Enhanced surface plasmon resonance absorption in metal-dielectric-metal layered microspheres

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We present a theoretical study of the dispersion relation of surface plasmon resonances of mesoscopic metal-dielectric-metal microspheres. By analyzing the solutions to Maxwell’s equations, we obtain a simple geometric condition for which the system exhibits a band of surface plasmon modes whose resonant frequencies are weakly dependent on the multipole number. Using a modified Mie calculation, we find that a large number of modes belonging to this flat-dispersion band can be excited simultaneously by a plane wave, thus enhancing the absorption cross-section. We demonstrate that the enhanced absorption peak of the sphere is geometrically tunable over the entire visible range.

In recent years there has been a growing interest in surface plasmon resonances (SPRs) of metal-dielectric structures as means to concentrate electromagnetic (EM) field in subwavelength volumes. The geometric tunability and the enhanced field intensity at the metal-dielectric interface have led to a number of theoretical and experimental demonstrations of SPR-assisted EM energy focusing. In particular, extensive studies have been conducted on SPRs of nanoshells—thin metal shells surrounding sub-micron dielectric cores. Both single and concentric nanoshell systems have been addressed. It was shown that the resonant frequencies, where incident EM radiation is efficiently focused to the nanoshells, are tunable from the visible to near-infrared. Moreover, the large EM field concentration at the metallic shell produces a giant surface enhanced Raman scattering.

The size scale of a typical nanoshell is of the order of 100nm or less, a small fraction of the excitation wavelength. As a result, only a single, low order multipole resonance plays a vital role in channelling the incident EM energy towards the metallic shell. On the other hand, mesoscopic layered particles open up the possibility for simultaneous excitation of a large number of SPRs, further increasing the efficiency of the EM field focusing. This, in turn, enhances optical phenomena such as absorption and nonlinear response.

In this Letter, we show how to utilize dispersion engineering to enhance the EM field focusing and the absorption cross-section of mesoscopic multilayered spheres. The system consists of a spherical resonator comprised of thin, alternating layers of dielectric and metal shells around a concentric metal core. The composite particle is embedded in a homogeneous, isotropic dielectric host with permittivity $\varepsilon_0$. More specifically, we address metal-dielectric-metal (MDM) microspheres: metallic cores comparable in size to optical wavelengths, surrounded by a sequence of lossless dielectric shell of thickness $L$ followed by a metal shell of thickness $T$. We show that it is possible to obtain a band of SPRs with nearly identical resonant frequencies (flat-dispersion band) by adjusting the above geometric parameters. By solving Maxwell’s equations using a spherical multipole expansion, we calculate the dispersion relations for the flat band and the resultant enhanced absorption cross-section.

To analyze the SPRs excited in the system, we initially address the dispersion relations of a simplified geometry in which the outer metal shell is infinitely thick. This model is complementary to a metal nanoshell on a dielectric core, the DMD. Unlike the DMD, the presence of a properly designed dielectric shell in the MDM is necessary and sufficient for achieving a flat-dispersion band.

We first consider a metal characterized by a lossless Drude model, $\varepsilon_m(\omega) = \varepsilon_b - \omega_p^2/\omega^2$, where $\varepsilon_b$ is the contribution of inter-band transitions and $\omega_p$ is the plasma frequency. The dielectric shell has a real permittivity $\varepsilon_d$. The eigenfrequencies of the simplified MDM system are determined by the eigenmode equation

$$0 = \left\{ \frac{\eta h_l(k_d S)}{h_l(k_m S)} - \frac{k_d S h_l(k_d S)}{h_l(k_m S)} \right\} \times \left\{ \frac{\eta j_l(k_d R)}{j_l(k_m R)} - \frac{k_d R j_l(k_d R)}{j_l(k_m R)} \right\} - \left\{ \frac{\eta h_l(k_d S)}{k_m S h_l(k_m S)} \right\} \times \left\{ \frac{\eta h_l(k_d R)}{k_m R h_l(k_d R)} \right\}$$

