A Statistical Review of Nanoparticle Plasmonics

Abstract

Nanoparticle plasmonics is an area of physics gaining increased traction in recent research due to its distinctive optical properties. From influence in the medical field with improved cancer treatment to increased sustainability by allowing for significantly more efficient energy conversion from sunlight, it cannot be understated that the field of nanoplasmonics is highly important and necessary to be studied and further developed upon. This report reviews how geometry may affect plasmons within nanoparticles according to their geometry. In particular, it was found that Aspect Ratio follows a linear relationship with a parameter known as sensitivity. By understanding this interconnection between geometry and the optical properties they are able to be manipulated: a paramount goal in advancing these fields.

1 Introduction

Since Michael Faraday's 1856 discovery that colloidal gold nanoparticle solutions display a striking red hue[1], scientists have been intrigued by the optical characteristics of metal nanostructures. Pines and Bohm later identified the source of these unique optical properties in the early 1950s, attributing them to the quantized oscillations of free electron gas (plasma)[2] now known as plasmons. These exhibit unique properties that can be finely tuned by controlling factors such as particle geometry, size, material and the wavelength of incident light[7]. Over recent decades, plasmons have garnered extensive study for their capacity to strongly absorb light and concentrate electric fields at the nanoscale[3], enabling advancements in spectroscopy[4], biosensing[5], and solar energy conversion technologies[6]. To be able to manipulate plasmons on such a fine scale opens new avenues for precise control in various applications.

Nanoparticle plasmonics is a field focused on the manipulation and understanding of plasmons within nanoparticles. It has emerged as a highly active area of research in modern physics due to its remarkable potential for diverse applications. This field builds upon the fundamental understanding of how light interacts with matter on the nanoscale, leading to highly localised electromagnetic fields and enhanced optical phenomena. These properties are tuneable and therefore allow nanoparticle plasmonics to play a pivotal role in enhancing processes across numerous sectors, including medicine, energy, spectroscopy[8] and environmental science. This report specifically examines how different conditions applied to nanoparticles influence plasmonic behaviour, as well as the impact of incident radiation wavelength. By exploring these conditions, this report aims to shed light upon the different ways nanoparticles can be tailored to manipulate plasmonic behaviour.

The medical field, for instance, would benefit from plasmonic nanoparticles in areas such as cancer therapy. Where the nanoparticle's precise interaction with light facilitates targeted treatments through photothermal effects. Furthermore, as our understanding of plasmon behaviour deepens, the potential for innovative applications in sensing, imaging, and medical care continues to expand. Such advancements could enable early disease detection, highly sensitive bioassays, and non-invasive imaging techniques. Plasmonic nanoparticles also contribute to the development of lab-on-a-chip devices, which have broad implications in diagnostic healthcare. The potential socioeconomic effects of further scientific development in nanoplasmonics could strike deep. Within the medical sector alone, it would have incredible benefits. Cancer is one of the biggest killers in the UK accounting for 27-28% of all deaths in England in a typical year[9]. This is over a quarter of all deaths every year. If nanoplasmonics becomes developed enough to tackle cancer on a nationwide scale, thousands of lives could be saved every year.

A particularly critical parameter influencing plasmon behaviour is the aspect ratio of nanoparticles. This is defined as the length of the nanoparticle divided by the depth of the nanoparticle. The reason this influences plasmon behaviour is because variations in this ratio alter the oscillation modes and resonance frequencies of the plasmons. This is important as understanding the relationship between aspect ratio and plasmonic resonance gives way to further development in specific fields. This report will examine how adjusting the aspect ratio affects the plasmonic behaviour. Specifically focusing on the influence of nanoparticle geometry thus changing the aspect ratio and affecting the behaviour of the surface plasmons.

2 Understanding Nanoplasmonics

2.1 Theory Governing Nanoplasmonics

This report wishes to explore how to manipulate plasmons within nanoparticles, and hence the underlying theory of both the nanoparticles and the plasmons must be considered. To ultimately direct findings towards the most important factors surrounding the optical properties of nanoparticles it is paramount to have a solidified understanding of the complex phenomenon. Unfortunately, a malleable, fully descriptive model of these nanoparticle plasmons does not exist. There are many predictive models which each rely on very different assumptions which hold well in their respective cases, but the best of this report's understanding comes from observed data.

As previously defined, a plasmon is an excitation of the free electrons within a metal.[10] Plasmons excited via electromagnetic radiation can only propagate on the surface of the metal due to radiative losses. The depth of these oscillations is characterised by the skin depth of the metal in question which explains why the plasmons propagate along the metal as opposed to throughout.

