Effect of nanoparticle geometry on sensitivity of metal nanoparticle based sensor

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Abstract. Biochemical detection using metal nanoparticles has been intensively investigated due to availability of robust nanoparticle synthesis methods whether chemically or using lithographic approach. SPR based sensor employs the shift of plasmonic resonance wavelength when local surrounding medium of metal nanoparticles change even slightly. The shift of the resonance wavelength depends sensitively on geometry and size of nanoparticle. The resonance wavelength and its shift were calculated numerically using boundary element method. Here, we compare the sensitivity of gold and silver nanoparticles to sense small change in refractive index of medium. Four different geometries (spherical, ellipsoidal, cylindrical, and donut-like nanoparticles) of different size were investigated to find the highest sensor sensitivity.

1. Introduction
Currently, we witness an increasing demand for robust and versatile biochemical sensing techniques for industrial, environmental, medical, and chemical analysis purposes [1]. Among many other approaches, surface plasmon resonance (SPR) sensing is now considered as a promising approach for detecting biological and chemical species in liquid or gaseous samples [2,3]. SPR sensing allows for real-time and label-free measurement by using only a small amount of sample. Surface plasmons are coherent oscillations of conducting electrons of a metal at the boundary with dielectric medium when illuminated with electromagnetic wave of appropriate wavelength [4]. The oscillations cause local field enhancement at the very surface of metal, therefore any small changes on the metal surface can be detected. Surface plasmon polariton (SPP) sensing on the surface of planar metal has been well studied and used for investigating biological structures for example binding and releasing mechanism of proteins. The excitation of SPP needs special optical set up such as prism, grating, or scatterer which then inhibits miniaturization. Consequently, metal nanoparticle based sensor using localized surface plasmonic resonance (LSPR) is often more preferred because of simplicity in its excitation and strong dependency of its sensitivity on shape and size of nanoparticles [5,6].

SPR based sensing is performed based on the shift of plasmonic resonance peak when local refractive index of medium that is in contact with particle changes. The wavelength at which coherent oscillation occurs (resonance wavelength) is determined by the dielectric constants of metal and surrounding
dielectric medium, size, and shape of nanoparticles. SPR sensing make use of local change of medium refractive index upon adsorption of biological or chemical species on the surface of metal nanoparticles [7,8]. Dependency of the resonance wavelength on local dielectric environment has been used to develop label-free optical sensing. Localized SPR based sensing are progressing very rapidly due to the possibility to control size and shape of metal nanoparticle precisely using either lithographic technique or wet chemical synthesis. Gold and silver nanoparticles are two of most investigated materials. The reasons are still their high free electron density and low loss (negative part of dielectric constant). Gold and silver nanoparticles can be synthesized into many different geometries such as spherical, cylindrical, bar, ellipsoidal, and triangular [9,10,11,12].

Here, we report the effect of nanoparticle geometry on the sensitivity of SPR-based sensor. Four different shape of nanoparticles namely spherical, cylindrical, ellipsoidal, and donut-like will be compared to obtain the highest sensitivity. Shape and size of nanoparticle determine resonance wavelength and consequently affects the sensitivity of SPR based sensor.

2. Experimental

2.1 Calculation method

Boundary element method [13,14] was used to calculate extinction spectra of gold and silver nanoparticles. This method solves full Maxwell’s equations for a metal nanoparticle embedded in a homogeneous dielectric medium. The metal nanoparticle having frequency-dependent dielectric constant is separated by an abrupt boundary with the surrounding dielectric medium. The metal and the dielectric medium are non-magnetic, therefore their relative magnetic permeability was assumed to be one. Free electrons in metal nanoparticle are polarized when illuminated with a plane wave. The polarization induces Coulombic restoring force that is proportional to particle size. Periodic change of the restoring force results in periodic coherent oscillation of free electrons. For calculation, the surface of metal is discretized and Maxwell’s equations are solved using appropriate boundary conditions.

