Enhancement of surface plasmons in an Ag aggregate by optical gain in a dielectric medium

M. A. Noginov, G. Zhu, M. Bahoura, J. Adegoke, and C. E. Small

Center for Materials Research, Norfolk State University, Norfolk, Virginia 23504

B. A. Ritzo

Summer Research Program, Center for Materials Research, Norfolk State University, Norfolk, Virginia 23504

V. P. Drachev and V. M. Shalaev

School of Electrical & Computer Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907

We have observed the compensation of loss in a metal by a gain in a dielectric medium in the mixture of an Ag aggregate and a Rhodamine 6G dye. The demonstrated sixfold enhancement of the Rayleigh scattering is the evidence of the enhancement of the surface-plasmon resonance. The reported experimental observation facilitates many applications of nanoplasmonics. © 2006 Optical Society of America

OCIS codes: 240.6680, 160.4760, 350.4990.

Light is the fastest and most efficient means to send information to and extract information from the nanoscale. Yet there is a fundamental incompatibility in scale between light at the microscale and devices and processes at the nanoscale. Plasmonic nanostructures can act as optical nanoantennae and nanocircuits, taking light across the nanomicrointerface. The rapid development of plasmonic nanomaterials is enabling inroads into various aspects of this problem. The major issue that needs to be addressed for opening new avenues for the next wave technology and enabling numerous applications is high loss in plasmonic nanostructures.

Localized surface plasmon (SP) is an oscillation of free electrons in a metallic particle, whose resonance frequency is the plasma frequency adjusted by the size and shape of the particle. A phenomenon relevant to localized SPs is a surface-plasmon polariton (SPP) or a surface electromagnetic wave propagating along the interface between two media possessing permittivities with opposite signs, such as the metal–dielectric interface.

Localized plasmons have been found on rough surfaces,[1,2] in engineered nanostructures,[3–6] as well as in clusters and aggregates of nanoparticles.[7–9] In the spots where local fields are concentrated, both linear and nonlinear optical responses of molecules and atoms are enormously enhanced. This leads to a number of important applications, the most matured of which is the suface-enhanced Raman scattering (SERS).[2] A number of interesting optical phenomena (such as harmonic generation, SERS, and the Kerr effect) caused by dramatic field enhancement in hot spots of fractal aggregates of Ag nanoparticles are discussed in Ref. 10. Other applications of resonating metallic nanostructures and related phenomena, described by the common name nanoplasmonics, include near-field microscopy,[11–13] extraordinary transmission of light through arrays of subwavelength holes in metallic films,[14] and negative index metamaterials.[15]

Most of existing and potential future applications of nanoplasmonics suffer from damping caused by metal absorption. In 1989, Sudarkin and Demkovich[16] suggested increasing the propagation length of the SPP by creating the population inversion in the dielectric medium adjacent to the metallic film. Recently, gain-assisted propagation of the SPPs at the interface between a metal and a dielectric with optical gain has been analyzed theoretically.[17,18] The enhancement of the SPP (of the order of 10^{-5} to 10^{-4}) at the interface between silver film and the dielectric medium with optical gain (laser dye) has been recently demonstrated in Ref. 19.

In a similar way, the localized SP resonance in metallic nanospheres is predicted to exhibit a singularity when the surrounding dielectric medium has a critical value of optical gain.[20] This singularity, resulting from canceling both real and imaginary terms in the denominator of the field enhancement factor in metal nanospheres $\propto (\varepsilon_d - \varepsilon_m)/(2\varepsilon_d + \varepsilon_m)$ can be evidenced by an increase of the Rayleigh scattering[20] (here ε_d and ε_m are complex dielectric constants of the dielectric and the metal, respectively). A relevant phenomenon of SP amplification by stimulated emission of radiation (SPASER), based on the Förster energy transfer from excited molecules to resonating metallic nanostructures, was discussed in Ref. 21.