Nanoparticles are small nanostructures which exist on a scale < 100nm; [11] it is this fact that introduces their interesting optical properties. For visible light, which is often the source of plasmon excitation in [12] nanophotonics, the skin depth of many highly conductive metals[13] such as gold or silver approaches the size of the nanoparticle itself. This is important as it allows a significant amount of the electrons within the nanoparticle to be excited, ultimately characterizing the way the plasmons propagate. This is one of the reasons why the type of metal used, and the size of the nanoparticle plays such a large role in plasmon behaviour. On this nanoscale, the oscillation is localised over the whole particle volume[14] which merits the title of localised surface plasmons, which is unique to these nanoparticles.

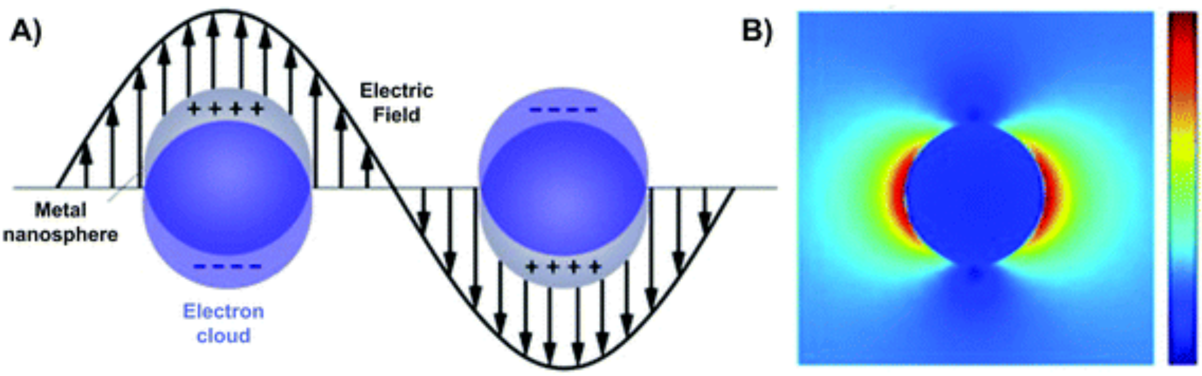

Figure 1 (A) Illustration of the effect of light on small nanoparticles leading to localised surface plasmon resonance. Taken from [15].

It is important to note that there are conditions which exist for electron excitation. Due to the nature of localised surface plasmons, they can be treated like a driven mass-spring harmonic oscillator[16]. As known, classically, all oscillators have some characteristic resonant frequency of oscillation. This resonant frequency must be matched [10]by the incoming radiation for plasmon excitation to occur. It is evident that the conditions which alter this resonant frequency are highly important as they essentially define how the enhanced optical properties of the nanoparticle occur.

The optical properties of nanoparticles can be examined by considering optical and electromagnetic theory. For simplicity, this report will only consider a specific case with the aim of gaining some level of understanding on which factors play the largest role in enhancing optical features. [18] This report will assume the nanoparticle is a homogeneous sphere which exists at a scale significantly less than the wavelength of incident electromagnetic radiation, this is the quasistatic approximation. The radiation in question will be treated as planar and the medium the particle exists in is also homogenous. Under these conditions, Mie theory will be consulted, which provides exact solutions to Maxwell's equations in the form of an infinite sum of multipole expansions which considers the distortion of the electron cloud in response to the incident electric field. Consult the listed literature for in depth definitions of the Mie variables.[19].

$$a_L = \frac{m\psi_L(mx)\psi_L'(x) - \psi_L'(mx)\psi_L(x)}{m\psi_L(mx)\chi_L'(x) - \psi_L'(mx)\chi_L(x)} \tag{1}$$

$$b_L = \frac{\psi_L(mx)\psi_L'(x) - m\psi_L'(mx)\psi_L(x)}{\psi_L(mx)\chi_L'(x) - m\psi_L'(mx)\chi_L(x)} \tag{2}$$

$$\sigma_{ext} = \frac{2\pi}{|k|^2}\sum_{L=1}^{\infty}(2L+1)[Re(a_L + b_L)] \tag{3}$$

Under the quasistatic approximation, only the first term of the sum will be taken, as it is majorly dominant. After considering a series of expressions and relations one arrives at an equation for the extinction cross section of a small homogeneous spherical nanoparticle[20].

$$\sigma_{ext} = \frac{18\pi[\varepsilon_m(\lambda)]^{3/2}}{\lambda} V_{NP} \frac{Im[\varepsilon(\lambda)]}{[Re[\varepsilon]+2\varepsilon_m(\lambda)]^2 + Im[\varepsilon(\lambda)]^2} \tag{4}$$

where ε_m is the dielectric function of the medium and ε is the dielectric function of the nanoparticle

