Nanoplasmonics: The physics behind the applications

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Abstract

The quite new field of nanoplasmonics is described starting from the historic beginnings in art, covering the basic physics and phenomena needed to grasp the principles. Numerous uses of such phenomena in sensing and detection for different fields of interest are presented as is a prediction for future applications.
1 Introduction

Although it has already been used in ancient times, only now have the principles of nanoplasmonics been understood well enough at the physical level for us to widely benefit from this knowledge, not only in art, but also in fields of biomedicine, sensing or detecting. It is necessary to understand that confinement of electric field of subwavelength is possible, although at first sight might be hard to grasp. Quanta of electron density oscillations, called plasmons, are important in nanoplasmonics (as even the name would suggest), as is the creation of local highly enhanced intensities of electric field, called hot spots. All those things will be encountered during the seminar and explained more thoroughly.
2 Historic examples of nanoplasmonics

The field of nanoplasmonics is thought to be quite new; however, one can find examples of its basic principles from as long ago as fourth century AD. Lycurgus cup from the British museum is a fascinating object, its glass looks green in reflected light (for example if one took a picture of it with a flash) and ruby red in transmitted light (a picture taken with light behind the object). How can one explain those complementary colors? It was shown that this dichroic\textsuperscript{1} glass contains nanocrystals of a gold-silver alloy represented in less than 1% of the cup\cite{1}. These metallic nanoparticles can both absorb and scatter light, intensity of the light transmitted depends very strongly on the viewing and incident angles (arriving at or striking at a surface).

![Figure 1: (a) Lycurgus cup, taken from Nature Photonics (2007), we can observe the changing of colour (b) Le Sainte Chapelle, taken from Physics Today (2011)](image)

Another example is the stained glass of Le Sainte Chapelle in Paris. At sunset, the angle scattering by gold particles creates a strong red glow, which moves downwards with the setting sun, while the intensities of blue tints of copper and cobalt stay the same. It was probably intended to resemble a stream of blood flowing downwards. Usual glass-staining metal ions such as iron (green, brown), chromium (dark green), copper or cobalt (blue)\cite{2} do not result in those fascinating changing colours, but stay unchanged no matter what the direction of incident light.

3 Nanoplasmonics - a few basics

Nanoplasmonics is, put simply, the study of optical phenomena (control and monitoring of the localization of optical energy) in the nanoscale vicinity of metal surfaces (more accurately between 2 and 20 nm). This may sound contradictory as we are used to the notion that no electromagnetic radiation can be confined to a region of size smaller than that of half of the light’s wavelength. If we look at an ideal Fabry-Perot resonator, consisting of two parallel mirrors, the minimum modal volume is that of $\lambda^3/8$, which is about 0.01 $\mu$m$^3$. This is still far away from the elusive nanoscale, however, as it is often the case, we have forgotten the

\textsuperscript{1}Having different transmitted and reflected colours (different polarizations are absorbed by different amounts). Should not be confused with exact same term meaning to cause visible light to be split up into distinct beams of different wavelength.
few constraints we have made along the way. We have assumed that optical energy is electromagnetic energy and that the best confinement is provided by ideal mirrors with zero skin depth and no penetration. Let us consider a system of size smaller or comparable to that of its skin depth $l_s$ (the indexes are $m$ for metal and $d$ for the ambient dielectric)[3]

$$l_s = \frac{\lambda}{2\pi} \left[ \text{Re} \left( \frac{-\epsilon_m}{\epsilon_m + \epsilon_d} \right) \right]^{-1/2}.$$  

(1)

