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Light scattering in gold nanorings

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Abstract

The optical response of gold nanoparticles of disk-like and ring-like shape is studied by analyzing their extinction cross section in the visible and near infrared regions. A strong dependence of the excitation modes on the actual geometry of the nanoparticles is found for particle diameters of ≈ 120 nm. The nanorings exhibit pronounced extinction peaks at much larger wavelengths than the nanodisks. We present both experimental results and numerical calculations, which are in excellent agreement when the geometry is correctly described. Nanorings are also shown to enhance the spontaneous emission at the resonance, where the emission is focused primarily along the ring axis.
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1. Introduction

The optical response of nanoparticles has recently received considerable attention due to their promising technological applications [1], ranging from non-linear phenomena to photonic devices.

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The optical excitation modes depend very strongly on (i) inter-particle coupling (e.g., in surface enhanced Raman scattering [2]), (ii) the local environment (e.g., in various spectroscopy and scanning probe techniques, ranging from near field scanning optical microscopy (NSOM) to light emission in scanning tunneling microscopy (STM)), and (iii) the actual intrinsic modes of the particles [3–5]. In general, coupling among particles and between particles and the environment leads to energy shifts and splittings of degenerate modes where short and long range coupling drives the properties of the plasmon resonances [6–9]. In this work, intrinsic nanoparticle modes are investigated by measuring the extinction cross section of dispersed systems where the interaction among particles (of identical size and shape) and with the environment is negligible due to the large separation distance between particles and the lack of long-range order in the colloidal lithography arrays. In this case, the mode wavelengths depend on the material and geometrical shape of the particles. Disk-like and ring-like gold particles of sizes of the order of ≈ 120 nm are considered, so that quantum confinement effects are also negligible. Particles with different geometries show strong differences in their optical response. The modes of the nanorings produce enhanced fields inside the cavity that offer the possibility to produced enhanced spontaneous emission, as shown below.

2. Experimental results

We carry out light scattering experiments for Au particles that have a bulk disk-like shape, and particles that exhibit a ring-like shape. The Au disks and rings are made on sodaglass substrates using colloidal lithography. For rings the procedure is as follows: (i) polystyrene (PS) colloidal particles (110 nm sulphate modified latex) are deposited by electrostatic self assembly onto the glass substrates; (ii) a 20 nm Au film is evaporated onto the particle coated glass substrates; (iii) Ar ion beam etching is used to remove the Au film, during which secondary sputtering of material creates a shell around the sides of the particles; (iv) the PS particles are removed by a UV-ozone treatment and a subsequent water rinse to create free standing Au nanorings. The disks are made by reversing the order of steps (i) and (ii), and by changing the shape of the PS particles by heat pre-treatment to avoid the secondary buildup of material around the PS particles. The samples are characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The characteristic diameter of both disks and rings is around 120 nm. We consider rings with three different wall thickness d: $d = 14 \pm 2$ nm(r_1), $d = 10 \pm 2$ nm(r_2), and $d = 9 \pm 2$ nm (r_3), respectively. A close SEM image of the nanorings is shown in Fig. 1(a). Both disks and rings show approximately the same particle density ($\approx 10^9$particles/cm^2).

We carry out measurements of the relative light extinction for both disks and nanorings. The experimental results in Fig. 1(b) show a remarkable difference in the position of the extinction peak for disks (dashed line) and rings (solid lines). The disks show a typical extinction peak around 700 nm typical of bulk particles, whereas the nanorings exhibit near infrared (NIR) extinction peaks in the range of 1000–1500 nm. The NIR peaks only appear for the ring structures. Solid disks of this small size never show this long wavelength extinction peak. The differences in geometry of the two must be the reason for the anomalous NIR anomalous extinction of the nanorings.

