NIR window and Near-Field detection of gold nanoshells

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The optical properties of metal nanoparticles play a fundamental role for their use in a wide range of applications. In hyperthermia treatment, for example, the nanoshells (core+metal shell) pre-embedded in a tumor cell absorb energy when exposed to the appropriate wavelengths of a laser beam and heat up thus destroying the tumor cell; nevertheless, the healthy tissues along the laser path are not affected. This is because most biological soft tissues have a relatively low light absorption coefficient in the NIR regions, characteristic known as the tissue optical window. Over such window, NIR light transmits through the tissues with the scattering-limited attenuation and minimal heating preventing the healthy tissues. In this paper, we place emphasis on the NIR response of ultrasmall metal nanoparticles and nanoshell clusters. The necessity to focus the attention on such ultra-small aggregates is based on the availability of experimental SNOM data recorded in the recent past. The optical responses of such aggregates have been analytically deduced by the reformulation of the Mie theory in evanescent wave regime. In addition, FDTD simulations were addressed to validate the numerical results. In turn, the experimental results obtained with an aperture SNOM were also enlightened.

Introduction

The optical properties of metallic (gold, silver) nanoparticles in the visible and near-infrared (Vis-NIR) domains are governed by the collective response of conduction electrons, the so-called plasmon excitations. These form an electron gas that moves away from its equilibrium position when perturbed by an external light field inducing surface polarization charges that act as a restoring force on the electron gas. The result is a collective oscillatory motion of the electrons characterized by a dominant resonance band that, depending by the shape and size of the gold nanoparticles, falls in the Vis-NIR range [1]. Plasmons produce strong effects in both the near- and far-field response of gold nanoparticles. The far-field is fundamental for describing the macroscopic properties of absorption and scattering in colloidal dispersions and metamaterials.

The near-field properties play a key role for describing the surroundings of the particle within a distance smaller than the wavelength of light, i.e., the optical properties between nanoparticles, and the interaction with nearby molecules and sensing powering as in the SERS techniques. Since two decades, the near-field is experimentally detected via scanning near-field optical microscopy (SNOM). It is rather surprising that near-field properties of gold nanoshells can act as nanolens with near-field enhancements that vary from 3 times for gold nanoshells with outer radii of 12-15nm, until an enhancement factor of ~450 for assemblies of gold nanospheres that can be thought of rows of nanolenses [1].

As a consequence the optical properties of nanoshell clusters play a fundamental role for their use in a wide range of applications. For example, in hyperthermia treatment, the nanoshells pre-embedded in a tumor absorb energy when exposed to the appropriate wavelengths of a laser beam and heat up thus destroying the tumor; nevertheless, the healthy tissues along the laser path are not affected [2]. This is because most biological soft tissues have a relatively low light absorption coefficient in

the Vis and NIR regions, characteristic known as the tissue optical window. Over such window, NIR light transmits through the tissues with the scattering-limited attenuation and minimal heating preventing the healthy tissues.
In this paper, we place emphasis on the NIR response of ultra-small nanoshell clusters, aggregates from 2 to 3 nanoshells or 3×3 clusters. The necessity to focus the attention on such ultra-small aggregates is based on the availability of experimental SNOM data recorded in the recent past. The optical responses of such aggregates have been analytically deduced by the reformulation of the Mie theory in evanescent wave regime. In addition, FDTD simulations were addressed to validate the numerical results. In turn, the convolution effect of the SNOM probe tip with the nanoshell clusters was also enlightened.

Optical response from single to randomly distributed clusters of gold shell nanoparticles: numerical and simulated results

Absorption and scattering of light by an arbitrary *N*-spherical nanoshell cluster depend on the sizes of the primary nanoshell, the size and topology of the cluster, the particles materials and the polarization and propagation direction of the incident wave. The simplest aggregate is a pair of nanoshells. In this case, two principal excitation modes of the aggregate are obtained: the longitudinal mode, when the electric field vector of the incident wave is along with the axis of the pair, and transverse mode with the electric field being perpendicular to this axis. In the general case of arbitrary incidence of the plane wave both modes contributes to a certain amount to the absorption and scattering by the pair. In the case of a three nanoshell cluster (triplet aggregates), the situation is very close to pair particles when the three particles are located along a line (linear triplet cluster), like in figure 1. In the case of triplet aggregates, planes waves *p*-polarized, characterized by the transversal oscillation of the electric field, produce the most relevant plasmon oscillation between the nanoshells, with the appearance of supplemental modes due to the geometry of the cluster. For higher and complex clusters, extinction and scattering responses become more complicate, so we will focus the attention on the difference between a single nanoshell and a linear triplet cluster.