In such a system, the optical electrical field penetrates the whole system and drives the oscillations of the metal electrons. Total energy for this case is the sum of potential energy of electrons in the electric field and their mechanical kinetic energy. The contribution of magnetic field is much smaller as the nonrelativistic electrons react much weaker ($v_F/c \approx \alpha$ is around 0.01, to which the interaction is proportional ($v_F$ is speed at the Fermi surface)). Thus we can address this in the quasistatic limit, where we have mostly electromechanical energy. The energy density $\mathcal{E}$ of such system is given by the Brillouin formula ($\omega$ is frequency and $\tilde{\epsilon}$ represents the effective permittivity)

$$\mathcal{E} = \frac{1}{16\pi} \frac{\partial (\omega \text{Re} \tilde{\epsilon})}{\partial \omega} |E|^2.$$  

(2)

From here we can see that $\lambda$, which determines the length scale of the energy exchange between electric and magnetic components of the EM wave, does not define the limit of spatial localization as it did in the case of Fabry-Perot as it is not present in the equation. Therefore the spatial scale of the optical energy localization is defined by the size of the system $R$, for example the radius of a nanosphere, instead of $l_s$.

We have determined that the size of our system should not exceed the skin depth, however, there also exists a yet unmentioned lower limit, nonlocality length $l_{nl} \approx v_F/\omega \approx 1$ nm - the distance an electron with velocity $v_F$ travels during a characteristic period of the optical field. For smaller particles the SP resonances disappear.

![Figure 2](image)

Figure 2: (a) Localization of optical fields in a Fabry-Perot resonator, (b) localization by gold particles, (c) schematic of charge separation, taken from [3]

As an example, we will consider a gold nanosphere of radius $R \approx 10$ nm, which is subjected to a plane EM wave. As the field penetrates the sphere, it causes displacement of electrons with respect to the lattice, resulting in opposite charges appearing on the opposing surfaces (see
Figure 2). Attraction of those charges causes a restoring force that along with the (effective) mass of the electrons defines an electromechanical oscillator, a **surface plasmon**, or SP for short.

Plasmons are quanta of plasma oscillations or, put differently, quasiparticles (similar to photons or phonons) which result from quantization of plasma oscillations. They are oscillations of free electron gas density and when coupled with photons, called polaritons (which will be made important later in the seminar).

Surface plasmons can keep the energy concentrated on a nanoscale. They exist only because the dielectric function $\epsilon_m$ has a negative real part, which becomes true for many metals at optical frequencies when the conduction electrons in the metals can be assumed to be reasonably free in the background of static ion cores[4]. A good plasmonic metal also has very little losses, so the resonances of SPs are well pronounced, and this stands if the imaginary part of $\epsilon$ is quite smaller than the absolute value of the real part. A substance will be a good plasmonic metal if it satisfies both conditions.

$$\text{Re } \epsilon_m < 0, \quad \text{Im } \epsilon_m << -\text{Re } \epsilon_m$$ (3)

When the frequency $\omega_{SP}$ is close to the frequency of the incoming (excitation) light wave, a resonance occurs, which leads to an enhanced local field at the surface. However, resonance is closely linked to loss of energy. The rate of loss is proportional to the imaginary part of the dielectric function, which leads to a finite lifetime of SPs. The decay rate of the plasmonic field $\gamma$ is inversely proportional to $\text{Im } \epsilon_m$:

$$\gamma = \frac{\text{Im } s(\omega)}{\text{Im } \epsilon_m(\omega)} \approx \frac{\text{Im } \epsilon_m(\omega)}{\text{Im } \epsilon_m(\omega)} - \frac{\epsilon_d}{\epsilon_d - \epsilon_m(\omega)}; \quad s(\omega) = \frac{\epsilon_d}{\epsilon_d - \epsilon_m(\omega)},$$ (4)

where $s(\omega)$ is Bergman’s spectral parameter[3]. We must note that $\gamma$ implicitly depends on the geometry of the system as this determines the SP frequency. Different shapes (and sizes) such as triangles, discs or rods, carved by electron beam litography will have distinct light emissions[1], which means we can finely tune the desired frequency.

