Plasmonic Nanostructures

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Introduction

With recent advancements in photonics, we have been able carry vast amounts of information across oceans with exceptional clarity. This has been made possible by the development of wires coated in a material of a specific dielectric constant to block the passage of a certain band of wavelengths. The hope born of this accomplishment was that optics would one day replace electronic circuits. The issue here was that because of diffraction constraints, the width of the medium a wave passes through must be at least half the light's wavelength. For infrared light, with wavelengths around 1,500 nanometers, this would require devices of at least 750 nanometers in width. This is not a significant step up from some of our current circuits, some of which have components smaller than 100 nanometers. Scientists are now searching for a solution to this problem in plasmonics.

Background

Photonics can be simply described as utilizing sections of nonconductive material with alternating dielectric constants to create a band gap of frequencies that are completely rejected. These can be used in conjunction with sections that allow the specified wavelengths to create waveguides. Plasmonics, on the other hand, relies on a metal-dielectric interface to capture or reflect certain wavelengths of light. Normally, metal is a poor choice for optics, as the field induced in the metal interacts with free electrons deeper in the metal which collide with other free electrons, interrupting the oscillations and causing the field to dissipate. By placing a nonconductive dielectric on top of the metal, we can allow the field to extend into the dielectric, where there are no free electrons, while still interacting with the surface electrons in the metal. This produces a scenario in which a wave of electrons, along with its field carried in the dielectric, can progress along a path defined by the plane between the two materials. This wave is called a plasmon.

This process results in the progression of a wave at a wavelength reduced by the reduction in the traveling speed of the wave. Normally, light waves are calculated at the speed of light, which forces any reduction in wavelength to require a similar increase in frequency. In this case, however, the transition from a light wave to an oscillation of electrons slows the wave progression, allowing a proportional decrease in wavelength. This would allow for the creation of small waveguides or junctions that compress the incident light and eject it at the end of the guide. This is a key step towards creating small scale light-based circuitry. For the simple case of a dielectric with a thin metal film, the wavelengths and frequencies of the plasmons can be adjusted by choosing different thicknesses of the film and could carry as far as a few centimeters before dying out. Structures of this type could be manipulated to replicate electronic devices, but the electric fields produced would be too large to convey signals at the nanoscale level. To solve this issue, a few nanostructures have been explored that have produced interesting results.

Nanoshell Plasmons

Rather than place the dielectric around the metal, structures have been fabricated that consist of a dielectric core with a metal shell deposited around it. These "nanoshells" can be described in terms of their inner and outer radii. This type of structure provides two interfaces, or plasmons, that interact to create resonance frequencies based on the shell size. These frequencies are determined as a function of the bulk plasmon frequency, which is described as:

$$\omega_B = \sqrt{\frac{4\pi n_0 e^2}{m_e}}$$

Where e is the electron charge, n_0 is the uniform electron gas density, and m_e is the mass of an electron. The resonant frequencies of the individual plasmons can be found by evaluating the Lagrangian of a charged, incompressible, irrotational fluid[1]:

$$L = \frac{n_0 m_e}{2}\int \eta \vec{\nabla}\eta \, dS - \frac{1}{2}\int \frac{\sigma(\vec{r})\sigma(\vec{r}')}{|\vec{r}-\vec{r}'|} dS dS'$$

In this function, the deformation of the fluid is described in terms of the scalar function η[2]:

$$\eta(r_C, \Omega_C, r_S, \Omega_S) = \sum_{lm}\left[\sqrt{\frac{a^{2l+1}}{l+1}}\dot{C}_{lm}(t) r_C^{-l-1} Y_l^m(\Omega_C) + \sqrt{\frac{1}{lb^{2l+1}}}\dot{S}_{lm}(t) r_S^{\,l} Y_l^m(\Omega_S)\right]$$

