The Use of Surface Plasmons as Sensors

Jonathan Mishler

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The electromagnetic properties of gold are important for applications in healthcare, food safety, and the enviornment. The uses of gold, in particular gold nanoparticles (Au NPs) in fields such as medicine is of growing interest among researchers for applications in cancer treatment, drug delivery, bioimagaing, biolabeling, and biosensing, all of which rely on gold's ability to support what is known as a surface plasmon in the presence of a dielectric. A surface plasmon is a quasiparticle resulting from the rapid as well as collective ocsillation of an electron density wave propogating along the surface of a metal-dielectric interface, the phenomenon is known as surface plasmon resonance (SPR). While other metals such as silver and copper have the ability to support surface plasmons, gold's unique properties such as its biocompatibility, chemical nobility, and exceptional interaction with dielectric media provide features optimal for its exploitation in healthcare applications. Other propertes of gold make it the metal of choice for modern day applications involving surface plasmons, and will be discussed in greater detail throughout the paper.

In every conducting metal, there are localized electrons associated with the atom in the valence band, and there are delocalized electrons found in the metal's conduction band that are essentially free to travel anywhere in the metal. When in close proximity to a dielectric of choice (will explain what this means shortly), the electrons in the conduction band at the metal-dielectric interface can, under certain circumstances (will also explain what this means shortly) form an electron density wave which propogates along the surface of the metal-dielectric

interface. The electrons in every metal oscillate at some frequency. When the wave vector of the incident light is harmonic to the electron oscillation frequencies, the electrons resonate at some resonant frequency, creating the electron density wave. However, to match the frequencies of light, a dielectric must be coupled with the metal, only some of which with specific permitivites will support the electron density wave. This wave, known as a surface plasmon has many applications in healthcare, in particular commerical biosensors. Electrons in metal-dielectrics such as gold-dielectrics and a silver-dielectrics resonate with frequenices of light in the visible spectrum, and are therefore ideal candidates for biosensing. However, gold is usually chosen because silver readily oxidizes and is more reactive than gold.

Au NPs can also support surface plasmons, however due to the local confinement of electrons in the Au NPs, the electron density wave is referred to as a localized surface plasmon (LSP), the phenomenon is known as localized surface plasmon resonance (LSPR). The characteristics of the LSP are dependant on the size and shape of the Au NPs, and are highly sensitive to any change in their dielectric enviornment, making them excellent biological detectors. In commerical SPR sensors, a surface plasmon is produced at the surface of a thin-metal-film-dielectric interface. In configurations as such, it is not sufficient to shine light with a resonant wave vector on the electrons in the metal-dielectric's conduction band; other tequniques must be used, and will be discussed later. However due to the ability of Au NPs to support localized surface plasmons through a simple matching of the incident light's wave vector and the metal-dielectric's conduction band electrons, Au NPs play important roles in medicine, and more specifically cancer treatment. Au NPs are as well important due to their ability to be coupled with a larger variety of dielectrics.

Aside from the previously stated benefits of using Au NPs in sensors, the properties of the excited LSP are much easier to model than those of a surface plasmon. For instance the Mie solution is commonly used to model the characteristic LSPR peak that would be excited based on the size of spherical Au NPs and their surrounding dielectric enviornment. The Mie solution is one of perhaps many solutions to Maxwell's equations and was developed to approximate the magnitude of the metal sphere's optical extinction (The Mie solution is also used for other approximations, however is out of the scope of this paper). These approximations are nearly one-hundred percent accurate and are used in programs such as MiePlot for fast and accurate modelling.

Converse to Au NPs, the excitation of surface plasmons at the interface of a thin-metal-film-dielctric is more complicated. There are a few ways to excite a surface plasmon, perhaps the most common being the Otto or Kretschmann geometries, both of which are known as the attenuated total reflection (ATR) methods. In the Kretschmann geometry, a prism with a higher refractive index than the dielectric film is used and is placed on top of the thin-metal-film. When light is shone through the prism, some light is reflected back through the prism, while the other portion propogates along the metal surface as an exponentially decaying evanescent wave. If the metal film is thin enough, the wave can penetrate the metal surface and couple at the interface with the metal-dielectric's delocalized electrons and excite a surface plasmon. The excitation is influenced by the dielectric and can not occur without it (J. Homola, Surface Plasmon Based Sensors, 27).

