Surface plasmon absorption of metallic nanospheres in an amplifying medium

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ABSTRACT

Numerous applications that rely on the local field enhancement associated with the Surface Plasmon Resonance (SPR) have been suggested. With host material being an integral part in forming SPR, systems with optically transparent host have been studied exhaustively, while the case of an absorbing host still generates discussions in the literature. Amplifying host in the context of SPR has until now received no attention in the literature.

This paper considers the problem of resonant absorption of electromagnetic radiation by small metallic particles embedded in an amplifying medium. A recent theoretical analysis showed for the first time that presence of gain in the host medium could result in a considerable enhancement of the SPR of colloidal metals in that host. Local field intensities can be enhanced by as much as two orders of magnitude, compared with those obtained near surface plasmon resonance of metal nanoparticles in non-amplifying media. We further develop these ideas in a rigorous manner as a generalized Mie solution. Possible applications for these systems include rapid single molecule detection for gas and biological sensors and ultra-low intensity optical tweezers for manipulation of nanostructures.

Keywords: plasmon resonance, gold nanoparticles, Mie scattering, amplifying medium, plasmon enhancement

1 INTRODUCTION

The classic phenomenon of surface plasmon resonance (SPR) of small metallic particles has recently become the focus of renewed interest and intensive exploration due to the development of generally attainable techniques of synthesis of these materials. Numerous applications that rely on the local field enhancement associated with SPR have been suggested, including surface-enhanced Raman scattering [1] and harmonic generation [2]. The magnitude of the local electromagnetic field is, therefore, the key to efficiency in any of the SPR applications. With host material being an integral part in forming SPR, systems with optically transparent host have been studied exhaustively [3], while the case of an absorbing host still generates discussions in the literature [4]. Amplifying host in the context of SPR has until now received no attention in the literature.

This paper considers the problem of resonant absorption of electromagnetic radiation by small metallic particles embedded in an amplifying medium. In a recent theoretical analysis [5], performed in electrostatic approximation, it was shown for the first time that the presence of gain in the host medium could result in a considerable enhancement of the SPR of colloidal metals suspended in that host. This effect is the result of the mutual cancellation of the imaginary parts of dielectric functions of the metal sphere and host medium in the denominator of the first-order partial electric wave of the sphere. Complex dielectric function of the particle's surrounding, obtained by means of introduction of gain, transfers the normally complex natural frequencies of the sphere into the real domain, and thus makes it possible to increase local field intensities by as much as an order of magnitude, compared with those obtained near surface plasmon resonance of metal nanoparticles in non-amplifying media. We further develop these ideas in a rigorous manner as a generalized Mie solution for absorption of a coated gold nanosphere, utilizing numerical algorithms for evaluation of Bessel-Riccati functions and their derivatives.

2 COMPUTATION OF EFFICIENCY FACTORS FOR COATED SPHERE

We follow the formalism developed by Aden and Kerker [6] for scattering of light by stratified spheres in notations of Kerker [7]. In this theory, the exact solution of wave equation is obtained for scattering of electromagnetic radiation by a particle whose complex index of refraction varies radially from the center to the outer surface. We limit our treatment by the case of two-layer particle, i.e. a coated sphere. The inner layer (core) has radius a and refractive index n_1, and the outer layer (shell) has radius b and refractive index n_2. The refractive index of the host medium is n_3.

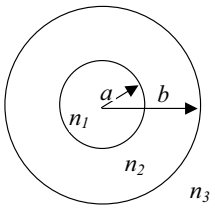

Figure 1. Geometry of a scattering coated sphere.

As usually, the calculation is performed in terms of dimensionless size parameters:

$$\alpha = \frac{2\pi a n_3}{\lambda},$$
$$\nu = \frac{2\pi b n_3}{\lambda}$$

where λ is the wavelength of light in vacuum, as well as relative indices of refraction, which are introduced as follows:

$$m_1 = \frac{n_1}{n_3},$$
$$m_2 = \frac{n_1}{n_3}$$

Kerker [7] gives the solution for the scattering coefficients in terms of Riccati-Bessel functions $\psi_n(z)$, $\chi_n(z)$, and their linear combination $\zeta_n(z)=\psi_n(z)+i\cdot\chi_n(z)$, which relate to the spherical Bessel functions of order n of the first kind $j_n(z)$ and of the second kind $y_n(z)$:

$$\psi_n(z) = z \cdot j_n(z),$$
$$\chi_n(z) = -z \cdot y_n(z)$$

The scattering coefficients are:

$$a_n = \frac{\begin{vmatrix} \psi_n'(m_2\alpha) & \chi_n'(m_2\alpha) & \psi_n'(m_1\alpha) & 0 \\ m_2\psi_n(m_2\alpha) & m_2\chi_n(m_2\alpha) & m_1\psi_n(m_1\alpha) & 0 \\ \psi_n'(m_2\nu) & \chi_n'(m_2\nu) & 0 & \psi_n'(\nu) \\ m_2\psi_n(m_2\nu) & m_2\chi_n(m_2\nu) & 0 & \psi_n(\nu) \end{vmatrix}}{\begin{vmatrix} \psi_n'(m_2\alpha) & \chi_n'(m_2\alpha) & \psi_n'(m_1\alpha) & 0 \\ m_2\psi_n(m_2\alpha) & m_2\chi_n(m_2\alpha) & m_1\psi_n(m_1\alpha) & 0 \\ \psi_n'(m_2\nu) & \chi_n'(m_2\nu) & 0 & \zeta_n'(\nu) \\ m_2\psi_n(m_2\nu) & m_2\chi_n(m_2\nu) & 0 & \zeta_n(\nu) \end{vmatrix}},$$

$$b_n = \frac{\begin{vmatrix} m_2\psi_n'(m_2\alpha) & m_2\chi_n'(m_2\alpha) & m_1\psi_n'(m_1\alpha) & 0 \\ \psi_n(m_2\alpha) & \chi_n(m_2\alpha) & \psi_n(m_1\alpha) & 0 \\ m_2\psi_n'(m_2\nu) & m_2\chi_n'(m_2\nu) & 0 & \psi_n'(\nu) \\ \psi_n(m_2\nu) & \chi_n(m_2\nu) & 0 & \psi_n(\nu) \end{vmatrix}}{\begin{vmatrix} m_2\psi_n'(m_2\alpha) & m_2\chi_n'(m_2\alpha) & m_1\psi_n'(m_1\alpha) & 0 \\ \psi_n(m_2\alpha) & \chi_n(m_2\alpha) & \psi_n(m_1\alpha) & 0 \\ m_2\psi_n'(m_2\nu) & m_2\chi_n'(m_2\nu) & 0 & \zeta_n'(\nu) \\ \psi_n(m_2\nu) & \chi_n(m_2\nu) & 0 & \zeta_n(\nu) \end{vmatrix}}.$$

Efficiency factors for extinction and scattering are obtained from the scattering coefficients as follows:

$$Q_{sca} = \frac{2}{\nu^2} \cdot \sum_{m=1}^{\infty} (2m+1) \cdot \mathrm{Re}(a_m + b_m),$$

$$Q_{ext} = \frac{2}{\nu^2} \cdot \sum_{m=1}^{\infty} (2m+1) \cdot \left(|a_m|^2 + |b_m|^2 \right)$$

The efficiency factor for absorption can be obtained as $Q_{abs} = Q_{ext} - Q_{sca}$. We truncated the series when relative increment decreased below 10^{-6}.

Our model system consists of a gold core and an amplifying shell immersed in water. Refractive index of gold was taken from experimental data [8]. Idealized shell material was considered to model an aqueous solution of amplifying "dye" whose gain line shape is described by the Lorenzian:

$$g(\omega) = \frac{\Delta_\omega}{(\omega - \omega_0)^2 + \left(\frac{\Delta_\omega}{2}\right)^2}$$

where Δ_ω is the linewidth, and ω_0 is the center frequency of the gain line. Dielectric function of such a dye follows as:

$$\varepsilon_2(\omega) = n_3^2 + 4\pi A g(\omega) \left(\frac{\omega_0 - \omega}{\Delta_{\alpha\omega}} + i \cdot \frac{1}{2} \right),$$

where n_3 = 1.33 is the refractive index of water and A is gain factor, proportional to the concentration of the dye. We choose our dye to have peak gain at 520 nm, and linewidth $\Delta_\omega = 4 \cdot 10^{14}$ s^{-1}. Plotted in Figures 2-4 is absorption efficiency of the core, defined as the total absorption cross-section divided by the geometrical cross-section of the gold core:

$$\alpha_Q^{abs} = \frac{C_{abs}}{\pi a^2} = Q_{abs} \cdot \frac{b^2}{a^2}$$

This quantity is proportional to the absorption coefficient of a suspension of corresponding particles in water, and allows direct comparison of Figures 2-4.