### 3.1 Some more parameters important to nanoplasmonics

One of other crucial parameters for surface plasmons is the quality factor $Q$

$$Q = \frac{\omega}{2\gamma} \approx \frac{\omega}{2\text{Im } \epsilon_m(\omega)},$$ (5)

which determines how many oscillations an SP undergoes before it decays and also measures the accompanying increase in the local field amplitude when SPs are in resonance. Another often used definition of such factor is

$$Q = \frac{-\text{Re } \epsilon_m(\omega)}{\text{Im } \epsilon_m(\omega)}.$$ (6)

Both quality factors agree reasonably well in red to near-infrared region, but differ in the yellow to blue region of the visible spectrum (Figure 3). If the metals’ permittivity was described precisely with the Drude-type formula ($\text{Re } \epsilon_m(\omega) = -\omega_p^2/\omega^2$, $\omega_p$ is the bulk plasma frequency), the definitions would be equivalent, but because in the yellow to blue part the D-band transitions also play an important role, the formula is not applicable for those regions[3].
Figure 3: Q factor: We can see that silver (a) is a much better plasmonic material than gold (b) - its quality factor is several times that of gold. But still we must not forget, that we are not interested in the whole region (only where enhancement will be high enough). Another thing we must take into account is that these Q factors are considerably smaller than those of optical resonators, for example whispering gallery mode (WGM) resonators which can be as high as $10^6$.

Square of the factor, $Q^2$, is proportional to the resonant enhancement of the local optical field intensity and it also indicates the enhancement of absorption and emission rates for molecules adsorbed on the metal particles, which is important for many applications (called the nanoantenna effect). Furthermore, for two-photon absorption processes, such as SERS (surface-enhanced Raman scattering), the enhancement follows the factor $Q^4$ and can thus be enormous (between $10^4$ and $10^8$). Additional factor related to the geometrical arrangement can raise the factor even still[1].

Modal volume $V_m$, in which the SP is localized, is usually on the order of the volume of the nanoparticle, which is about $10^{\text{nm}^3}$. This subwavelength confinement forms the basis of numerous applications, from optical filters, waveguides and other photonic-circuit components[5].

Oscillatory strength $f$, yet another important property of SP, is equal to the number of conduction electrons in a particle, typically around $10^5$, while in a dye molecule or a semiconducting quantum dot (a portion of matter whose excitons$^2$ are confined in all spatial dimensions), $f$ is about 1. Because the absorption cross section is proportional to $f$ and the scattering cross section to $f^2$, we can see why plasmonic nanoparticles are more efficient scatterers and absorbers. Efficiency is key to their applications in detection and sensing.[1]

Another effect related to nanoplasmonic confinement because of finite skin depth is that the phase shift $\Delta\phi$ for light reflected from a metal mirror differs from $\Delta\phi = \pi$, which is characteristic for ideal metals.

Lifetime $\tau$ of the SP is related to spectral width as $\tau = (2\gamma)^{-1}$. As seen in Figure 4, the lifetimes in range from 1 to 60 fs mean that nanoplasmonic phenomena are ultrafast. However, an ever faster response can be achieved. The fastest linear response time $\tau_C$ depends solely on the bandwidth and can be calculated as a quarter period of the beating between the extreme

$^2$exciton is a bound state of an electron and hole which are attracted to each other by electrostatic Coulomb force
spectral components. With the inclusion of aluminium as a plasmonic metal (as it has plasmonic response even in the UV range), a system can have a coherent reaction time $\tau_C$ around 100 as and thus nanoplasmonics is potentially attosecond science.

4 Hot spots

On a scale of nanometers, every optical wave looks like a uniform plane wave, however, when light is incident on nanoplasmonic particles, it gives rise to an inhomogeneous distribution of intense and highly localized electrical fields. These intensity spikes have been called hot spots and are one of the most important phenomena in nanoplasmonics, resulting in numerous applications. They arise from the multiplication of enhancement factors due to 1.) SP resonance, 2.) constructive interference of fields from different SPs and 3.) specific geometries such as sharp tips or narrow gaps.

The most exploited hot spot is due to the lightning rod effect, where we have a sharp tip at which a high local field is produced when the polarization of the exciting light is parallel to the tip’s axis; these enhancements are mostly nonresonant.