The extinction cross section in this case is a value which describes how much light the nanoparticle both scatters and absorbs. [21]This ultimately describes the optical behaviour of the nanoparticles in the specific case of the sphere. The general dependencies can be noted as a basis for any shape although maybe not as exact, it is still valuable general information. There is a limit where this equation breaks down for nanoparticles that are too small (around <10nm) [22]where quantum effects become significant. Electron pressure, which is previously ignored in the used electromagnetic theory, becomes highly relevant and detrimentally changes results. As well as this, the probability an electron may quantum tunnel away from the nanoparticle becomes large enough for electron losses to occur such that the description of plasmons is no longer correct[12]. Despite this, with reasonable assumptions it should be expected the optical behaviour of nanoparticles to be dependent on their volume/size, wavelength of incident light, the dielectric function of the surrounding medium and of the nanoparticle itself.

To take advantage of the enhanced optical properties of these nanoparticles this report considers which conditions maximise the extinction cross section. A majorly important condition is that of the Frolich condition[16], which when imposed in a given context to minimise the denominator, tells us the frequency for which localised plasmon resonance occurs.

$$Re[\varepsilon_{NP}(\omega)] \approx -\chi\varepsilon_m(\omega) \tag{5}$$

Where χ is a geometrical factor equal to 2 for a sphere and ω is the associated plasmonic frequency

We can infer a relative dependence between the resonant point of the plasmons, incident light wavelength and nanoparticle size. Since these factors seem so important and intertwined, it seems reasonable to dissect their relationship and make any confirmations with some real data. The most abundant data for such variables worked with nanoparticle aspect ratio and sensitivity.

2.2 Exploring the Effects of Aspect Ratio on Plasmonic Resonance

Aspect ratio is defined as the ratio between the length and depth of a nanoparticle.

$$R = \frac{L}{d} \tag{6}$$

There are many different types of nanoparticles; characterised by their geometry. Aspect ratio primarily will take the length of the most prominent side and find the ratio of that with the depth of the particle with respect to the side that was chosen as the length. A nanosphere hence has R=1.

It is known that high aspect ratio nanostructures experience greater electromagnetic enhancement as well as a redshift in localised surface plasmon resonance (LSPR) absorption maximum. [24] The absorption maximum refers to the wavelength at which a plasmonic nanoparticle exhibits the maximum absorption due to the resonance of surface electrons with incident light.

This report plans to explore this and its correlation with the sensitivity of a nanoparticle and in turn the Resonant frequency of LSPR. The sensitivity of nanoparticles describes how the resonant frequency of LSPR changes with the refractive index of the nanoparticle environment. Sensitivity can be defined as:

$$S = \frac{\Delta\lambda_{lspr}}{\Delta \mathrm{n}} \tag{7}$$

$$S = kR + C \tag{8}$$

The aspect ratio of a nanoparticle has a clear linear relationship with its sensitivity; to prove this relationship is a goal of this review.

3 Methodology

As previously determined, sensitivity has an approximately linear dependence on aspect ratio. This lends itself to a least squared fitting modelling method such as OLS (Ordinary Least Squared) eq.1-5 if σ^2 equalled 1 [26], WLS (Weighted Least Squared) eq.1-5, GLS (General Least Squared) eq.(6).

$$\chi^2 = \sum_i^n \frac{(y_i - ax_i - b)^2}{\sigma_i^2} \tag{9}$$

$$0 = \sum_i^n \frac{x_i(y_i - ax_i - b)}{\sigma_i^2} \tag{10}$$

$$0 = \sum_i^n \frac{(y_i - ax_i - b)}{\sigma_i^2} \tag{11}$$

$$a = \frac{N\sum_i^n x_i y_i - \sum_i^n x_i \sum_i^n y_i}{N\sum_i^n x_i^2 - (\sum_i^n x_i)^2} \tag{12}$$

$$b = \frac{\sum_i^n (y_i - ax_i)}{N} \tag{13}$$

The route chosen was the WLS fitting method because it is a balance between the simplicity of OLS and the beneficial features of GLS [27]. GLS would have been the best choice for the project as there is a covariance between errors of points in the data set from sensitivities dependence on size, composition and shape to name a few. As the analysis focuses only on one variable, AR, affecting sensitivity.

$$\beta = (X^T Cov^{-1} X)^{-1} X^T Cov^{-1} y \tag{14}$$

The reason GLS wasn't chosen however was because to get the covariance between each data point would take a large amount of extensive research which could of course be how the project is continued. A future feature that could be added is an estimator of the covariance matrix [28] [29] [30].