Where a and b describe the inner and outer radius of the shell, and the $\dot{C}_{lm}$ and $\dot{S}_{lm}$ functions describe the amplitude of the cavity and sphere plasmons, respectively. The values l and m are called the multipolar index and azimuthal angle. The surface charge σ is also described as the time integral of a normal derivative of this deformation function[1]:

$$\frac{d}{dt}\sigma = n_0 e \frac{d\eta}{d\hat{n}}$$

The deformation function is expressed as a normal derivative in both this case and in the Lagrangian, so it would help to define it here:

$$\frac{d\eta}{d\hat{n}} = \vec{\nabla}\eta = \frac{d\eta}{dr} = \sum_{lm}\left[-\sqrt{(l+1)a^{2l+1}}\dot{C}_{lm}(t) r_C^{-l-2} Y_l^m(\Omega_C) + \sqrt{\frac{l}{b^{2l+1}}}\dot{S}_{lm}(t) r_S^{\,l-1} Y_l^m(\Omega_S)\right]$$

We can now express σ as an integral of this function over time. To do so, we will make the assumption that the $C_{lm}(t)$ and $S_{lm}(t)$ functions are of the form:

$$C_{lm}(t) = Ne^{i\omega t} \qquad \dot{S}_{lm}(t) = Mi\omega e^{i\omega t}$$

This allows us to express σ as:

$$\sigma = \int n_0 e \frac{d\eta}{d\hat{n}} dt = \frac{n_0 e}{i\omega}\sum_{lm}\left[-\sqrt{(l+1)a^{2l+1}} C_{lm}(t) r_C^{-l-2} Y_l^m(\Omega_C) + \sqrt{\frac{l}{b^{2l+1}}} S_{lm}(t) r_S^{\,l-1} Y_l^m(\Omega_S)\right]$$

We can now calculate the kinetic term of the Lagrangian:

$$\int \eta \vec{\nabla} \eta \, dS = \int \sum_{lm} \left[-a^{2l+1} \dot{C}_{lm}(t)^2 Y_l^m(\Omega_C)^2 r_C^{-2l-3} + b^{-2l-1} \dot{S}_{lm}(t)^2 Y_l^m(\Omega_C)^2 r_S^{2l-1} \right] \left(4\pi r_{C,S}^{\ 2} dr_{C,S} d\Omega \right)$$

$$= 4\pi \sum_{lm} \left(\left(\frac{-1}{2l} \right) a^{2l+1} \dot{C}_{lm}(t)^2 r_C^{-2l} + \left(\frac{1}{2l+2} \right) b^{-2l-1} \dot{S}_{lm}(t)^2 r_S^{2l+2} \right)$$

Here we should note that the spherical harmonic functions serve to eliminate any elements that have unequal multipolar indexes or azimuthal angles (*l* or *m*) by means of the following equality:

$$\int Y_l^m(\theta,\phi) Y_{l'}^{m'}(\theta,\phi) \sin\theta \, d\theta \, d\phi = \delta_{l,l'} \delta_{m,m'}$$

This allows us to retain our summation in its proper form. The potential term of the Lagrangian is a bit more difficult. For the individual sphere and cavity plasmons, we do not need to consider coupling between the two. This allows us to express the following portion in this form:

$$\int \frac{\sigma(\vec{r})\sigma(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} dS dS' = \int \frac{\sigma(\vec{r}_C)\sigma(\vec{r}_C\,')}{|\vec{r}_C - \vec{r}_C\,'|} dS_C dS_C' + \int \frac{\sigma(\vec{r}_S)\sigma(\vec{r}_S\,')}{|\vec{r}_S - \vec{r}_S\,'|} dS_S dS_S'$$

The expanded form for both integrals appears as such:

$$\int \frac{\sigma(\vec{r}_C)\sigma(\vec{r}_C\,')}{|\vec{r}_C - \vec{r}_C\,'|} dS_C dS_C' = \left(\frac{n_0 e}{i\omega} \right)^2 \iint \sum_{lm} \frac{(l+1) a^{2l+1} C_{lm}(t)^2 Y_l^m(\Omega_C) Y_l^m(\Omega_C') r_C^{-l-2} r_C'^{-l-2} r_C^{\ 2} r_C'^{2} \, dr_C \, d\Omega_C \, dr_C' \, d\Omega_C'}{|\vec{r}_C - \vec{r}_C\,'|}$$

$$\int \frac{\sigma(\vec{r}_S)\sigma(\vec{r}_S)}{|\vec{r}_S - \vec{r}_S|} dS_C dS_S = \left(\frac{n_0 e}{i\omega} \right)^2 \iint \sum_{lm} \frac{\left(\frac{l}{b^{2l+1}} \right) S_{lm}(t)^2 Y_l^m(\Omega_S) Y_l^m(\Omega_S') r_S^{l-1} r_S'^{l-1} r_S^{\ 2} r_S'^{2} \, dr_S \, d\Omega dr_S' \, d\Omega_S}{|\vec{r}_S - \vec{r}_S\,'|}$$

