. We found that size, aspect ratio, and type of metal influences the sensing sensitivity of ellipsoidal nanoparticles significantly.

2. Simulation details

2.1 Numerical method

Extinction spectra of gold and silver nanoparticles were calculated using boundary element method [14,15]. Full Maxwell’s equations were solved for a metal nanoparticle in a homogeneous dielectric medium. Metal nanoparticle having frequency-dependent dielectric constant is separated abruptly with its surrounding dielectric medium. Relative magnetic permeability of metal and dielectric is assumed to be unity. When metal particle is excited by external field (e.g. plane wave), electrons in metal will be polarized and resulting in induced electromagnetic fields. The surface of metal is discretized and Maxwell’s equations are solved at the boundary using appropriate boundary conditions.

2.2 Nanoparticle Parameters

Calculations were performed for gold and silver nanoparticles with three different aspect ratios (0.25, 0.50, and 0.75) and five different particle diameters (10 nm, 30 nm, 50 nm, 70 nm, and 100 nm). Here, aspect ratio is the ratio of minor axis to major axis. The nanoparticles were excited using plane wave at wavelength of 200 – 1000 nm polarized along ellipsoidal minor axis and propagate along ellipsoidal major axis. Refractive index of medium surrounding particles was varied from 1.0 to 2.0. The variation of medium refractive index is aimed at mimicking refractive indices of liquids or gases containing biological and chemical species. Refractive indices of many gasses lie between 1 – 1.1, while those of chemicals are between 1.25 – 1.70.

![Ellipsoidal nanoparticles](image)

**Figure 1.** Ellipsoidal nanoparticles with different aspect ratio, (a) 0.25, (b) 0.50, and (c) 0.75.

The key parameter of SPR based sensing is sensitivity. Sensitivity of metal nanoparticle were calculated from extinction spectra. The sensitivity describes the shift of extinction spectra when refractive index of surrounding medium increases by one, therefore it has a unit of nm/RIU where RIU refers to refractive index unit. Adsorption of biological or chemical species may increase effective refractive index of medium resulting in a stronger screening of the Coulombic restoring force.
3. Results and Discussion

3.1 Effect of aspect ratio
The dependency of extinction (absorption + scattering) spectra of 20-nm silver nanoparticle on aspect ratio is plotted in figure 2. The intensity of extinction peaks increases monotonously with aspect ratio, while resonance wavelength decreases non-linearly. The resonance wavelength blue-shift with aspect ratio because of an increase in Coulombic restoring force when particle size becomes smaller. It is clearly visible that the shift of the resonance wavelength is much stronger for aspect ratio less than one. Larger shift means higher sensing sensitivity. Therefore, in this work aspect ratio was assumed to be 0.25, 0.50, and 0.75.

![Figure 2](image2.png)

**Figure 2.** Surface plot of extinction spectra versus aspect ratio of ellipsoidal silver nanoparticle embedded in air. Diameter of nanoparticle is assumed to be 20 nm. Intensity of extinction spectra is given in colorbar. Resonance wavelengths are indicated as white circles.

3.2 Effect of refractive index of medium
Example of normalized extinction spectra of 30 nm gold and silver nanoparticles for three different aspect ratio are given in figure 3. Similar calculation was performed for particles with a diameter of 10 nm, 50 nm, 70 nm, and 100 nm.

![Figure 3](image3.png)

**Figure 3.** Intensity normalized extinction spectra of 30 nm nanoparticle for different aspect ratio as a function of refractive index of medium, (a) Au aspect ratio 0.25, (b) Au aspect ratio 0.50, (c) Au aspect ratio 0.75, (d) Ag aspect ratio 0.25, (e) Ag aspect ratio 0.50, and (f) Ag aspect ratio 0.75.
Red-shift of extinction peak with refractive index of surrounding medium can be observed for all particle diameter and aspect ratio. The shift of extinction peak does not vary linearly with refractive index of medium. The slope of the shift seems to depend on aspect ratio and particle size. Larger red-shift with refractive index means a higher sensing sensitivity. Resonance wavelength of silver is shorter than that of gold nanoparticles. Red-shift of extinction peak with refractive index of medium is also clearly visible. Broadening of extinction peak for silver nanoparticle is not as significant as that of gold nanoparticles.

Red shift of the extinction peak with refractive index of medium is caused by a lowering in Coulombic restoring force as a result of an increase in polarization charge at the surface of nanoparticles on the dielectric medium side. Broadening of extinction peak is also clearly visible when nanoparticle diameter is larger than 50 nm. The broadening is caused by retardation effect where oscillations of free electrons are delayed and damped [16]. Radiation losses and damping is dominant for particles larger than 100 nm, therefore affecting sensing sensitivity.