where $\eta = 1$ for transverse electric (TE) modes and $\eta = \varepsilon_d/\varepsilon_m$ for transverse magnetic (TM) modes, and $k_{m,d} = \sqrt{\varepsilon_{m,d}} \omega/c$. The radius of the inner metal core is $R$ and $S \equiv R + L$. The spherical Bessel and Hankel functions of the first kind of integer order $l$ are denoted respectively by $j_l$ and $h_l$, and the prime denotes differentiation with respect to the argument. We limit our discussion to large enough particles, satisfying $1 \ll k_d R$ and $1 \ll |k_m| R$. Using a real $\varepsilon_m(\omega)$ leads to straightforward analytic solutions of Eq. (1) with real $\omega$. We show later that using a realistic (lossy) metal only modifies quantitative aspects of the flat band, while its fundamental physical origins remain unaltered.

For each polarization there is an infinite number of solutions to Eq. (1), each characterized by a multipole
number, \( l \) and \( n \geq 0 \) roots, the latter yielding a radial excitation number (i.e. band index). We first examine the resonant modes for asymptotic limits of Eq. 1. For high-order multipoles satisfying \( l \gg |k_m|S \) and \( l \gg k_dS \) we expand \( j_l \) and \( h_l \) to obtain the resonance condition

\[
e_m(\omega_l) + \epsilon_d = 0.
\]  (2)

for TM polarization. No similar resonance condition exists for TE polarization. We next look for an expression for \( L \) such that Eq. 2 is also satisfied for the TM mode with the smallest multipole number. For \( l = 1 \) where expansions of \( j_l \) and \( h_l \) may be applied, Eq. 1 reduces to

\[
(2n - 1) \pi = 2k_dL,
\]  (3)

with \( n \geq 1 \).

The high order multipole modes of Eq. 2 belong to the \( n = 1 \) radial excitation band, hence by setting \( n = 1 \) in Eq. 3, we obtain the geometric condition

\[
L = L^* = \frac{\lambda_{sp}}{4\sqrt{\epsilon_d}}
\]  (4)

where \( \lambda_{sp} = 2\pi c/\omega_{sp} \) and \( \omega_{sp} \) is given by \( \epsilon_m(\omega_{sp}) + \epsilon_d = 0 \). The position of the flat band given by Eq. 4 and the geometric condition, Eq. 1, do not depend on \( R \) and are identical to those for the planar MDM geometry [7].

Figure 1(a) shows the resonant frequencies of the system plotted as function of the multipole number \( l \). To approximate the optical response of silver, we have chosen \( \epsilon_b = 5.1 \) and \( \hbar \omega_p = 9.1 eV \) [8]. The dielectric shell has \( \epsilon_d = 3.53 \), corresponding to the measured value of amorphous titania. For clarity, we have chosen a high dielectric constant to place \( \omega_{sp} \) well away from the bulk plasma resonance at \( \omega_p \). Using Eq. 4 \( L^* = 53.4 \text{nm} \), and we set \( R = 500 \text{nm} \). From the figure, it is clear that there is a band of TM modes whose frequencies are weakly dependent on the multipole number. This flat-dispersion band is near \( \omega_{sp}/\omega_p = (\epsilon_b + \epsilon_d)^{-1/2} \approx 0.34 \) as expected, and the width of the band is given by \( \delta \omega/\omega_{sp} = 0.014 \) where \( \delta \omega \) is the difference of the largest and the smallest frequencies in the band. For comparison, Fig. 1(b) shows the dispersion relation of a dielectric sphere of radius \( R + L \) embedded in a metallic host.

By analyzing the dispersion relation of MDM spheres with various core radii, we have found that when \( R \geq 100 \text{nm} \), \( \delta \omega \) depends weakly on the core radius \( R \). For example, \( \delta \omega/\omega_{sp} = 0.018 \) for \( R = 100 \text{nm} \) and \( \delta \omega/\omega_{sp} = 0.014 \) for \( R = 1000 \text{nm} \). We have observed that the material dispersion of the metallic medium affects the flatness \( \delta \omega/\omega_{sp} \) more significantly; a larger and positive \( d\delta \omega/\omega_{sp} \) leads to a flatter dispersion relation.