In order to integrate these functions, we need to employ multipole expansion. We can choose a simplified form, as the charge density is independent of the azimuthal angle φ. This allows us to assume that all *m*=0 and the function is a sum of *l* only. The expansion occurs in the following form:

$$\iint \frac{\sigma(r)\sigma(r')drdr'}{|\vec{r}-\vec{r}\,'|} = \sum_l \left(\frac{4\pi}{2l+1} \right) \sigma(r) \int \frac{r_<^{\ l}}{r_>^{\ l+1}} \sigma(r') Y_l^m(\Omega') Y_l^0(\Omega') dr' \, d\Omega'$$

Where is $r_<$ the minimum value of (*r*, *r'*) and $r_>$ is the maximum. This corresponds to an interior moment for the cavity term and an exterior moment for the sphere term. Applying the expansion results in:

$$\iint \frac{Y_l^m(\Omega_C) Y_l^m(\Omega_C') r_C^{-l-2} r_C^{\ 2} r_C'^{-l-2} r_C'^{2} \, dr_C dr_C'}{|\vec{r}_C - \vec{r}_C\,'|} = \left(\frac{(4\pi)^2}{2l+1} \right) r_C^{\ l} r_C^{-l-2} r_C^{\ 2} \int \frac{r_C'^{-l-2} r_C'^{2}}{r_C'^{l+1}} dr_C'$$

$$r_C^{\ l} r_C^{-l-2} r_C^{\ 2} = 1$$

$$\int \frac{r_C'^{-l-2}}{r_C'^{l+1}} r_C'^{2} dr_C' = -\left(\frac{1}{2l} \right) r_C^{-2l}$$

$$\iint \frac{Y_l^m(\Omega_S)Y_l^m(\Omega_S{}')r_S{}^{l-1}r_S{}^2 r_S{}'^{l-2}\, r_S{}'^2\, dr_S dr_S{}'}{|\vec{r}_S - \vec{r}_S{}'|} = \left(\frac{(4\pi)^2}{2l+1}\right)\frac{r_S{}^{-l-2} r_S{}^2}{r_S{}^{l+1}} \int r_S{}'^{l}\, r_S{}'^{-l-2}\, r_S{}'^2\, dr_S{}'$$

$$\frac{r_S{}^{l-1}}{r_S{}^{l+1}} r_S{}^2 dr_S = 1$$

$$\int r_S{}'^{l-1}\, r_S{}'^{l}\, r_S{}'^2\, dr_S{}' = \left(\frac{1}{2l+2}\right) r_S{}^{2l+2}$$

$$\int \frac{\sigma(\vec{r})\sigma(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} dS dS' = \sum_l \frac{(4\pi n_0 e)^2}{2l+1}\left(-\left(\frac{l+1}{2l}\right) a^{2l+1} C_{lm}(t)^2 r_C{}^{-2l} + \left(\frac{l}{2l+2}\right) b^{-2l-1} S_{lm}(t)^2 r_S{}^{2l+2}\right)$$

We can now write out the Lagrangian for the whole, uncoupled system.

$$L = \frac{4\pi n_0 m_e}{2}\left(\sum_{lm}\left(\left(\frac{-1}{2l}\right) a^{2l+1} \dot{C}_{lm}(t)^2 r_C{}^{-2l} + \left(\frac{1}{2l+2}\right) b^{-2l-1} \dot{S}_{lm}(t)^2 r_S{}^{2l+2}\right)\right)$$

$$-\frac{(4\pi n_0 e)^2}{2}\sum_l \frac{1}{2l+1}\left(-\left(\frac{l+1}{2l}\right) a^{2l+1} C_{lm}(t)^2 r_C{}^{-2l} + \left(\frac{l}{2l+2}\right) b^{-2l-1} S_{lm}(t)^2 r_S{}^{2l+2}\right)$$