In clusters of silver or gold in fractal or other self-similar structures, we can observe hot spots as very pronounced enhancements in the local field. A chain of nanospheres of vastly different sizes produces even brighter signal, for example, a chain of three nanospheres, seen in Figure 5, produces field enhancement in the areas between the particles that can be as high as three orders of magnitude. The enhancement, which is due to the multiplicative, cascade effect of its geometry and high Q factor, grows along the chain, starting from the bigger particle. In the case of SERS, the arrangement can enhance the signal by 12 orders of magnitude for silver or 9 for gold - it is potentially bright enough to observe single molecules.

Such enormous enhancements only appear if we have zero losses as the local field can be quite reduced when the resonances are dulled by the radiative losses or we deal with particles whose size is no longer comparable to skin depth. There exists a way to counteract with such losses by using interference of dark and bright plasmonic modes and thus creating something called Fano resonances. Because the spectral width of those resonances is narrower than those of ordinary SP, the local field is again enhanced extraordinarily.
4.1 Fano resonance

More thoroughly, a Fano resonance is a type of resonant scattering which produces an asymmetric line shape by interference of two scattering amplitudes, the background (scattering with a continuum of states) and a resonant scattering process (excitation of a discrete state). The energies must lie in the same range. The asymmetry is due to background scattering amplitude changing slowly with energy while the resonant scattering amplitude and phase change considerably.

Total scattering section then assumes the form of (index \( \text{res} \) means resonance) [7]

\[
\frac{(q\Gamma_{\text{res}}/2 + E - E_{\text{res}})^2}{(\Gamma_{\text{res}}/2)^2 + (E - E_{\text{res}})^2}
\]

where \( q \), the Fano parameter, measures the ratio of resonant scattering to background scattering amplitude. When \( q \) approaches infinity, we are left with the well-known Breit-Wigner (or Lorentzian) formula.

5 Surface plasmon polaritons

Until now, we have described only surface plasmons. However, more important for our seminar are surface plasmon polaritons (or SPPs for short) - surface bound waves that result from the resonant coupling of charge density oscillations of the conduction electrons in the metal (SPs) with the electromagnetic field[6]. They represent a homogenous solution of the Maxwell equations on a flat metal-dielectric interface and propagate over the surface as a longitudinal surface charge density oscillation and decay in both perpendicular directions to the surface (they are transverse magnetic). The dispersion relation, which can be derived from boundary conditions for the fields on the surface, is

\[
k_{sp} = \frac{\omega}{c} \frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}
\]

The wave vector of SPP is higher than that of EM wave of the same frequency that is found solely in the dielectric. Because of the conservation of the wave vector in the plane, it
is impossible to excite SPP at an interface by an EM wave propagating in the dielectric and furthermore, SPP cannot radiate into the dielectric. This is why SPPs are called ‘dark waves’. Considering this, it seems we do not have a way to produce those oscillations. However, there exists a way to excite them and it is by using Kretschmann geometry [1].

5.1 Kretschmann geometry

The incident light with wave vector $k$ passes through a glass hemisphere with permittivity $\epsilon_1$ and is incident on the lower interface of the metal nanofilm of permittivity $\epsilon_m$ and whose thickness is comparable to skin depth. The plane above the film is filled with a medium of permittivity $\epsilon_2$ (Figure 6). The evanescent field of the light wave at the upper interface of the metal is now able to excite an SPP wave if the angle of incidence $\theta$ is equal to the so called Kretschmann angle

$$\sqrt{\epsilon_1 \sin \theta_K} = \sqrt{\frac{\epsilon_m \epsilon_2}{\epsilon_m + \epsilon_2}}.$$  \hspace{1cm} (9)

The equality 9 makes sense only if $\epsilon_1 > \epsilon_m \epsilon_2 / (\epsilon_m + \epsilon_2) > \epsilon_2$. Therefore the SPPs are excited under total internal reflection condition. When the angle almost corresponds to Kretschmann angle, the reflection coefficient $R$ of the incident wave experiences a sharp drop which signals that efficient transformation of the incident wave into phase-matched SPP is under way. Value of $\epsilon_2$ can be increased if even a monolayer of molecules is present on the metal’s upper surface and thus $\theta_K$ is perceptibly shifted.