Imaginary part of dielectric constant of silver is much smaller than that of gold nanoparticles. As a consequence, damping and broadening of silver extinction peak is much lower than those of gold nanoparticles. Small peak width is advantageous for sensing because it allows for precise assignment of resonance wavelength and thus refractive index of investigated sample.

3.3 The shift of resonance wavelength

Red shift of extinction peak of gold and silver particles as a function of refractive index of surrounding medium, diameter, and aspect ratio is displayed on figure 4.

![Figure 4](image-url)

**Figure 4.** Dependency of red shift of extinction spectra of ellipsoidal gold nanoparticle with aspect ratio of (a) 0.25, (b) 0.50, and (c) 0.75, and ellipsoidal silver nanoparticle with aspect ratio of (d) 0.25, (e) 0.50, and (f) 0.75. Diameters of nanoparticles are given in the legend of Figure (a). The color and type of data marker are the same for all sub-plots.
One can clearly see that resonance wavelength red shifts with particle diameter and refractive index of medium, but blue shift with aspect ratio. The red shift shows nicely quadratic dependency on refractive index of medium within the simulation range. The slope of red shift of silver nanoparticle spectra (figure 4 (d), (e), and (f)) is larger than that of gold nanoparticles (Figure 4 (a), (b), and (c)). In the work reported by Anker, et al. [17], the red shift is assumed to be linear with refractive index of medium. The linear trend seems to fit quite nicely with their data where refractive index of solvent less than 1.6. However, as can be seen from figure 4, linear trend is just a rough estimation because quadratic dependency is valid over a larger range of medium refractive index. Quadratic dependency is even more clearly visible for larger particles. Larger slope of silver nanoparticle red shift corresponds to a steeper wavelength dependency of real part of dielectric constant of silver.

### 3.4 Sensing Sensitivity

Sensitivity of SPR based sensor is determined by the slope of resonance wavelength to the refractive index of medium. The obtained sensitivity has a unit of nm/RIU. Sensitivity of ellipsoidal nanoparticles is shown in figure 5. Sensitivity increases linearly with refractive index as expected from quadratic dependency of red-shift. In addition, sensitivity of ellipsoidal nanoparticles decreases with aspect ratio and increases with particle diameter. The increase of sensitivity with refractive index can be explained as a result of polarization charge build up in the dielectric medium. Polarization reduces oscillation restoring force that results in red shift of extinction peak. High sensitivity at higher refractive index is related to a strong light localization at the interface of metal and dielectric. Linear variation of sensitivity with refractive index was also predicted by Miller and Lazarides [18].

![Figure 5](image-url)

**Figure 5.** Dependency of sensitivity of ellipsoidal gold nanoparticles with aspect ratio of (a) 0.25, (b) 0.50, and (c) 0.75, and ellipsoidal silver nanoparticles with aspect ratio of (d) 0.25, (e) 0.50, and (f) 0.75. Diameters of nanoparticles are given in the legend of Figure (a). The color and type of data marker are the same for all sub-plots.
The increase of sensitivity with particle diameter is caused by larger variation of real part of dielectric constant of metal nanoparticles at longer wavelength. Real part of dielectric constant of metal determines resonance wavelength of surface plasmon. Silver has a steeper variation of real part of dielectric constant with wavelength than that of gold, therefore the sensitivity of silver nanoparticles to refractive index of medium is higher. However, gold has important advantages compared to silver, namely biocompatibility and chemical inertness. Silver can easily be oxidized and corroded in a humid environment.

Lowering sensitivity with aspect ratio is likely due to reduction of particle anisotropy when aspect ratio increases close to unity. Ellipsoidal nanoparticles shows incident light polarization dependency where longitudinal and transversal plasmonic mode may occur. The resonance wavelength of longitudinal mode depends sensitively on particle size and refractive index of medium. When aspect ratio reach unity, the modes overlap and then reduces sensitivity.

4. Conclusions
Sensitivity of SPR sensing using ellipsoidal metal nanoparticle depends on ellipsoid aspect ratio, diameter, type of metal, refractive index of surrounding medium. Smaller ellipsoidal aspect ratio is more promising for sensing due to its much higher sensitivity. Larger particles consistently show a higher sensitivity than the smaller one. Sensitivity increases linearly with refractive index of medium. Silver nanoparticles show a higher sensitivity than gold. The obtained sensitivity for gas (refractive index slightly above 1) and chemical species (refractive index 1.3 – 1.6) sensing is relatively high that are well above 200 nm/RIU and in best case up to 600 nm/RIU. For sensing application, small aspect ratio and large particle diameter are recommended.

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