Figure 1: Kretschmann Geometry

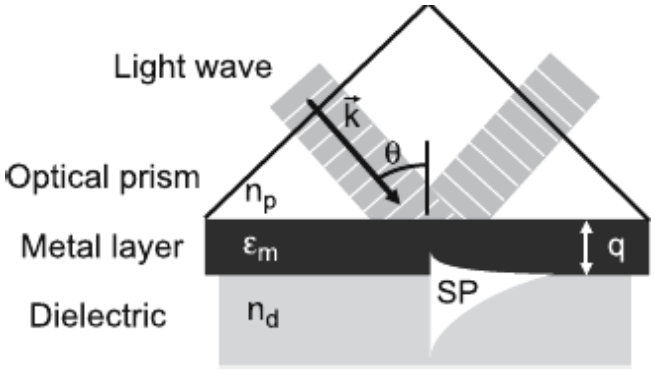

Figure 1 shows the Kretschmann geometry associated with the excitation of a surface plasmon. As shown, a light wave is incident on the prism, both being reflected at an angle equal to the angle of incidence and penetrating the metal surface exciting a surface plasmon which propagates parallel to the metal-dielectric interface. In this figure, $\vec{k}$ is the wave vector, n_p is the refractive index of the prism, ϵ_m is the permittivity (dielectric constant) of the metal, θ is the angle of incidence, q is the thickness of the metal film, and n_d is the refractive index of the dielectric. It should be noted that in the Kretschmann geometry, $n_p > n_d$ (J. Homola, Surface Plasmon Based Sensors, 27).

In the Otto geometry the prism is on top of the dielectric, rather than the metal. The angle of incidence is chosen as to be greater than the critical angle associated with the configuration's interface. The light incident on the prism is totally internally reflected parallel to the prism-dielectric interface. If the thickness of the dielectric is chosen correctly, the exponentially

decaying evanescent wave can couple with the delocalized electrons at the metal-dielectric interface and excite a surface plasmon (J. Homola, Surface Plasmon Based Sensors, 28).

Figure 2: Otto Geometry

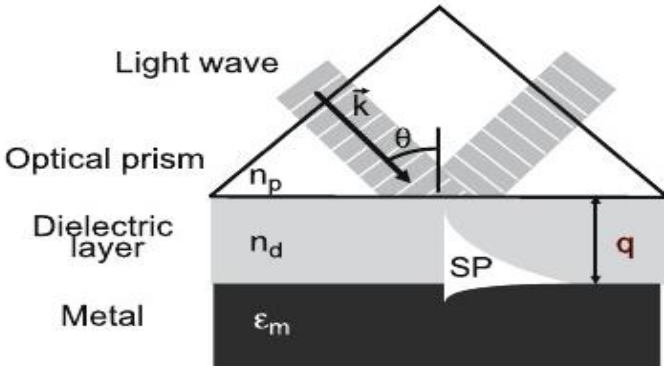

Figure 2 shows the Otto geometry associated with the excitation of a surface plasmon. As shown, a light wave is incident on the prism, both being reflected at an angle equal to the angle of incidence and being totally internally reflected parallel to the prism-dielectric interface. Because the angle of incidence is above the critical angle associated with the configuration's interface, and $n_p > n_d$, the light is refracted at a 90° angle through the interface. The variables in this figure are identical to the ones in the Kretschmann figure. It should also be noted that in both the Kretschmann and Otto geometries, the reflectivity is dependant on the frequencies of light used to excite a surface plasmon. The wavelengths corresponding to the frequencies of light used for surface plasmon excitation will not reflect and is noticed on a reflectivity versus wavelength graph where there is atleast one wavelength with zero reflectivity (J. Homola, Surface Plasmon Based Sensors, 29).