We would also like to obtain a hot spot at a desired position over a vast band of frequencies (from the near UV to THz). A systematic and reproducible way is to adiabatically concentrate optical energy with the use of a tapered metal-nanowire surface-plasmonic waveguide (a waveguide in which the diameter varies along the length). As SPPs propagate toward the tip of the metal cone, they also slow down (never quite reaching the end) and deposit a significant fraction of their energy, which results in a giant concentration of energy on the nanoscale. The SPPs are adiabatically transformed into localized SPs, pure electric oscillations, which leads to three-dimensional nanofocusing. Such concentration has proved to be especially useful in nanoscopy-based applications as it is sensitive enough to reveal surface chemical details at the nano scale.
6 Application of nanoplasmonics[1]

Spectral shift of the plasmonic resonances toward longer wavelengths, when metal nanoparticles aggregate on the surface, is one of the most commonly exploited effects of SPs. This effect is the foundation of many sensors.

6.1 Uses in medicine

Take for example the home pregnancy test. It is an assay, designed to detect human chorionic gonadotropin hormone (hCG), a hormone produced by the uterus from the beginning of pregnancy. Primary antibodies immobilized on a strip of chromatography paper specifically target the hormone, so that when a drop of urine from expectant mother is placed on the strip, hCG binds with the antibodies, however, this binding is invisible since hormone molecules scatter little light. If we want confirmation in the form of change of colour (as it was widely used to test drunk driving, using acidified potassium permanganate solution), we add a suspension of gold nanospheres which are chemically linked to secondary antibodies. These antibodies also bind with hCG and the nanospheres now form a dense monolayer at the surface. Because of their high polarizability, they screen each other’s plasmonic charges, which causes reduction of the restoring force and frequency of the SP, consequently redshifting the emission from vaguely green colour (the colour of the initial suspension), to a bright red - confirmation of pregnancy.

The procedure is generalizable and can be used for many more substances, as long as the principle of binding with the antibodies is the same. Other widely used tests on the same principle can detect medical conditions such as prostate cancer, a heart attack and HIV-AIDS.

A very promising future application of localized surface plasmons is implantable robust sensors that can continuously monitor, for example, the glucose levels of diabetics. Given that millions of people have been diagnosed with the disease already and that the disease can lead to heart attacks, blindness, kidney failure and many more unpleasant consequences, the significance of such sensors cannot be overestimated.

6.2 Sensing analyte molecules

This method of sensing is based on the redshift as a response to covering a metal surface with analyte molecules (this is also due to the dielectric screening of SP surface charges). For it to work, the analyte molecules must have a permittivity that differs from the surrounding dielectric by some amount $\Delta \varepsilon_d$ (Figure 7).

Let us assume that the analyte molecules replace the host medium in the hot spots of the local plasmonic field. The frequency shift $\Delta \omega_n$ of a plasmonic resonance relative to its spectral width $\gamma_n$, can be described by a simple formula

$$\frac{\Delta \omega_n}{\gamma_n} = -Q \frac{\Delta \varepsilon_d}{\varepsilon_d}$$

and the estimation of the minimum number of molecules that can be sensed $N_a$ is

$$N_a = \frac{|\Delta \omega_n| \varepsilon_d V_m}{\gamma_n \alpha Q},$$

where $|\Delta \omega_n|$ is a detectable frequency shift and $\alpha$ the analyte’s polarizability. Small modal volume increases the sensitivity much more than the relatively low quality factor. The large spectral width of SP resonances compared to those of dielectric microcavities also has its advantages, as it makes the plasmonic sensing stable with respect to perturbations of the field environment. Vibrations, temperature changes and drifts in the laser frequency are no problems for this sensing method.
Figure 7: (a) example of a home pregnancy test, (b) sensing of analyte molecules through the change in permittivity, (c) testing of six different analyte proteins as a change in permittivity results in change of absorbance [1]