Next we use the Euler-Lagrange equations to develop a matrix describing our system. We can separated these into matrices M and K for each part of the equation:

$$M = \frac{\partial}{\partial t}\begin{pmatrix} \left(\dfrac{\partial L}{\partial \dot{C}}\right) \\ \left(\dfrac{\partial L}{\partial \dot{S}}\right) \end{pmatrix} = \frac{4\pi n_0 m_e i\omega}{2}\begin{bmatrix} -2\left(\dfrac{1}{2l}\right) a^{2l+1} r_C{}^{-2l} & \\ 2\left(\dfrac{1}{2l+2}\right) b^{-2l-1} r_S{}^{2l+2} & \end{bmatrix}\begin{bmatrix} C_{lm}(t) \\ S_{lm}(t) \end{bmatrix}$$

$$K = \begin{pmatrix} \left(\dfrac{\partial L}{\partial (C/i\omega)}\right) \\ \left(\dfrac{\partial L}{\partial (S/i\omega)}\right) \end{pmatrix} = \frac{-1}{2i\omega}(4\pi n_0 e)^2 \begin{bmatrix} -2\left(\dfrac{l+1}{(2l+1)(2l)}\right) a^{2l+1} C_{lm}(t) r_C{}^{-2l} \\ 2\left(\dfrac{l}{(2l+1)(2l+2)}\right) b^{-2l-1} S_{lm}(t) r_S{}^{2l+2} \end{bmatrix}$$

$$= \frac{1}{2i\omega}(4\pi n_0 e)^2 \begin{bmatrix} 2\left(\dfrac{l+1}{(2l+1)(2l)}\right) a^{2l+1} r_C{}^{-2l} & 0 \\ 0 & -2\left(\dfrac{l}{(2l+1)(2l+2)}\right) b^{-2l-1} r_S{}^{2l+2} \end{bmatrix}\begin{bmatrix} C_{lm}(t) \\ S_{lm}(t) \end{bmatrix}$$

The matrices can now be subtracted and we can evaluate the determinant for the frequency.

$$M - K = 0$$

$$= 4\pi n_0 m_e \begin{bmatrix} -\dfrac{(4\pi n_0 e)^2}{4\pi n_0 m_e}\left(\dfrac{l+1}{(2l+1)(2l)}\right) a^{2l+1} r_C{}^{-2l} + \omega^2\left(\dfrac{1}{2l}\right) a^{2l+1} r_C{}^{-2l} & 0 \\ 0 & \dfrac{(4\pi n_0 e)^2}{4\pi n_0 m_e}\left(\dfrac{l}{(2l+1)(2l+2)}\right) b^{-2l-1} r_S{}^{2l+2} - \omega^2\left(\dfrac{1}{2l+2}\right) b^{-2l-1} r_S{}^{2l+2} \end{bmatrix}\begin{bmatrix} C_{lm}(t) \\ S_{lm}(t) \end{bmatrix}$$

After substituting in for the bulk frequency and dividing out the outside constants and matrices into zero, we arrive at the following polynomial expression:

$$\left(\omega_B{}^2\left(\frac{l+1}{(2l+1)(2l)}\right)a^{2l+1}r_C{}^{-2l}-\omega^2\left(\frac{1}{2l}\right)a^{2l+1}r_C{}^{-2l}\right)\left(\omega_B{}^2\left(\frac{l}{(2l+1)(2l+2)}\right)b^{-2l-1}r_S{}^{2l+2}-\omega^2\left(\frac{1}{2l+2}\right)b^{-2l-1}r_S{}^{2l+2}\right)=0$$

Factoring these will yeild the vibration frequencies of the cavity and sphere plasmons.

$$\omega_C=\omega_B\sqrt{\frac{l+1}{2l+1}}\qquad\qquad \omega_S{}^2=\omega_B\sqrt{\frac{l}{2l+1}}$$