2.2 Geometry of nanoparticles

Calculations were performed for gold and silver nanoparticles with four different shapes and different particle diameters (see Figure 1). The nanoparticles were excited using a monochromatic plane wave with a frequency that varies between 200 – 1000 nm. Refractive index of medium surrounding particles was varied from 1.00 to 2.00 with a step of 0.05 to match the refractive indices of liquids or gases containing biological and chemical species. Refractive index of gasses is a little bit above that of vacuum (i.e. 1.0 – 1.1), while refractive index of most of chemicals are 1.3 – 1.6.

![Figure 1. Metal nanoparticles of different shapes, (a) spherical, (b) cylindrical, (c) ellipsoidal, and (d) donut-like.](image)

The sensing sensitivity of metal nanoparticle was calculated from its extinction spectra. The sensitivity describes how big the shift of extinction peak when refractive index of medium surrounding nanoparticle increases by one. The sensitivity has a unit of nm/RIU, where RIU refers to refractive index unit. A good sensor should have a high sensitivity so that it can detect any tiny change surrounding medium.
3. Results and Discussion

3.1. Extinction Spectra

Sample of extinction spectra of gold and silver nanoparticles are shown in figure 2. Here, extinction spectra are defined as surface plot of extinction cross section versus wavelength of incoming light and refractive index of surrounding dielectric medium. Figure 2(a), (b), (c), and (d) are spectra of gold nanoparticles, while figure 2(e), (f), (g) and (h) are spectra of silver nanoparticles.

Maximum of extinction spectra of spherical nanoparticles increases significantly with the increase of medium refractive index and particle diameter. In addition, the extinction peak position (resonance wavelength) red shifts in a non-linear manner when refractive index of medium increases. The slope of the red shift depends on particle size and type of metal. Broadening of extinction spectra of silver nanoparticles is less than the broadening of gold nanoparticles. A narrow secondary extinction peak at a shorter wavelength than the primary one is only visible in the extinction spectra of silver nanoparticle.

The red shift of the extinction peak with refractive index of medium is caused by an increase of polarization charge at the surface of metal. The polarization reduces Coulombic restoring force determining resonance wavelength. The red shift of extinction peak with particle size is caused by
retardation of the exciting field. The separation distance of free electrons on the opposite surface of nanoparticle increases with particle size. The increase of separation distance lowers the restoring force appearing as red shift of resonance wavelength. The broadening of extinction peak with particle size is caused by retardation of electron oscillation for large particle. Lower imaginary part of dielectric constant of silver results in much narrower extinction peak than that of gold nanoparticle. The red shift of extinction peak with refractive index of medium and particle size is also obvious for non-spherical nanoparticles like cylindrical, ellipsoidal, and donut-like geometries. The explanation for the red shift is also similar with that of spherical particles. An increase of medium refractive index causes an increase in polarization charge at the medium part of the boundary which then decreases restoring force of oscillation and thus increases resonance wavelength. The slope of red shift depends on particle shape and size. The ellipsoidal nanoparticle seems to have the narrowest peak width. The broadening of extinction spectra for large particle size is caused by excitation of higher multipole radiation. The contribution of quadrupole mode is indicated by non Lorentzian extinction peak for big particles.

A quadrupolar peak at shorter wavelength than the primary (dipolar) peak is visible for silver nanoparticles. The quadrupolar peak is much narrower than that of the dipole. The quadrupole peak does not red shift significantly with refractive index of medium, therefore shows a lower sensitivity.

3.2. Resonance Wavelength
Resonance wavelengths of gold and silver particles for different refractive index of medium for different particle size and shape are shown in figure 3 and figure 4, respectively. The resonance wavelength shifts to a longer wavelength as refractive index of medium increases. The red shift fits quadratic dependency with refractive index. Except for donut-like particle, an increase of particle dimension (diameter or height) results in a red shift with a slope that depends on particle shape. There is no much difference between the shift of resonance wavelength between gold and silver nanoparticles.