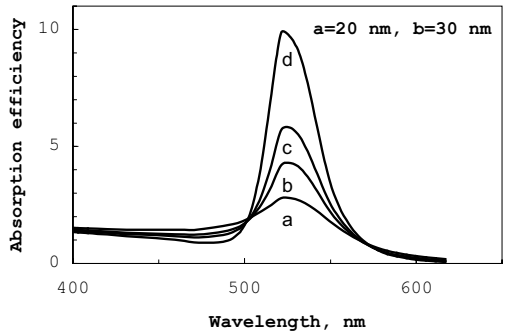

Figure 2. Absorption efficiency for a 20 nm core, 30 nm shell. Gain coefficient is (in cm^{-1}): a-0, b- $2.8 \cdot 10^4$, c-$3.9 \cdot 10^4$, d-$5.4 \cdot 10^4$.

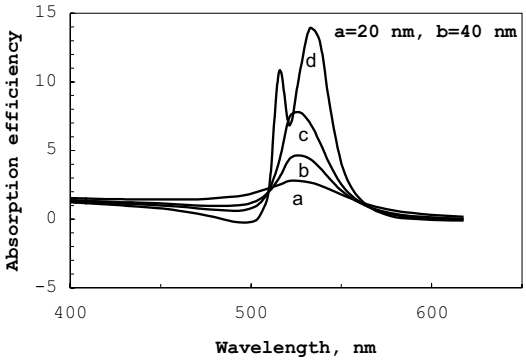

Figure 3. Absorption efficiency for a 20 nm core, 40 nm shell. Gain coefficient is (in cm^{-1}): a-0, b- $2.8 \cdot 10^4$, c-$3.9 \cdot 10^4$, d-$5.4 \cdot 10^4$.

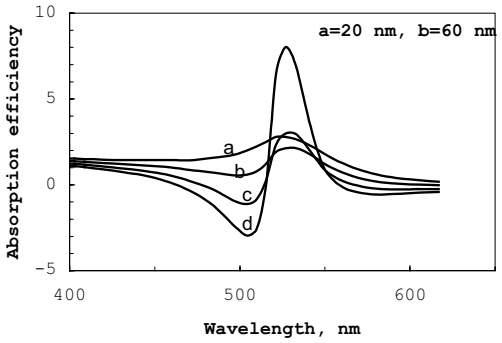

Figure 4. Absorption efficiency for a 20 nm core, 60 nm shell. Gain coefficient is (in cm^{-1}): a-0, b- $1.4 \cdot 10^4$, c-$2.8 \cdot 10^4$, d-$3.9 \cdot 10^4$.

Thus introducing amplification into a shell around a gold particle can lead to increase in absorption cross-section, in our case by a factor of 7 or more. This enhancement of absorption is necessarily accompanied by comparable increase of optical field in the vicinity of the particle, i.e the effects of the SPR are more pronounced.. Further shell amplification increase leads to absorption efficiency becoming negative in parts of the spectrum, which means overall amplification at the appropriate wavelength. However, the local field calculation, which has more direct and immediate relation to phenomena such as surface-enhanced Raman scattering and ultimately to the applications is the subject of another paper, which will be published elsewhere. Among suggested applications for the systems of metal nanostructures in amplifying host is rapid single molecule detection for gas and biological sensors and ultra-low intensity optical tweezers for manipulation of nanostructures.

REFERENCES

[1] K. Kneipp, H. Kneipp, I. Itzkan, R.R. Dasari, and M.S. Feld, J. Phys. **14**, R597-R624 (2002).

[2] P.M. Hui, C. Xu, and D. Stroud, Phys. Rev. B **69**, 014203 (2004).

[3] C.F. Bohren and D.R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1998)

[4] A.N. Lebedev and O. Stenzel, Eur. Phys. J. D **7**, 83 (1999), I.W. Sudiarta and P. Chylek, Appl. Opt. **41**, 3545 (2002), G. Videen and W. Sun, Appl. Opt. **42**, 6724 (2003).

[5] N.M. Lawandy, Appl. Phys. Lett. **85**, 5040 (2004).

[6] A.L. Aden, and M. Kerker, J. Appl. Phys. **22**, 1242 (1951)

[7] M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation*, chapter 5 (Academic Press, New York, 1969)

[8] P.B. Johnson and R.W. Christy, Phys. Rev. B **6**, 4370 (1972).