6.3 Plasmonic nanoscopy

A technique, near-field scanning optical microscopy (NSOM), is based on scanning nanometer-scale surface features with hot spots at the end of a pointed probe illuminated by light (Figure 8). Of the two types of instruments, the one with an aperture at the tip is commonly used to image biological cell structures. It uses a tapered optical fiber whose tip is covered with metal, typically aluminium because of its small skin depth (about 13nm), which ultimately limits the resolution of the microscope.

Instruments without an aperture may use a sharp metal tip, directly excited by focused laser radiation; however, a plasmonic metal nanosphere at the end of the probe is also often used. Its role is similar to that of a nanoantenna that delivers optical energy to the nanoscale and enhances light scattered or emitted by an object, above which it is positioned.

Newer application is that of spectroscopic nanoscopy which allows researchers identification of chemical structure on the nanometric resolution. A promising approach is that of adiabatic nanofocusing, mentioned earlier. Consider mapping the chemical composition of a silica surface which contains an ultranarrow (30 nm) trench of exposed silicon. The sensor consists of a silver cone on a two-dimensional photonic surface (see Figure 8) and is mounted on a cantilever used both for atomic force microscopy (AFM) or NSOM measurements. With this configuration researchers were able to map a silicon surface's chemical fingerprint at very fine scales. No more than a thousand atoms of silicon contribute to the optical signal, which suggests a roughly 5 nm resolution; a feat unprecedented in Raman nanoscopy and comparable to best existing specialized SERS sensors.
6.4 Other uses

Other developing applications have a potential to benefit humankind. One of most important may be thermal phototherapy of tumors using nanoparticles composed of a dielectric core and a gold shell whose thickness determines the peak of its optical absorption and can therefore be made such that they absorb mostly near-IR, light not absorbed by biological tissue (it means it will not be damaged by that kind of irradiation). The nontoxic nanoshells tend to spontaneously accumulate in tumors, when injected into the body and efficiently absorb intense IR light, but scatter very little due to their small size. Thus the generated heat kills neighbouring tumor cells but leaves the healthy tissue intact.

The ability to quickly and robustly detect very small amount of chemical substances and biological pathogens thus makes nanoplasmonic sensing important not only in science or biomedicine, but also in environmental monitoring, homeland security and national defence.

For nanoplasmonics to continue its development, an active device, a near-field generator and amplifier of nanolocalized optical fields, is needed[3]. An amplifier MOSFET has been used, however, its limits in frequency and bandwidth have already been reached and its high sensitivity to temperature, electrical fields and ionizing radiation limit its use even more.

A nanoplasmonic counterpart to laser has been proposed - a spaser[9], a nanoscale quantum generator of nanolocalized coherent intense optical fields. It has been further developed theoretically and recently also observed experimentally, along with SPP equivalents (also called nanolasers). In spasers, SPs replace photons which are the basis for lasers, a nanoparticle plays a role of the resonator, and as in all ‘amplification by stimulated emission of radiation’ devices, they also have a gain medium. The likely applications of such devices would be in ultrafast
information processing, lithography, also nanoscopy or optical loss compensation in nanocircuits and metamaterials.

7 Conclusion

In conclusion, we have seen that the field of nanoplasmonics, although quite new, has a lot to offer. From better methods of sensing, detecting, almost breakthrough novelties in biomedicine to nanoscopy. There are still many applications that remain, for example plasmon-assisted solar energy conversion, nanoplasmonic circular polarizers or optical superlenses, which have not been covered in this seminar, and also promises of optical cloaking. As the author of [1] nicely put it: "... nanoplasmonics has come a long way since the stained glass of Roman times."

References