In the same manner, we could add coupling to the Lagrangian and would arrive at the hybridization frequencies of the nanosphere[1].

$$\omega_{l\pm}{}^2=\frac{\omega_B{}^2}{2}\left\{1\pm\frac{1}{2l+1}\left[1+4l(l+1)\left(\frac{a}{b}\right)^{2l+1}\right]^{1/2}\right\}$$

These frequency equations reflect the asymmetric and symmetric coupling between the two plasmon modes. The asymmetric mode $|\omega_+\rangle$ interacts weakly with the interacting optic field, while the symmetric mode $|\omega_-\rangle$, the lower energy of the two, interacts strongly.

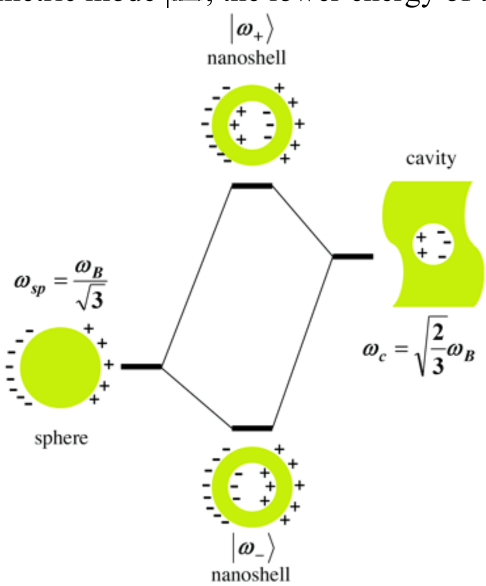

Figure 1. Energy level diagram of resonant modes[5]

Structures of this type have been successfully fabricated on the scale of 50 to more than 100 nanometers and have responded as expected from the calculations. One method for developing nanoshells consists of a reduction of tetrachloroauric acid with sulfide ions, which results in a Au_2S core with a gold shell layer. Other methods allow for the growth of the core separate from the shell, which allows much more control and precision in the design of nanoshells. This type of structure, however, has a tendency to peak sharply at a certain wavelength, which doesn't allow much freedom in designing a means of transporting information. Another nanoparticle, the nanoegg, can provide us with another degree of adjustability to our system.

<u>Nanoegg</u>

In a spherical nanoshell, the resonance between modes occurs only with those of the same multipolar index *l*. In a nanoegg, the center of the dielectric core is offset by a distance D. This offset allows all modes of the sphere and shell plasmons to hybridize to a certain degree. This causes the initially sharp peaks to spread and shift to higher frequencies. The result is a wide, multipeaked response that increases in complexity with increasing D.