$$\Sigma = \begin{bmatrix} \sigma_{11}^2 & \cdots & cov(\sigma_1 \sigma_j) \\ \vdots & \ddots & \vdots \\ cov(\sigma_i \sigma_1) & \cdots & \sigma_{ij}^2 \end{bmatrix} \tag{15}$$

With this in mind the code was designed in a way that allows for ease of scaling, the way this was done was by taking a matrix interpretation of the problem and assuming homoscedastic errors which in turn leads to a diagonal covariance matrix of the variance of each point on the diagonal. By making this known incorrect assumption it allowed the code to be built as a GLS modelling tool but with WLS features only so if the covariance between each data points do get found there is little to no hassle implementing them in the existing model.

$$\beta = (X^T W X)^{-1} X^T W y \tag{16}$$

This leads on to feature design within the project there were three main goals for features in the code in order of consideration: ease of scientific interpretation, ease of complexity scaling and speed of the code. First ease of scientific interpretation, the use of dictionaries was heavily present especially within the data segmenting and error calculation/propagation of the code; this was done as dictionaries allow for the storing of sorted information and require minimal knowledge of the code itself to change how the data is segmented. For example, in the case of the used data it allows for easy addition of new shapes and composition of nanoparticles which allows for both easier visualisation of how each set of shapes and composition behaves, and future addition of data related to different shapes or composition or more data for existing ones. This is a result of most of the sorting and segmentation being generalised (not hard coded) through the use of dictionaries. Another main feature of the code were the prediction and 95% confidence bands [32] [33] which show the region in which a new set of data points is predicted to be in and the region the model curve is estimated to lie within, based on the residuals of the WLS model. This was a useful tool as it allows for additional analysis from outside functions of the figures. It also gave an indication as to how well our model performed against other similar functions.

Alongside the functions defined for the actual model the code also contains functions for testing how well the model performs, such as reduced chi squared, R squared and Mean Squared error.

$$\chi^2_{red} = \sum_i^n \frac{[D_i - M_i(x)]^2}{\sigma_i^2} \tag{17}$$

$$R^2 = 1 - \frac{\sum_i^n \left(D_i - M_i(x)\right)^2}{\sum_i^n (D_i - \mu_i)^2} \tag{18}$$

$$MSE = \frac{1}{n} \sum_i^n [D_i - M_i(x)]^2 \tag{19}$$

This further allowed for greater analysis and understanding of the data. The final major feature that the code includes with relation to scientific interpretation is a regression model called Huber regression [37] from the sklearn module, this was included as it models a line with reduced effects of noise. This is beneficial as the data is an approximately linear fit, however the linear fit does have a limit which for each shape and composition is different [38] this means that the data will begin to behave nonlinearly at the higher ends of each model. As it will only slightly begins to behave non-linearly the feature treats the higher end deviation from the model as noise, if the model was to further predict past this limit of linearity it could not do this as there would be an obvious relationship between the variables however as it is only analysing near the limit the deviation from the linearity can be treated as noise this is why the confidence band is useful as it shows the Huber regression line is still contained within this 95% confidence band.

The second feature goal, ease of complexity scaling. As previously mentioned, the main way that the code allowed for complexity scaling was the matrix representation of the problem, this allows for both OLS decreased complexity and GLS increased complexity (once the covariances have been obtained or the matrix estimated). Dictionaries also allow for increased complexity scaling by allowing for easy adding of more variables and more data points. Another feature to ease in increased complexity is a feature that warn/alert if features don't work as intended such as if a matrix cannot be Cholesky decomposed the code breaks and prints the problem, if errors propagate through, they are displayed in the discrepancies between the results of the professional models and the codes. These professional models include numpy.polyfit, scipy.curvefit and statsmodels.api.GLS or WLS so if any major deviations from these other models arise it will be seen on the figures and the problem determined.

The third and final goal the code's features were trying to achieve was speed. Speed was difficult as simplicity in interpretation of the code is often reduced when speed is increased this meant a middle ground had to be struck between the two features. For example, with the inverted matrix instead of doing three matrix multiplication of was formulated semi manually for speed this reduced ease of scaling.

However, the main speed increase came from the implementation of the Cholesky decomposition [39] and backwards and forwards substitution of tridiagonal matrices [40]; this allowed for a major increase in speed when inversing the matrix. This is also where the warning comes in as a Cholesky matrix can only be inverted if certain conditions are met .

$$A = LL^T \tag{20}$$

By design one is met (symmetry) as the covariance matrix is symmetrical and X^T@X is symmetrical, finding the determinant then checks for zero eigenvalues however this still leaves the positive definite parts unchecked which is where the discrepancy checking comes in.