Let us estimate a critical gain needed to compensate for the metal loss of localized SPs. The polarizability (per unit volume) for isolated metallic nanoparticles is given by $\beta = (4\pi)^{-1}[\varepsilon_m - \varepsilon_d]/[\varepsilon_d + p(\varepsilon_m - \varepsilon_d)]$, where p is the depolarization factor.[10] (We note that a fractal aggregate can be roughly thought of as a collection of spheroids, with different aspect ratios, formed by various chains of nanoparticles in the aggregate.[10] If the dielectric is an active medium with $\varepsilon_d = -p\varepsilon_m/(1-p)$, then the imaginary part in the

denominator becomes zero, leading at the resonance wavelength λ_0 to extremely large local fields limited only by saturation effects.[20,22] The resonant wavelength λ_0 is defined by the requirement to nullify the real part of the denominator, $\varepsilon_m' = -\varepsilon_d'/(1/p-1)$, which, using the Drude formula $\varepsilon_m = \varepsilon_b - \omega_p^2[\omega(\omega + i\Gamma)]$ (ε_b, ω_p, and Γ are the interband dielectric constant, plasma frequency, and relaxation rate, respectively), results in $\lambda_0 = \lambda_p \sqrt{\varepsilon_b + \varepsilon_d'(1/p-1)}$. The gain coefficient $\gamma = 4\pi n''/\lambda_0$ can be written as $\gamma = -(2\pi/\lambda_0)\varepsilon_d''/\sqrt{\varepsilon_d'}$, where we used the basic relation $n = n' + in'' = \sqrt{\varepsilon' + i\varepsilon''}$ and the approximation $n' \approx \sqrt{\varepsilon_d'}$. Thus the gain needed to compensate for the loss of the localized SP is given by

$$\gamma = (2\pi/\lambda_0)[p/(1-p)]\varepsilon_m''/n$$
$$= (2\pi/n\lambda_0)(\Gamma/\omega_p)[p/(1-p)][\varepsilon_b + n^2(1-p)/p]^{3/2},$$

where we again used the Drude formula, $n' \approx \sqrt{\varepsilon_d'}$, and set $n \equiv n'$, to simplify notations. For the resonant wavelength $\lambda_0 = 0.56$ μm, for example, we have $\varepsilon_m'' = 0.405$ and $p \approx 0.114$ so that the required $\varepsilon_d'' \approx -0.052$, and the gain coefficient is $\gamma \approx 4 \times 10^3$ cm^{-1} (we used $n = 1.33$ and known optical constants from Ref. 23).

The gain $\gamma \sim 10^3$ cm^{-1} needed to compensate for the loss of the SPP or the localized SP is within the limits of semiconducting polymers[24] or laser dyes (highly concentrated, $\sim 10^{-2}$ M,[20] or adsorbed onto metallic nanoparticles). One can estimate that a single excited molecule of R6G, characterized by the emission cross section $\sim 4 \times 10^{-16}$ cm^2, taken per volume occupied by a metallic nanoparticle with the diameter $d = 10$ nm, causes a local gain of the order of 10^3 cm^{-1}. If the number of adsorbed R6G molecules per nanoparticle exceeds 1, the effective local gain can be even higher. Note that the high gain should be in the vicinity of the metallic nanoparticles and the presence or absence of the gain far from the nanoparticles is not important as well as the percentage of the dye molecules absorbed onto the nanoparticles.

The objective of this work was to demonstrate the enhancement of the SP by a gain in a dielectric medium experimentally.[25]

We studied Rayleigh scattering in the mixtures of a R6G dye (Rhodamine 590 chloride from Exciton) and an aggregate of Ag nanoparticles. Poly(vinylpyrrolidone)-passivated Ag aggregate suspended in ethanol was prepared according to the procedure described in Ref. 26. In most of the experiments, the concentrations of R6G and Ag nanoparticles in the mixture were equal to 2.1×10^{-5} M and 8.7×10^{13} cm^{-3}, respectively. The absorption spectrum of the Ag aggregate has one structureless band covering the whole visible range and extending to the near infrared. The major feature in the absorption (emission) spectrum of R6G is the band peaking at ≈ 528 nm (≈ 558 nm).