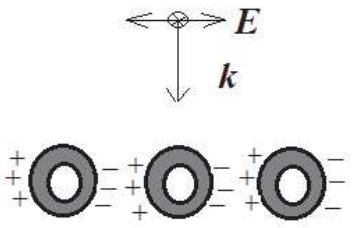

Fig. 1. A linear triplet cluster of nanoshells perpendicular to wave vector with *p*-polarized and *s*-polarized electric field vector (perpendicular to the plane wave and denoted by the cross symbol). Since the *p*-polarization presents an electric field oscillating along the axis of the cluster (longitudinal mode), the plasmonic effect is amplified and supplemental modes due to the interaction between subsequent nanoshells can be observed.

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The optical properties of nanoshell clusters, obtained using the extended Mie theory in near-field conditions, can be described in terms of normalized efficiencies for the extinction, scattering and absorption cross sections divided by the geometrical cross section of the clusters. The incident radiation can be *p*-polarized or *s*-polarized and its wave vector is directed perpendicularly to the nanoparticle array plane as in figure 1. The absorption efficiency of the numerical integration of Mie equations for a single nanoshell and a triplet or a 3×3 nanoshell clusters using the generalized multiparticle Mie approach in evanescent wave conditions are summarized in figure 2. Absorption efficiency is also the prevalent optical mechanism for particle with a varying gold layer in the range 0-100nm, with a $BaTiO_3$ core dimension fixed of 100nm [3].

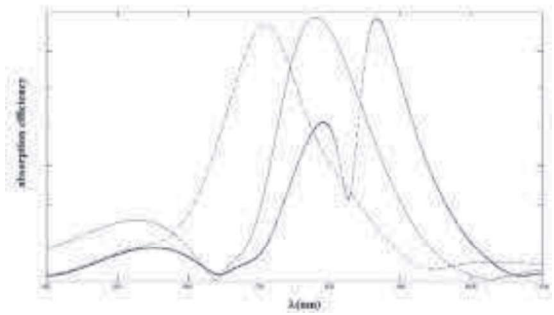

Figure 2. Absorption efficiency spectra as a function of external e.m. wavelength for, respectively, an isolated $BaTiO_3$-gold (80nm-40nm) nanoshell, dashed line, for a triplet aggregate for the same nanoshell composition, continuous line, and 3×3 nanoshell cluster, dot-dashed line.

A FDTD simulation model is applied to analyze the near-field properties around the irradiated nanoparticles. This computational technique is commonly recognized to give an adequate picture of the electromagnetic field distribution in the near and far-fields around structures with arbitrary shapes. The main signal observed in the FDTD simulation is the Poynting vector of the evanescent wave. Since the Poynting vector is also the collected signal by the SNOM, the FDTD simulation gives a results that can be immediately compared with the experimental results. However, the observed intensity collected by the SNOM aperture tip needs a comment. As I_{inc} we choose the incident intensity, averaged over the cross-sectional area of the SNOM aperture tip perpendicular to the Poynting vector ($\boldsymbol{S}=\boldsymbol{E}\times\boldsymbol{H}$) of the evanescent wave, then we have

$$I=\frac{1}{\pi a^2}\iint\langle S_{inc}\rangle ndA=I_{inc}\exp(-2\kappa d)\frac{I_1(2\kappa a)}{\kappa a}\frac{n_S}{n_M}\sin\theta_i \qquad (1)$$

where $I_1(2\kappa a)$ is the modified Bessel function of first order with argument $2ka$, and the normalization factor

$$\eta=\frac{I_1(2\kappa a)}{\kappa a}\frac{n_S}{n_M}\sin\theta_i \qquad (2)$$

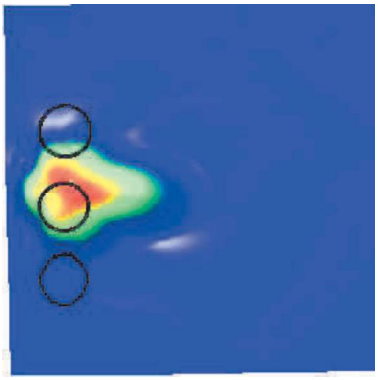

Figure 3. FDTD plot of the scattered intensity (Poynting vector) from a triplet cluster for a wavelengths of λ=795nm, as observed at z=20nm from the particle surface.