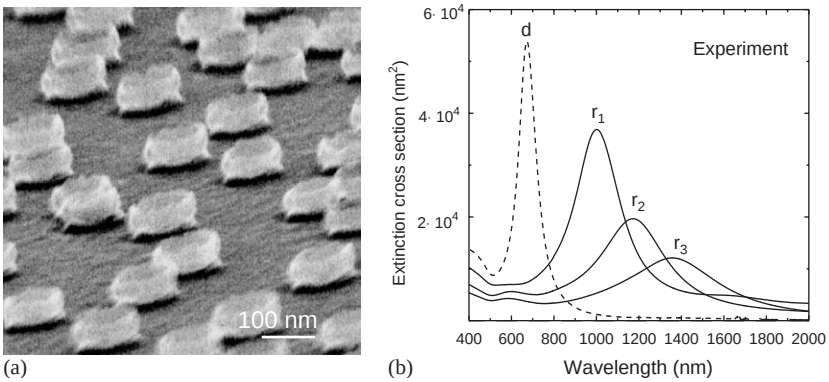

Fig. 1. (a) SEM image of ring structures. (b) Experimental extinction cross section for disks (dashed line) and rings (solid lines) of different wall thickness r_1 (thick), r_2 (medium), and r_3 (thin). Rings show near infrared peaks associated with intra-particle coupling whereas disks show a typical dipolar excitation around 700 nm.

3. Theory

The extinction cross section for disk-like particles can be understood in terms of the excitation of multipolar modes whose frequency depends on the size of the particle [10]. As the particle becomes bigger, the modes are red shifted following a dispersion relation similar to the lowest order modes of a spherical particle of radius a. The particular values for the modes energy can differ from a disk-like structure to a perfectly spherical case, nevertheless the red-shift with size follows the same pattern. In the case of the rings it is possible to excite two different patterns of polarization at the particles. On the one hand, a dipolar pattern may still be excited with an energy similar to the dipolar excitation of the disk-like particles. On the other hand, if the thickness of the ring walls d is thin enough compared to the particle radius a, there is a strong coupling between the inner and outer walls which leads to a new scheme of polarization and shifts the energy of the excitations in a similar way as in the case of a metallic thin slab where a symmetric and anti-symmetric branch of the modes is generated as the thickness becomes smaller [11].

To understand the nature of the near infrared excitations, numerical calculations of the extinction cross section for disks and rings have been performed. The parameters of the calculation are the outer radius of the particles, taken as 60 nm, and the thickness of the walls of the rings, taken as 14 nm(r_1), 10 nm(r_2), and 7 nm(r_3), which fall in the range of experimental uncertainty. The height of the rings is kept equal to 40 nm in all the cases. The material inside the particles is described by the dielectric constant of gold, as taken from optical data [12]. The SiO_2 planar substrate is also described by its dielectric function [12]. Maxwell's equations are solved under these conditions using the boundary element method [13]. In this method the electromagnetic field is expressed in terms of charges and currents distributed along the surfaces and interfaces of the structure. The customary boundary conditions for the electromagnetic field provide a set of linear integral equations with the charges and currents as the unknowns, which are solved self-consistently in the presence of an external incident light by discretizing the integrals. The light is incident normal to the substrate. The geometry of the particles is shown in the inset of Fig. 2(a) and their corresponding extinction spectra are represented by solid and