Once the Cholesky matrix has been calculated backwards and forwards substitutions are applied to invert the upper and lower tridiagonal matrices and a matrix rule allows for the fast and easy inversion of the matrix. This feature also scales well with increased linear parameter increase.

As said before rather than do more matrix calculations than necessary the solution to the matrix problem is hard coded. This of course doesn't scale well with increasing number of linear parameters or nonlinear fitting however it can easily be rectified if necessary.

The final feature added for increased speed is importing a data set of critical t values used in the prediction and confidence band features. Rather than calculating them manually, this is for the prediction and confidence band, and it increases speed by reducing the amount of statistical calculations the code has to do and by instead pre defining the variable, this however is scalable as whilst the number of data points increases to infinity the relevant critical t value tends to 1.96 or Z value for 95% confidence.

4 Results and Discussion

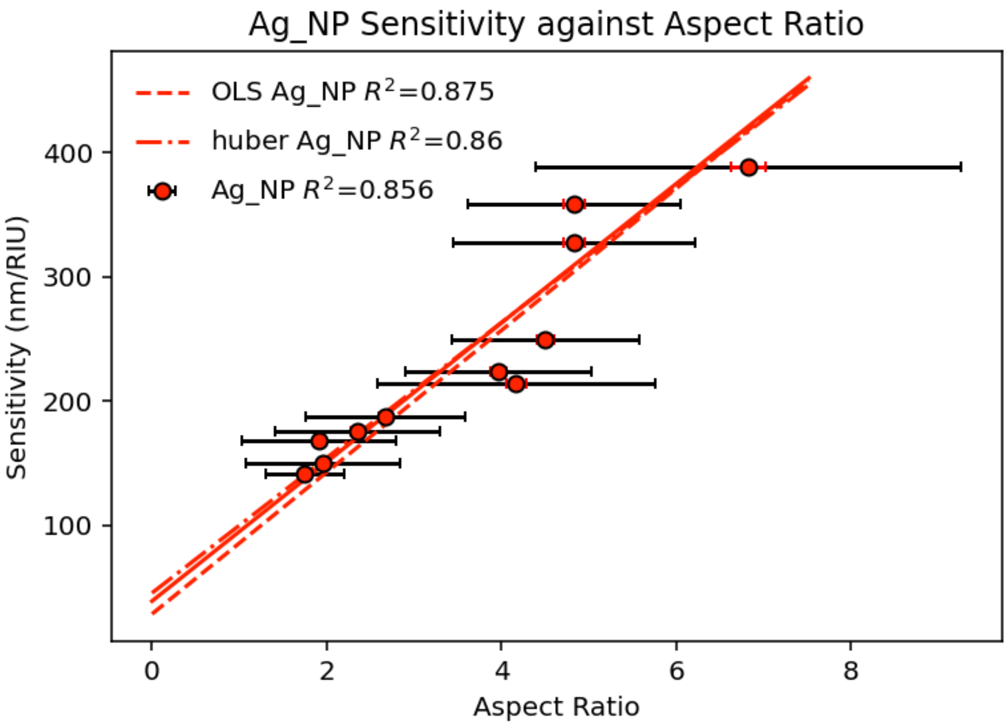

Figure 2 Sensitivity vs aspect ratio for silver nanoplates and nanoprisms.

With this analysis in mind, let's first consult Figure 2. It is immediately clear that for silver nanoplates, the aspect ratio increases linearly within reasonable statistical significance with sensitivity which is exactly what was expected. There is a coefficient of determination around 0.85 for every regression fit which implies a strong dependence on aspect ratio for sensitivity. Data from alternative reports suggest an upper limit to linearity for aspect ratio and sensitivity, our data does not surpass this value. Although irrelevant for this case, the Huber regression removes any upper noise by applying linear loss to the data with larger residuals and would hence persevere as a more reliable fit. While a linear trend is confirmed , model reliability cannot be confirmed according to our reduced Chi squared output of 5.05. This high result may arise from the fact that aspect ratio is one of many different variables that may alter nanoparticle sensitivity.