Next, we analyze the absorption cross-section of the MDM sphere with a metal shell of finite thickness, and study the coupling between the incident plane wave and the flat-dispersion modes. Such spheres may be realized by chemical synthesis of layered metal-dielectric particles [9, 10]. We have developed an exact and numerically stable algorithm for calculating the absorption cross-section of multilayered spheres based on previous publications [10, 11, 12, 13, 14]. We also account for absorption losses in the metal by modifying the Drude model to \( \epsilon_m(\omega) = \epsilon_b - \omega_p^2/(\omega^2 + i\Gamma)^{-1} \), with \( \Gamma \) describing the electron relaxation rate. We set \( \Gamma = 0.021 eV \) [8] and \( \epsilon_0 = 1 \).

A sharp absorption peak near \( \lambda_{sp} \) is seen in Fig. 2(a). For a core of \( R = 500 \text{nm} \) this is maximized when \( L = 62 \text{nm} \) and \( T = 77 \text{nm} \), and it is positioned at \( \lambda = 428 nm \). The deviations of the peak from \( \lambda_{sp} = 401 \text{nm} \) and of the optimal value of \( L \) from \( L^* = 53.4 \) are explained as follows: In addition to SPRs of the flat-dispersion band, SPRs of the outermost metal-host interface contribute to this peak. In fact, the two SPR branches are coupled through the finite metal shell. These plasmon hybridizations lead to slight modifications in peak position as well as in the optimal dielectric shell thickness.

The degree of coupling between the incident plane wave and the flat dispersion band is tuned by adjusting \( T \), the thickness of the outer metal shell. As we show later, the value of \( L \) may be varied in the vicinity of \( L^* \) to spectrally tune the absorption maximum while maintaining a nearly flat dispersion band. For each such value of \( L \) there exists a \( T \) which optimizes the coupling. Nevertheless, if the metal shell is made too thin, strong plasmon hybridization will eventually distort the flat band.

The mode decomposition of the spectrum, shown in Fig. 2(b), confirms that a large number of multipoles share nearly identical resonant frequencies and shows that the first 13 multipoles are excited concurrently by the incident plane wave. Higher order multipoles have negligible contribution to the absorption peak. Compared to the absorption spectrum of a metal sphere and of
metal core on the absorption diminishes, the spectrum

The enhanced absorption is also demonstrated numerically using the experimentally obtained dielectric function for silver. For $R = 500\, \text{nm}$, the absorption cross-section peak is maximized for $L = 94\, \text{nm}$ and $T = 31\, \text{nm}$, and it is at $\lambda = 533\, \text{nm}$ with $64\, \text{nm}$ FWHM as shown in Fig. 3. The absorption enhancement factors relative to a solid metallic sphere and to a core-shell sphere of a comparable size are 7 and 3, respectively. While the spectral position of the flat dispersion (i.e., $\omega_{sp}$) depends only on the optical properties of the constituent media, the absorption peak position can be tuned by adjusting $L$. As discussed above, an arbitrary $L$ does not produce a flat dispersion. However, the slope of the band, $\omega_l - \omega_{l-1}$, is generally small as long as $L \sim L^*$. Thus, it is possible to vary the value of $L$ by tens of nanometers and shift the resonant frequencies, and still retain a significant overlap of the absorption cross-section peaks of various multipoles. Figure 3 shows the geometric tunability of the enhanced absorption over the visible range.

In summary, we have analyzed the dispersion relation of mesoscale MDM spheres, and derived the condition for which the system exhibits a band of TM modes whose eigenfrequencies are weakly dependent on the multipole number. The numerically obtained absorption spectra exhibit enhanced absorption as a consequence of the simultaneous excitation of a large number of SPRs. Since the enhancement implies a large EM field concentration, these results suggest that the flat-dispersion MDM spheres may be used to enhance nonlinear optical phenomena, and more generally, they may lead to a new generation of mesoscale plasmonic systems in which numerous modes are excited to manipulate SPR-assisted light-matter interactions.

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