In Eq. (1), d is the z-height of the evanescent wave before the complete extinction, in the FDTD simulation we tested the Poynting vector for a z=10-30nm range, figure 3.

To exhibit the relative absorption and scattering ability of the nanoshells, the cross sections for absorption and scattering can be defined as $\sigma_{abs}=W_{abs}/I_{inc}$ and $\sigma_{scat}=W_{scat}/I_{inc}$ respectively, while the efficiencies are defined as $Q_{abs}=\sigma_{abs}/A$ and $Q_{scat}=\sigma_{scat}/A$, for the absorption and the scattering processes, respectively. Here, the $I_{inc}=(1/2)\varepsilon_0 cE^2$ represents the intensity of the incident wave, $A=\pi r^2$ is the particle cross-section projected onto a plane perpendicular to the incident wave, and r is the total radius on the nanosphere. Finally, the absorption and scattering energy $W_{abs/scat}$ are defined respectively as

$$W_{abs}=\frac{1}{2}\mathrm{Re}\left[\iint\left(\mathbf{E}_{tot}\times\mathbf{H}^*_{tot}\right)\cdot\mathbf{n}ds\right] \quad \text{and}$$
$$W_{scat}=\frac{1}{2}\mathrm{Re}\left[\iint\left(\mathbf{E}_{scat}\times\mathbf{H}^*_{scat}\right)\cdot\mathbf{n}ds\right] \qquad (3)$$

In far field, we can insert the components fields inside the eqs (3), and integrating on all a solid angle; on the contrary, in near field, if we consider a finite dimension of tip aperture, we have that the scattered and absorbed intensity are proportional to the solid angle.

In addition, if we consider a near field solution of electric and magnetic fields and the field enhancement in *z*-direction in proximity of the SNOM probe tip, under some specific conditions we can observe intense enhanced absorption. Since the E_z components under the SNOM tip is about 10 times larger compared to the in-plane components, it is reasonable to suppose that when the probe signal displays a point-like absorption peaks, this can be identified with a nanoshell [4]. This is because the field enhancement caused by the local surface plasmon resonance mainly focuses on the metal-dielectric interface (and decays exponentially) is not absorbed by the biological tissue due to the transparency window.

Experimental Results

The extinction signals of cells and small clusters of nanoshells seed on SiO_2 substrates in air were measured making use of a home-made SNOM operating in air in collection mode with different illumination wavelengths ranging from visible to near infrared.

The SNOM used for the reflection mode measurements is composed by two separable cylindrical supports: the lower one contains the sample holder mounted on top of a piezoelectric scanner which is embedded in a motor controlled *x*-*y*-*z* stage. A piezo-modulated stretched optical fiber with a few tens of a nanometer pinhole and a shear-force apparatus mounted inside the top cylinder allow for topographic measurements. In figure 4, a schematic sketch of the experimental setup is shown. Any additional information on the home-made SNOM can be found in [4]. Home-made procedure for tip manufacturing was based on chemical etching process producing tips with aperture of nearly 50nm diameter. After etching process, the tip are coated by a tiny metallic (evaporated aluminum) layer so as to prevent light from coupling into the fibre from anywhere other than at the aperture of the probe.

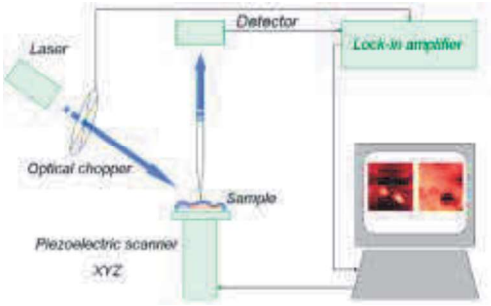

Figure 4. Schematic sketch of the experimental setup used for the SNOM acquisitions.

Conclusions

Metal nanoshells are a type of nanoparticle composed by a dielectric core and a metallic coating. They show distinctive absorption peaks at specific wavelengths due to surface plasmon resonance with the basic advantage that the wavelengths at which resonance occurs can be tuned by changing the core radius and coating thickness. In this paper, we show the changes of optical response in visible and near infrared wavelengths from single to randomly distributed ultra-small clusters of nanoshells. The results show that the optical signal of a randomly distributed cluster of nanoshells can be supplementary tuned with respect to the case of single nanoshell depending by the geometric configuration of the clusters.

References

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