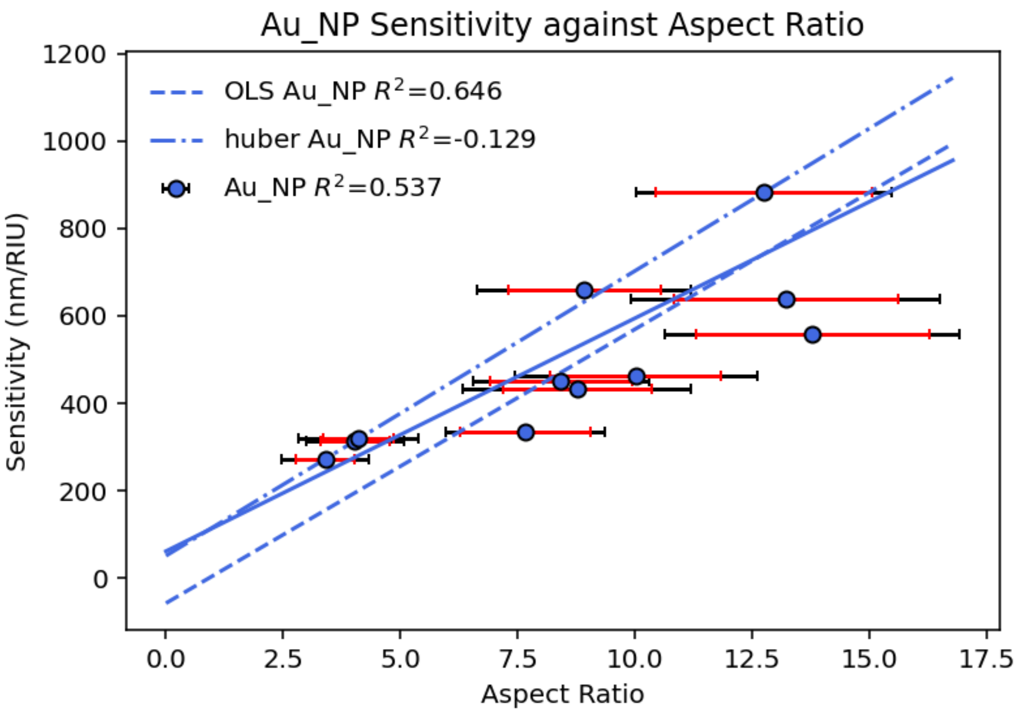

Figure 3 Sensitivity vs aspect ratio for gold nanoplates and nanoprisms.

Looking at, figure 3, it is swiftly evident that the data is more spread and our various regression models have significant issues when fitting to all of the points. One of the data points with large errors has no overlap with the regression models which may lead us to question the reliability of the data or the model. Unsurprisingly, it follows that our model has a Chi squared of 26 which suggests a very poor fit. Some potential errors may have occurred in data observation which should be considered. A positive correlation is clearly present but further data would be required to support such a trend confidently. It may be deemed the data in this case is inconclusive.

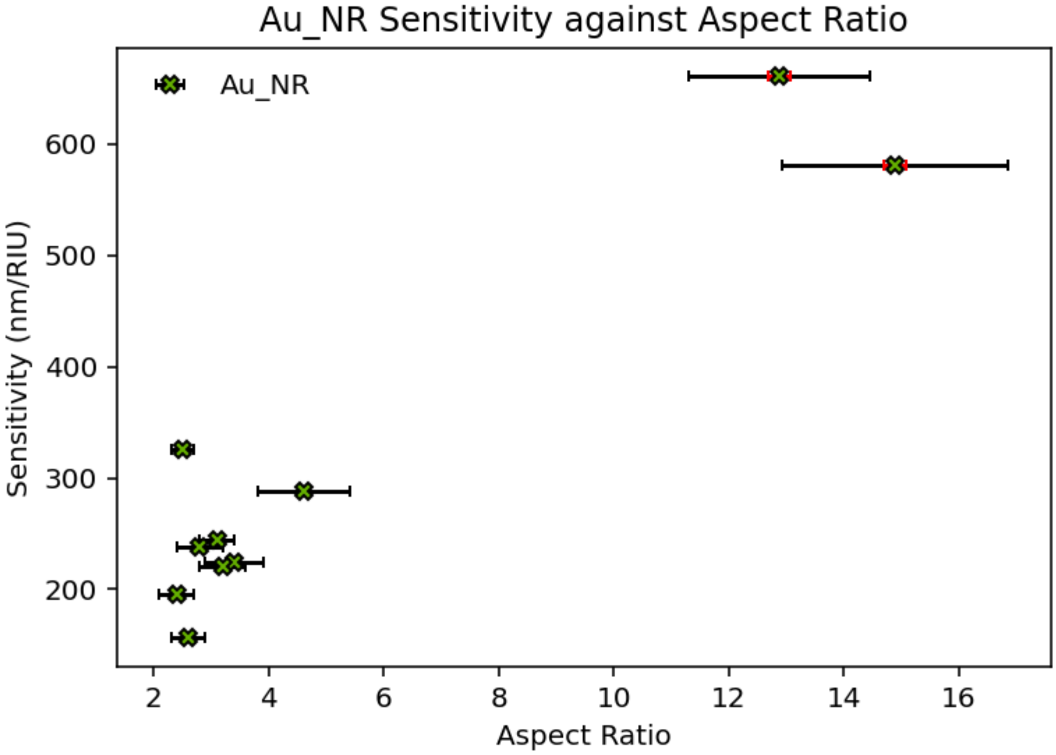

Figure 4 Sensitivity vs aspect ratio for gold nanorods.