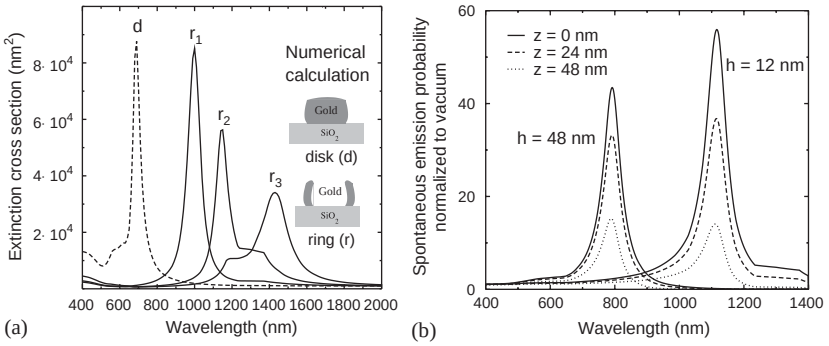

Fig. 2. (a) Calculated scattering cross section for the experimental system of Fig. 1. The height is 40 nm in all the cases. (b) Spontaneous emission probability for atoms at distance z along the axis from the center of a gold nanoring of height h and 16 nm thickness. The probability is normalized to the value in the absence of the ring.

dashed curves. The agreement between experiment and theory in position and weight of the extinction peaks is excellent.

4. Spontaneous emission near gold nanorings

Spontaneous photon emission from an excited atom is known to be influenced by the environment [14–16]. We consider a two-level atom, $\Psi_g(\mathbf{r})$ and $\Psi_e(\mathbf{r})$ being the wavefunctions of the ground state and the excited state, respectively. With these wavefunctions we can build a spontaneous emission electron current density

$$\mathbf{j}(\mathbf{r}) = -\mathrm{i}\frac{e\hbar}{m}\Psi_g^*(\mathbf{r})\vec{\nabla}\Psi_e(\mathbf{r})$$

which will be used as the semiclassical current density associated to the decay transition of the atom originally in the excited state. With this current density one can build the electric and magnetic fields originated by the transition, and therefore the Poynting vector $\mathbf{S}$, from which one can obtain the photon emission rate, or equivalently, the probability that the atom decays giving rise to an emitted photon. In the dipole approximation, that is, considering that the wavelength of the spontaneous emission transition is much larger than the atomic size, it is found that the spontaneous emission rate Γ from the atom takes the form

$$\Gamma = \frac{1}{\hbar\omega}\int_{r\to\infty} \mathrm{d}\Omega\, r^2 \mathbf{S}\hat{\mathbf{r}}.$$

In particular, for an atom near a nanoring, strong modifications in the spontaneous emission probability are expected, especially for photon energies close to the resonances of Figs. 1(b) and 2(a). Here, the emission probability is obtained from the angular integral of the Poynting vector far from the ring for a source current corresponding to a dipolar atomic transition at the position of the atom. The far field, and hence the emission probability, are also obtained from the boundary element method [13].

Fig. 2(b) shows the calculated emission probability near a ring with 120 nm diameter and 16 nm thickness for two different ring heights h (see labels in Fig. 2(b)). The atom is assumed to be in the ring axis at a distance z along the axis from the center, and the electric dipole moment is taken perpendicular to the ring axis. The probability is normalized to the value obtained in the absence of the ring. A strong enhancement is observed at the energies corresponding to the extinction peaks for the particular ring thickness (16 nm) and height (12 and 48 nm). However, this enhancement is not reproduced when the dipole moment is oriented along the ring axis. For $h = 12$ nm the enhancement occurs even for atoms well above the ring and the influence of the ring on the emission leads to a 15-fold enhancement even at a distance of $4h$. According to the different positions of spontaneous emission for rings with $h = 12$ and 48 nm, Fig. 2 is also representative of the resonance changes with ring height. As the height of the ring diminishes, the top and bottom borders of the ring can interact more effectively driving an additional red-shift to the spectrum.

5. Conclusion

In summary, it has been shown that the excitation wavelengths of metallic nanoparticles depend strongly on the particle geometry. In particular, ring-like nanoparticles exhibit near-infrared resonances that are not observed in similar disk-like particles without a hole. The observed optical response of these structures are well described by numerical simulations and the main features are qualitatively well understood from simple models for the oscillation modes. The predictive character of these calculations allows one to tailor the shape of a particle to achieve excitation spectra on demand. Spontaneous emission from atoms near rings can show a 50-fold enhancement near the nanoring resonances as a result of the enhanced fields.

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