![Figure 3](image)

**Figure 3.** The shift of resonance wavelength of gold nanoparticle as a function of refractive index of dielectric medium for different particle shape and size, (a) spherical, (b) cylindrical with a diameter of 50 nm, (c) ellipsoidal with an aspect ratio of 0.25, and (d) donut-like with a diameter of 100 nm. Other dimensions of nanoparticles are given in the corresponding plot legend.
Figure 4. The shift of resonance wavelength of silver nanoparticles as a function of refractive index of dielectric medium for different particle shape and size, (a) spherical, (b) cylindrical with a diameter of 50 nm, (c) ellipsoidal with an aspect ratio of 0.25, and (d) donut-like with a diameter of 100 nm. Other dimensions of nanoparticles are given in the corresponding plot legend.

The dependency of resonance wavelength on particle dimension is stronger for cylindrical and donut-like nanoparticles. The shift of resonance wavelength of silver nanoparticle is larger than that of gold nanoparticle. Larger shift of resonance wavelength of silver particle is caused by stronger wavelength dependency of real part of silver dielectric constant.

3.3. Sensing Sensitivity

The slope of resonance wavelength versus refractive index medium indicates the sensitivity of SPR sensor. Larger slope is demanded to be able to discriminate tiny local change of medium refractive index. The change can be caused by the presence of biological or chemical species. The sensitivity has a unit of nanometer per refractive index unit (nm/RIU). The sensing sensitivity of spherical, cylindrical, ellipsoidal, and donut-like gold and silver particles are shown in figure 5 and figure 6, respectively. The sensitivity is linearly dependent on refractive index medium as expected from quadratic dependency of resonance peak shift.

In general, sensitivity increases with refractive index of medium. It means that higher refractive index chemical or biological substances are much easier to detect. However, care must be taken because extinction peak tends to broaden at high medium refractive index due to retardation effect. On contrary to spherical and cylindrical particles, the sensitivity of ellipsoidal and donut-like particles do not always increase with refractive index of medium. The slope of sensitivity of decreases gold ellipsoidal particle with a diameter of 100 nm and donut-like particle with a 20 nm ring radius.
Figure 5. The sensitivity of gold nanoparticles as a function of refractive index of dielectric medium for different particle shape and size, (a) spherical, (b) cylindrical with diameter of 50 nm, (c) ellipsoidal with aspect ratio of 0.25, and (d) donut-like with diameter of 100 nm. Other dimensions of nanoparticles are given in the corresponding legend.

Figure 6. The sensitivity of silver nanoparticles as a function of refractive index of dielectric medium for different particle shape and size, (a) spherical, (b) cylindrical with diameter of 50 nm, (c) ellipsoidal with aspect ratio of 0.25, and (d) donut-like with diameter of 100 nm. Other dimensions of nanoparticles are given in the corresponding legend.
From figure 5 and figure 6 we can see that cylindrical nanoparticle has the highest sensing sensitivity, followed by ellipsoidal particles, donut-like particle, and the last spherical particles. High sensitivity of cylindrical and ellipsoidal nanoparticles is likely due to a stronger shape anisotropy. Anisotropic nanoparticles show longitudinal and transversal modes whose resonance wavelength depends sensitively on particle dimension. The highest sensitivity is obtained by using cylindrical nanoparticles with a high aspect ratio (ratio of height to diameter). The sensitivity of cylindrical nanoparticle is always higher than 400 nm/RIU. It is also clearly visible that spherical particles have the lowest sensitivity that lies in the range between 100 - 400 nm/RIU. The dependency of sensitivity on composition of metal is weaker than its dependency on particle shape and size.

4. Conclusion
Sensitivity of SPR sensor increases linearly with refractive index of surrounding medium. Particle size and shape affect sensitivity of SPR sensor significantly. The dependency of sensitivity on particle composition (e.g. gold and silver) is much weaker than on particle shape and size. Larger particle size is, in general, results in higher sensitivity. The highest sensitivity is shown by cylindrical nanoparticle, while the lowest sensitivity is displayed by spherical one. The sensitivity of rod shape nanoparticle is always above 400 nm/RIU, while that of spherical particles is below 400 nm/RIU.

Acknowledgement
The authors would like to thank the Ministry of Research and Technology and Higher Education of the Republic of Indonesia through the 2017-Hibah Fundamental Research Grant No. 059/SP2H/LT/DRPM/2017 and the 2018-PDUPT Research Grant No. 050/SP2H/LT/DRPM/2018.

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