Another less common method for the excitation of surface plasmons is achieved through diffracted light. Light incident on a dielectric film placed on grated metal will cause the light to

diffract when it comes in contact with the metal ridges and grooves. The diffracted light that travels along the metal grating (also known as a diffraction grating) can couple with the delocalized electrons at the metal-dielectric interface to excite a surface plasmon (J. Homola, Surface Plasmon Based Sensors, 35.)

Figure 3: Excitation of Surface Plasmon Using Diffraction Grating

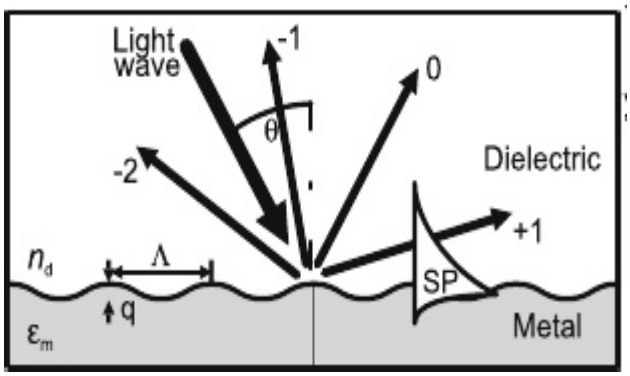

Figure 3 shows the process involved in exciting a surface plasmon by using a diffraction grating. As seen, light is incident on the metal grating where it diffracts into multiple light waves. The diffracted light waves along the metal-dielectric interface can excite a surface plasmon. All the variables in this figure are the same as in the others, however q in this figure represents the grating thickness, and Λ is the grating period (J. Homola, Surface Plasmon Based Sensors, 35.)

There are other ways to excite surface plasmons, however, they will not be discussed in this paper.

Over the last century, as the understanding of electromagnetic theory has improved, surface plasmons have gained popularity among researchers. Because surface plasmons are highly sensitive to their dielectric enviornments, they make excellent chemical as well as biological sensors. SPR sensors can be used to detect almost anything with different spectral characteristics than the metal-dielectric being used. They can be used for cancer detection, virus

detection, protein detection, as well as numerous other biological and chemical analytes. Because the analyte changes the incident light's reflective (or transmitted and absorbed if nanoparticles are used) intensity in a unique way specific to that analyte, a shift or change in the sensor's extinction can be measured and correlated to a positive or negative confirmation for whatever is being detected. Some benefits of SPR sensors include high sensitivity, real-time analysis, label-free detection, and no sample pre-treatment (Yuan Yao, "Surface Plasmon Resonance Biosensors and its Applications", 1044).

Commerical SPR sensors use thin metal films on a dielectric layer as the foundation for the sensor. There are a few ways that commercial SPR sensors work, all of which rely on some sort of spectral shift of the surface plasmon. In one method, monochromatic light of a specific frequency can be used to excite a surface plasmon using the ATR methods. The reflected light intensity is then measured as a function of the angle of incidence. Once these values are recored, the sensor with the analyte (adsorbed, absorbed, etc.) is then placed under identical conditions, and the method is repeated. Any shift in reflection intensity corresponds to a change in SPR which corresponds to a change in the thin metal film's dielectric surroundings. However, because virtually any impurity will cause a change in SPR and therefore reflected intensity, the change in reflected intensity must be compared to an experimentally determined reflection shift which only corresponds to the analyte being tested for. The device which detects a shift in reflection intensity is often a spectrometer. Another method used utilizes polychromatic light and the ATR methods to excite a surface plasmon. In this method, the angle of incidence is unchanged, and the reflectivity versus wavelength is measured using a device such as a spectrometer. Because the excitation of a surface plasmon corresponds to the wavelength with zero reflectivity, any shift in this wavelength can be measured and referenced again the known