The data acquired for figure 4 is unfortunately poor. The large gap in data between aspect ratios 5 and 12 means a valid model cannot be created in the region. The only valuable information that can be interpreted is that of the positive correlation between aspect ratio and sensitivity. The lack of regression implementation means there is no statistical data to infer anymore significant trends. The reason for such a gap follows from the fact that the data is a combination of two different datasets each focusing on a different shaped subset of nanorods at given aspect ratio scales. It was this combination of datasets that meant any regression models couldn't be applied. The larger aspect ratio data has a greater standard deviation at each point as a result the weighting of these points would be significantly reduced giving an almost vertical fit. The reason the data was combined was to highlight the further dependence of sensitivity on factors other than aspect ratio, in this case it is the specific shape. A manipulated nanostructure shape causes plasmons to oscillate differently across the longitudinal and transverse dimensions which in turn implies altered plasmon excitation requirements and hence a varying sensitivity independent of aspect ratio explicitly.

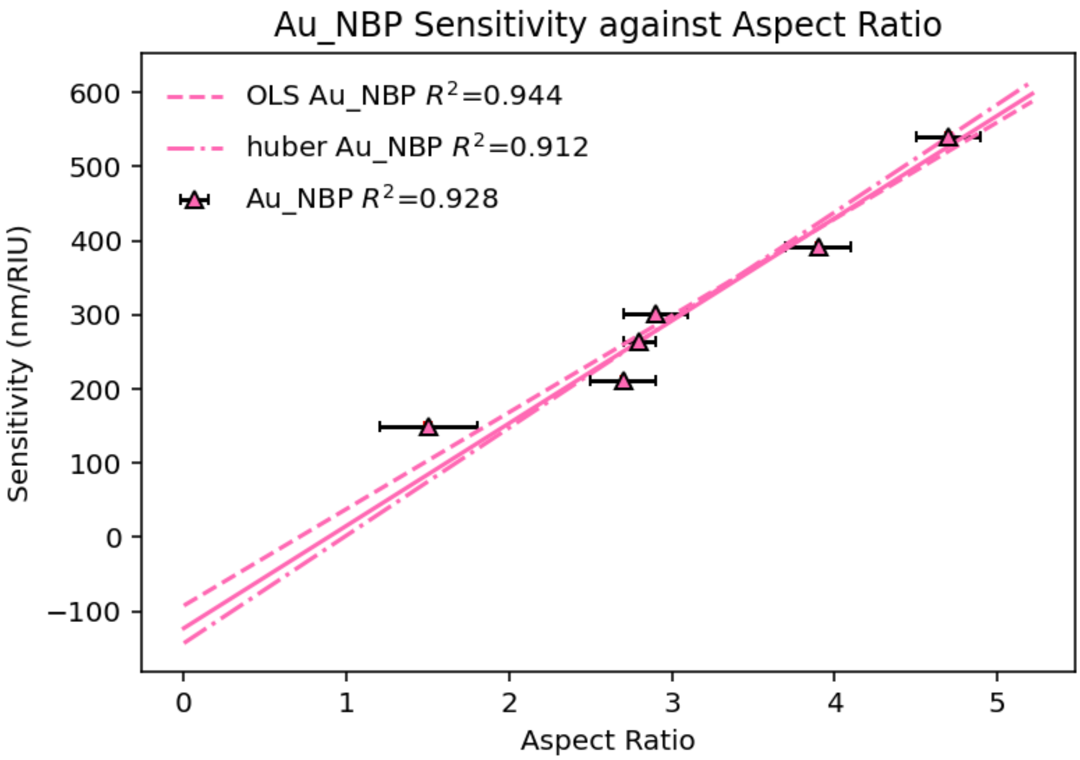

Figure 5 Sensitivity vs aspect ratio for gold nanobi-pyrimids.

This data figure 5 provides lots of information regarding nanoparticle shape tunability. In comparison to other shapes, nanobi-pyramids have a coefficient of determination closest to one. This tells us that of all potential variables that may influence sensitivity, changes in aspect ratio are the most significant. This is valuable information that can be used in the application of nanoparticles as it gives us the most control over the associated sensitivity and hence the wavefunction required for excitation. Interestingly, for nanobi-pyramids there also is the largest gradient which physically infers small aspect ratio changes that have the greatest effect on the way plasmons oscillate through this particular shape.