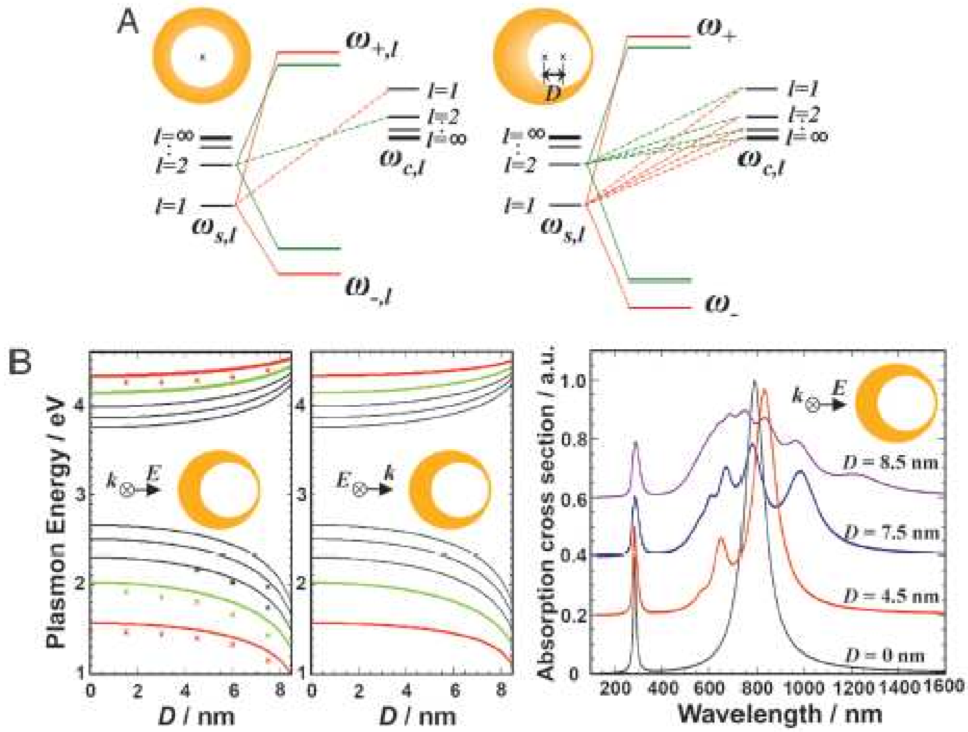

Figure 2. (A) Schematic of plasmon hybridization in nanoshell (Left) and nanoegg (Right). (B) Calculated l = 1-5 plasmon energies as a function of core offset for parallel polarization (Left) and perpendicular polarization (Center). (Right) Theoretical spectra as a function of the offset D for a (39,48) nm Au nanoshell with a vacuum cores[2]

These nanoeggs can be produced by depositing Au on already fabricated nanoshells. In this manner, the thinnest portion is dictated by the shell thickness initially and the offset can then be adjusted by the amount of Au deposited on one side of the nanoshell.

<u>Nanomatryushkas</u>

Another method of adding control to the frequency response has been titled "nanomatryushka." A nanomatryushka is a concentric nanoshell composed of a dielectric core with alternating layers of dielectric and metal laid on top. This structure not only allows adjustment of the response of individual nanoshells by means of their radii ($a_{1,2}$,$b_{1,2}$), but also adjustment of their coupling by means of the thickness of the dielectric spacer $|a_2-b_1|$.