In a pump–probe Rayleigh scattering experiment, R6G–Ag aggregate mixtures were pumped with a frequency-doubled Q-switched Nd:YAG laser ($\lambda_{pump} = 532$ nm, $t_{pump} \approx 10$ ns, repetition rate 10 Hz). A fraction of the pumping beam was split off and used to pump a simple laser consisting of the cuvette with the R6G dye placed between two mirrors, Fig. 1 (upper inset). The emission line of the R6G laser (~ 558 nm) corresponded to the maximum of the gain spectrum of the R6G dye in the mixtures studied. The beam of the R6G laser, which was used as a probe in the Rayleigh scattering, was aligned with the pumping beam in the beam splitter and sent to the sample through a small (0.5 mm) pinhole. The pump and probe beams were collinear, and their diameters at the pinhole were larger than 0.5 mm.

The scattered probe light, along with the scattered pumping light and the spontaneous emission of dye, was collected by an optical fiber that was placed within several millimeters from the cuvette at the angles ranging from $\sim 45°$ to $\sim 135°$ relative to the direction of the beam propagation. (We did not notice that the results of the SP enhancement measurement depended on the detection angle.) To separate the scattered probe light, we used a monochromator and recorded the emission spectrum between 540 and 650 nm. The scattered probe light was seen in the spectrum as a relatively narrow (~ 5 nm) line on the top of a much broader spontaneous emission band, Fig. 1 (lower inset). Thus it could be easily separated from the spontaneous emission.

Experimentally, we kept the energy of the probe light constant and measured the intensity of the scattered probe light as the function of the varied pumping light energy. The sixfold increase of the Rayleigh scattering observed in the dye–Ag aggregate mixture with the increase of the pumping energy (Fig. 1) is the clear experimental demonstration of the compen-
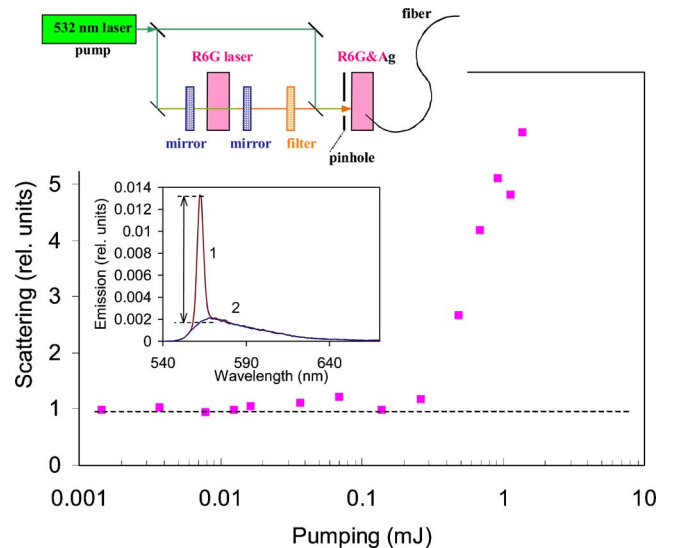

Fig. 1. (Color online) Intensity of the Rayleigh scattering as the function of the pumping energy, R6G, 2.1×10^{-5} M; Ag aggregate, 8.7×10^{13} cm^{-3}. Upper inset: Pump–probe experimental setup for the Rayleigh scattering measurements. Lower inset: 1, spectrum of scattered light and spontaneous emission; 2, spectrum of spontaneous emission only. The difference between the two spectra indicated by the arrow is plotted in the main frame.

sation of the loss in the metal and the enhancement of the quality factor of the SP resonance by optical gain in the surrounding dielectric.[25]

The dye–Ag aggregate mixtures were placed in 1 mm thick cuvettes. At the dye concentration of 2.1×10^{-5} M, the maximal optical amplification (of the pure dye solution or dye–Ag aggregate mixtures) at a 1 mm length did not exceed ~7%. (Note that low average gain is not inconsistent with the existence of high local gain in the vicinity of nanoparticles, which enhances SP resonances and Rayleigh scattering.) The lateral dimension of the pumped volume was smaller than 1 mm. The dye–Ag aggregate mixtures were visually clear, with the transport mean free path of the order of centimeters. Correspondingly, the probability of the elongation of the photon path in the pumped volume owing to scattering was insignificantly small. Thus we conclude that an increase of the intensity of scattered light in our experiment was due to an enhancement of the Rayleigh scattering cross section of metallic particles rather than simple amplification of scattered light in a medium with gain. (One can conjecture that enhancement of the Rayleigh scattering can elongate photon paths and make amplification effects more important. However, a significant increase of the Rayleigh scattering is still a necessary condition for this hypothetic effect.) Experimentally, no noticeable enhancement of scattering was observed in the pure R6G dye solution or pure Ag aggregate suspension. We also did not see evidence of irreversible photomodification that could lead to enhanced scattering at 558 nm.