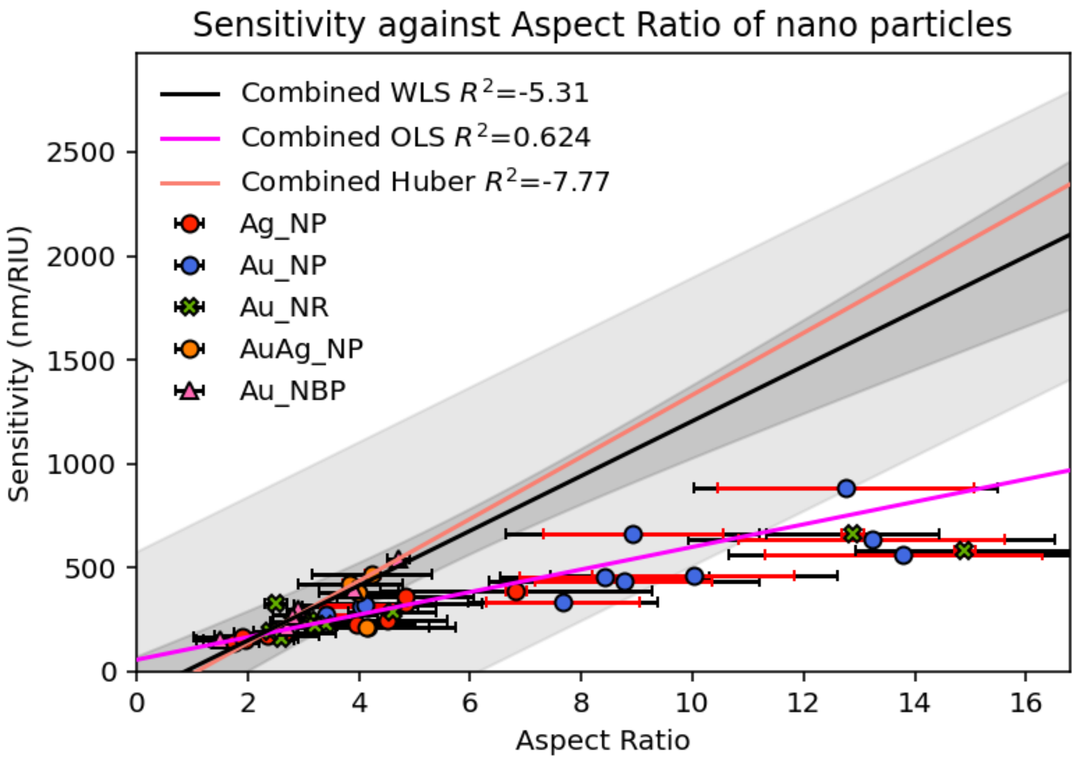

Figure 6 Sensitivity vs aspect ratio; combined data sets.

On a broader scale, figure 6 was consulted to consider the relationship between aspect ratio and sensitivity in full generality, a plot was created containing all data, combining the various shapes and their respective aspect ratio/sensitivity trends into one. Linear regression models were applied to statistically examine the relationship. As seen for the previous individual figures, the standard deviations associated to each point scale with aspect ratio. A consequence of this is that when incorporating WLS the model has a greater bias for lower aspect ratio points. This is why the data leaves the prediction band surrounding the model drastically. Ultimately an incredibly unreliable model remains with a chi squared value exceeding 1000.

5 Conclusion

Across its multitude of uses, Nanoplasmonics proves itself as an intriguing and powerful tool. Throughout this research the effects of changes in aspect ratio towards sensitivity have been studied across a variety of nanostructures and conclusions have been drawn. For many of the structures, plotted graphs show a solid linear correlation between aspect ratio and sensitivity, whilst some structures (with greater errors in data) proved unplottable, and correlations could not be found. When the wider model was plotted containing each structure the linear relation was not as clear: the plot (figure 6) contains an extensive confidence band and large chi-squared value. From this it can be concluded that there is a linear relationship between aspect ratio and sensitivity. The relationship governing sensitivity for nanoparticles is very complex, it relies on a plethora of factors and therefore not within the scope of this report. However, it is clear that a large proportion of the changes in sensitivity can be explained by changes in aspect ratio. From the main model of sensitivity, it is concluded that aspect ratio alone cannot explain the changes in sensitivity; the small changes in aspect ratio for structures are less significant compared to the greater changes of structures to one another. Whilst an overarching model cannot be plotted for this relation it is clear that across alike structures it a fundamental factor in the manipulation of nanoplasmonics.

6 Bibliography

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