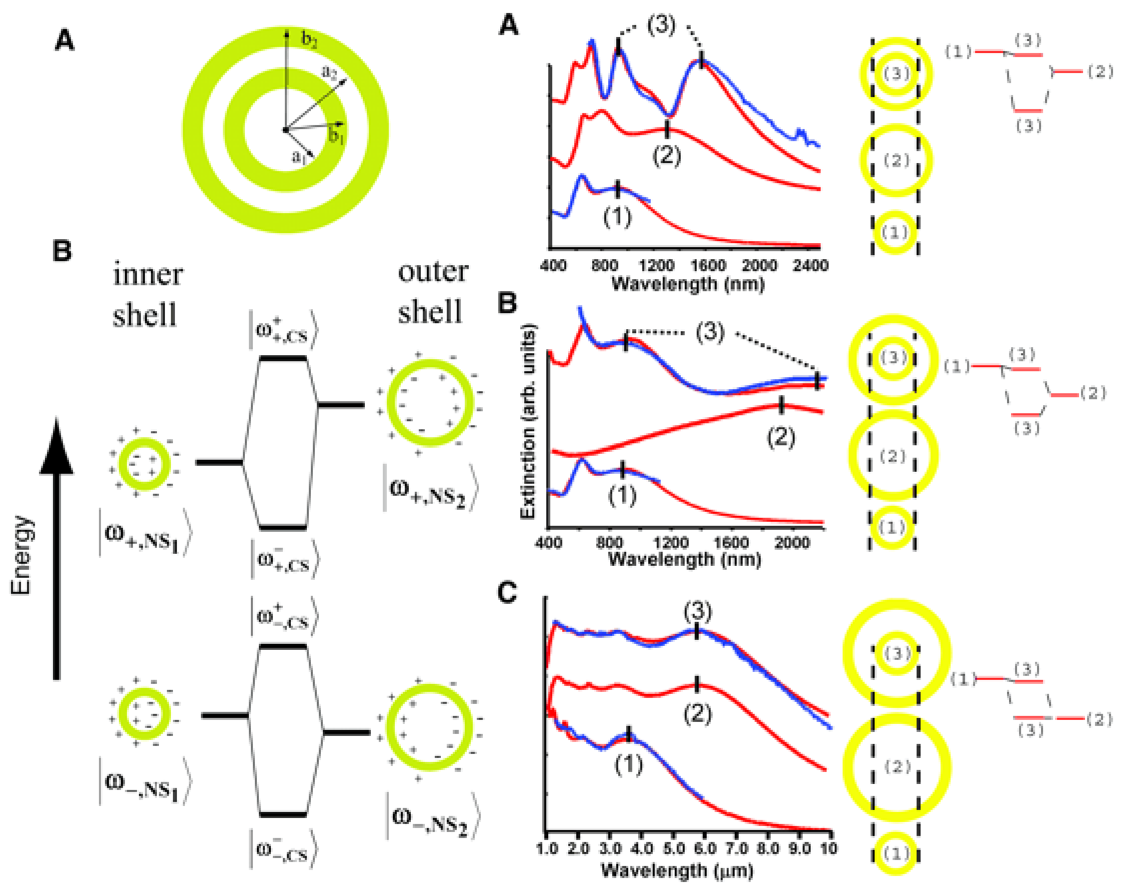

Figure 3. Nanomatryushka structure and response[5]

Image A on the left describes the basic structure of the nanomatryushka. B below it shows the energy structure of the system based on plasmon symmetry. The images on the right show an example of differing sizes of nanomatryushka. The red lines show theoretical extinction spectra, while the blue lines show experimental spectra. The smaller shell shows distinctly coupled peaks, while the nanomatryushka with larger outer shells exhibit low to almost no coupling. The dimensions for these structures are: A ($a_1/b_1/a_2/b_2$) = (80/107/135/157), B (77/102/141/145), C (396/418/654/693) with all values in nanometers.

Potential Uses

As stated before, the main draw of plasmonics is the ability to squeeze high frequency light into nanoscale waveguides that would allow for fast transmission of large amounts of data. The hope is that optics will one day replace electronic circuits and drastically increase processing potential. There have been a few ideas along these lines as well as a few others that have sprung out of the natural course of experimentation.

One of the more interesting uses stems from the nanostructure's ability to absorb light as heat as well as the biocompatibility of gold. Researchers have found that the gold plated nanoshells can be injected into the body without adverse effect. For testing purposes, they have been injected into the bloodstream of mice with cancerous tumors. The shells were found to have been deposited more on cancerous tissue than healthy ones, due to the heavy flow to the rapidly growing tumors. These shells were then targeted with infrared radiation at a wavelength that passes through animal tissue. The resonant absorption raised the temperature of the cells from about 37 degrees Celsius to about 45 degrees, killing the cancer cells while leaving healthy tissue unharmed. In the mice treated this way, all signs of cancer disappeared within 10 days, while tumors of the mice in the control group continued to grow rapidly.

Another proposed use involves a trait plasmonics discovered in the 1980s. It has been found that by enhancing the field in the dielectric, the emission rate of luminescent dyes near the metal's surface can be increased. This could potentially allow the fabrication of LEDs that shine just as brightly as traditional light sources. Systems have been created that couple silver or gold nanostructures with quantum dot arrays that boost emission by about 10 times. The hope is that eventually plasmonics will enable the creation of bright LEDs made out of cheap materials, such as silicon.

Another idea that has attracted a lot of attention is the potential use of nanostructures to create an invisibility cloak. It has been shown that by exciting a plasmon with radiation at a frequency close to its resonant frequency makes the structure's refractive index equivalent to that of air. It would be possible to create an object that, for a certain band of wavelengths, would appear to be invisible. This, however, would not apply to anything inside the object. The next step would be to create a method of diverting the light around the contents of the invisibility container and out the back in the same direction and intensity as light incident on the container. Though difficult, some scientists believe it possible.

Conclusion

Plasmonics appears to be paving the way towards optical circuitry. By providing a method of shrinking the wavelength of our information medium, we can now use smaller and more complex structures to process and deliver the information. Even with the length limitation dictated by field dissipation, plasmonics has found many uses as junctions and waveguides and some uses far outside those initially considered. The possibilities available due the advent of plasmonics gives it promise far exceeding that of photonics.

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