To summarize, we have observed the compensation of loss in a metal by a gain in the interfacing dielectric in the mixture of the aggregated Ag nanoparticles and the Rhodamine 6G laser dye. The demonstrated sixfold enhancement of the Rayleigh scattering is the evidence of the increase of the quality factor of the SP resonance. This paves the way for numerous applications of nanoplasmonics, which currently suffer from strong damping caused by absorption loss in a metal.

References

1. R. H. Ritchie, Surf. Sci. **34**, 1 (1973).
2. M. Moskovits, Rev. Mod. Phys. **57**, 783 (1985).
3. M. Quinten, A. Leitner, J. R. Krenn, and F. R. Aussenegg, Opt. Lett. **23**, 1331 (1998).
4. R. D. Averitt, S. L. Westcott, and N. J. Halas, J. Opt. Soc. Am. B **16**, 1824 (1999).
5. M. L. Brongersma, J. W. Hartman, and H. A. Atwater, Phys. Rev. B **62**, R16356 (2000).
6. J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz, and S. Schultz, J. Chem. Phys. **116**, 6755 (2002).
7. U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, 1995), Vol. 25.
8. K.-H. Su, Q.-H. Wei, X. Zhang, J. J. Mock, D. R. Smith, and S. Schultz, Nano Lett. **3**, 1087 (2003).
9. M. Quinten, J. Cluster Sci. **10**, 319 (1999).
10. V. M. Shalaev, *Nonlinear Optics of Random Media: Fractal Composites and Metal-Dielectric Films*, Vol. 158 of Springer Tracts in Modern Physics (Springer, 2000).
11. T. L. Ferrell, Phys. Rev. B **50**, 14738 (1994).
12. E. J. Sánchez, L. Novotny, and X. S. Xie, Phys. Rev. Lett. **82**, 4014 (1999).
13. M. I. Stockman, Optoelectron. Instrum. Data Process. **3**, 27 (1989).
14. H. F. Ghaemi, T. Thio, D. E. Grupp, T. W. Ebbesen, and H. J. Lezec, Phys. Rev. B **58**, 6779 (1998).
15. J. B. Pendry, Phys. Rev. Lett. **85**, 3966 (2000).
16. A. N. Sudarkin and P. A. Demkovich, Sov. Phys. Tech. Phys. **34**, 764 (1989).
17. M. P. Nezhad, K. Tetz, and Y. Fainman, Opt. Express **12**, 4072 (2004).
18. I. Avrutsky, Phys. Rev. B **70**, 155416 (2004).
19. J. Seidel, S. Grafstroem, and L. Eng, Phys. Rev. Lett. **94**, 177401 (2005).
20. N. M. Lawandy, Appl. Phys. Lett. **85**, 5040 (2004).
21. D. J. Bergman and M. I. Stockman, Phys. Rev. Lett. **90**, 027402 (2003).
22. V. P. Drachev, A. K. Buin, H. Nakotte, and V. M. Shalaev, Nano Lett. **4**, 1535 (2004).
23. P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).
24. F. Hide, B. J. Schwartz, M. A. Diaz-Garcia, and A. J. Heeger, Synth. Met. **91**, 35 (1997).
25. M. A. Noginov, G. Zhu, V. M. Shalaev, V. P. Drachev, M. Bahoura, J. Adegoke, C. Small, and B. A. Ritzo, arxiv.org, physics/0601001 (December 31, 2005), http://arxiv.org/ftp/physics/papers/0601/0601001.pdf.
26. M. A. Noginov, G. Zhu, C. Davison, A. K. Pradhan, K. Zhang, M. Bahoura, M. Codrington, V. P. Drachev, V. M. Shalaev, and V. F. Zolin, J. Mod. Opt. **52**, 2331 (2005).