shift for the particular analyte being sensed. The next detection method utilizes the ATR methods as well, however both the angle of incidence and frequency of light shone are fixed. The changes in reflected light intensity correspond to a change in SPR which correspond to a change in refractive index which is then referenced against a known shift in refractive index for the particular analyte used.. The last method which will be discussed in this paper to no surprise also utilizes the ATR methods. Once again, the angle of incidence and frequency of light shone are fixed. However, instead of measuring a change in refractive index, the phase differences between the incident and reflected light are measured. The analyte causes a shift in SPR which causes a phase shift, which is then referenced against the known phase shift for that particular analyte. It is of great importance that in each of these methods, the results are referenced against the known shift associated with the particular analyte being sensed. It should also be noted that not all these methods are equally effective for every analyte, and must be chosen depending on the analyte used (Yuan Yao, "Surface Plasmon Resonance Biosensors and its Applications", 1044). For example, not all biological analytes will cause a noticeable shift in refractive index.

Converse to chemical analytes which often require the analyte to adsorb or absorb onto the sensor, biological sensors often require the use of biorecognition elements such as antibodies for adequate sensing. For instance, if a sample of biofluid is being detected for a specific protein without a biorecognition element, there may not be enough proteins adsorbed on the sensor's surface to produce a strong enough signal from the proteins. While the biofluid will indeed cause a shift in the sensor's SPR, the known shift that the protein causes may not be large enough or even noticeable for a positive confirmation of that protein. When biorecognition elements are used, the proteins or whatever biological analyte is being looked for will bind to the biorecognition element and substantially increase the amount of biological analyte absorbed or

adsorbed onto the sensor. The biorecognition elements are usually flowed over the sensor in a flow cell in which they adsorb and possibly absorb into the sensor (J. Homola, "Surface Plasmon Resonance Sensors for Detection of Chemical and Biological Species", 472).

SPR sensors have been of growing importance in fields such as food safety, the enviornment, and healthcare. Due to their high sensitivity and efficiency, SPR sensors have been used to detect pathogens, drug residues, hormones, contaminants, pollutants, as well as many other harmful biological analytes found in food. In applications regarding the enviornment, SPR sensors can be used to test for chemical as well as biological toxic analytes found in sources such as drinking water and harmful metals or pesticides on farms. SPR sensors are also useful in applications regarding medicine. Such applications include the detection of cancer markers, viral markers, and real-time observation and detection of biomolecular interactions which will each cause a unique shift in SPR. Because of the relative simplicity of sample preparation, a label free detection method, and real-time observation, SPR sensors have become a valuable tool in modern medicine (J. Homola, "Surface Plasmon Resonance Sensors for Detection of Chemical and Biological Species", 472-485).

SPR sensors can also be relatively cheap to design and make. The coupling of Au NPs and transparent dielectric media for their uses as sensors is of growing interest among many researchers. Chloroauric acid can be be mixed with uncured polydimethylsiloxane (PDMS) to grow Au NPs in the mixture. Once mixed, the solution can be spin-coated onto a substrate and thermally cured. Once thermally cured, spectral data of the membrane can be easily recorded using a laser pointer (in the 532 nm range) and a charge-couple device (CCD) camera (for detection) because Au NPs only require a matching wave vector to their oscillation frequencies to excite a surface plasmon. Once the spectral data is recored, a solution of biological or

chemical analytes can be flowed over the sensor in a flow cell (biorecognition elements may also be flowed over if needed). Once the membrane is ready for spectral characterization, identical conditions may be used to compare the shift in LSPR due to the analyte through spectral analysis. However, the problem with this method is that there could be different spectral shifts associated with a different membrane thickness, Au NP density, etc. Also, because there is likely no previous spectral characterization of the particular sensor made, extensive characterization of the sensor is required for good results.

Over the course of the past couple of decades, SPR technology, specifically SPR sensors, has signifcantly advanced. In recent years, SPR sensors have become more widely used in fields such as healthcare, food safety, and the enviornment, and are of growing importance to these fields. Because of the high dielectric sensitivity of surface plasmons, SPR sensors are incredibly efficient at detecting small amounts of analyte using a fast, label-free method. Not until very recently have commerical SPR sensors become so widely available with such variety and since their release, new, inventive innovations are being made to these sensors to optimize them. In years to come, SPR sensors are predicted to have even more extraordinary features that will truly revolutionize the modern world.

Bibliography

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