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The effect of gain and absorption on surface plasmons in metal nanoparticles

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ABSTRACT The compensation of loss in metal by gain in interfacing dielectric has been demonstrated in a mixture of aggregated silver nanoparticles and rhodamine 6G dye. An increase of the quality factor of surface plasmon (SP) resonance was evidenced by the sixfold enhancement of Rayleigh scattering. The compensation of plasmonic losses with gain enables a host of new applications for metallic nanostructures, including low- or no-loss negative-index metamaterials.

We have also predicted and experimentally observed a suppression of SP resonance in metallic nanoparticles embedded in dielectric host with absorption.

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1 Introduction

Localized surface plasmon (SP) is an oscillation of free electrons in a metallic particle. Its resonance frequency is the plasma frequency adjusted by the size and, mainly, the shape of the particle. A relevant phenomenon, surface plasmon polariton (SPP) is a surface electromagnetic wave propagating along a metal–dielectric interface. The plasmon's electromagnetic field is concentrated in the close vicinity to the surface of the particle or metal–dielectric boundary.

Localized SPs exist on rough surfaces [1, 2], in clusters and aggregates of nanoparticles [3–5], and in engineered nanostructures [6–9]. In the spots where SPs concentrate local fields, linear and nonlinear optical responses are gigantically enhanced. This leads to a number of important applications. One of them is surface enhanced Raman scattering (SERS) [2], which enables rapid molecular assays for detection of biological and chemical substances [10], observation of Raman scattering from a single molecule [11, 12], etc. A number of interesting optical phenomena, such as highly efficient harmonic generation, SERS, and Kerr effect, have been observed in fractal aggregates of metallic nanoparticles, which provide extremely large enhancements of local fields exceeding those of single metallic particles [13–15].

Brus et al. [16] proposed using gigantic localized fields to influence photochemistry of reactions. Later this phenomenon was studied in application to photocells, detectors, and other processes including vision [17]. Other applications of SPs include near field scanning microscopy and photo-modification with nanoscale resolution [18–20], extraordinary high transmission of light through subwavelength holes in metallic films [21], enhanced response of *p-n* junctions [22], negative index metamaterials [23, 24], etc.

Many applications of nanoplasmonics suffer from loss caused by absorption in metal. In 1989, Sudarkin and Demkovich proposed to increase the propagation length of surface plasmon polaritons by creating the population inversion in the interfacing dielectric [25]. More recently, gain-assisted propagation of SPPs in planar metal waveguides of different geometries has been studied by Nezhad et al. [26]. SPPs at the interface between metal and a dielectric with strong optical gain have been analyzed theoretically by Avrutsky [27]. The first experiment aimed at amplification of SPP by gain at the interface between silver film and laser dye been recently reported by Seidel et al. [28]. The observation was done in an experimental setup similar to that proposed in [25] and the experimentally observed change in the metal reflectivity was as small as 0.001% to 0.01%.

Lawandy has predicted that localized surface resonance in metallic nanospheres can exhibit a singularity when the interfacing dielectric has a critical value of optical gain [29]. This singularity results from cancelling both real and imaginary terms in the denominator of the field enhancement factor in metal nanospheres $\propto (\varepsilon_d - \varepsilon_m) / (2\varepsilon_d + \varepsilon_m)$, where e_d and e_m are complex dielectric constants of dielectric and metal, respectively. It can be evidenced by an increase of the Rayleigh scattering within the plasmon band and lead to low-threshold random laser action, light localization effects, and enhancement of surface enhanced Raman scattering [29].

A relevant phenomenon of surface plasmon amplification by stimulated emission of radiation (SPASER) was discussed

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in [30]. Apparently, the two phenomena above have different physical nature [31]. In the former one (singularity of the field enhancement factor [29]) both media, metal and dielectric with gain, interact with the field, while in SPASAR [30] non-radiative energy transfer occurs from dielectric to metal.

The objective of this work was to demonstrate a sizable enhancement of the localized SP by gain in a dielectric medium experimentally.

2 Estimation of the critical gain needed to compensate metal loss of localized SPs

The polarizability per unit volume of isolated metallic nanoparticles can be calculated as $\beta = (4\pi)^{-1}[\varepsilon_m - \varepsilon_d]/[\varepsilon_d + p(\varepsilon_m - \varepsilon_d)]$, where p is the depolarization factor [15]. (A fractal aggregate can be roughly thought of as a collection of spheroids, with different aspect ratios and different values of p, formed by various chains of nanoparticles in the aggregate [15].) The maximal (resonant) polarizability response occurs at the wavelength at which the real part of the denominator $\varepsilon'_m = -\varepsilon'_d/(1/p-1)$ is equal to zero. Using the Drude formula $\varepsilon_m = \varepsilon_b - \omega_p^2[\omega(\omega + i\Gamma)]$, one obtains $\lambda_0 = \lambda_p\sqrt{\varepsilon_b + \varepsilon'_d(1/p-1)}$, where ε_b, ω_p, and Γ are the interband dielectric constant, plasma frequency and relaxation rate, respectively. If the dielectric is a gain medium with $\varepsilon''_d = -p\varepsilon''_m/(1-p)$, then the imaginary part in the denominator becomes zero, leading to extremely large local fields (at the resonance frequency) limited only by saturation effects [29, 32]. The gain coefficient can be written as $\gamma = 4\pi n''/\lambda_0 = -(2\pi/\lambda_0)\varepsilon''_d/\sqrt{\varepsilon'_d}$, where $n = n' + in'' = \sqrt{\varepsilon' + i\varepsilon''}$ and $n' \approx \sqrt{\varepsilon'_d}$. Thus, the gain needed to compensate loss of localized surface plasmon 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 set $n \equiv n'$ to simplify notations. For the resonant wavelength $\lambda_0 = 0.56\,\mu$m, one has $\varepsilon''_m \approx 0.405$ and $p \approx 0.114$ so that the required values of ε''_d and gain coefficient γ are equal to -0.052 and $4 \times 10^3\,\text{cm}^{-1}$, respectively (we used $n = 1.33$ and known optical constants from [33]).

The gain $\gamma \sim 10^3\,\text{cm}^{-1}$ needed to compensate loss of surface plasmons is within the limits of semiconducting polymers [34] or highly concentrated laser dyes [29]. Note that the high gain should be in the vicinity of metallic nanoparticles and the presence or absence of gain far from nanoparticles is not important. One can estimate that a single excited molecule of R6G, characterized by the emission cross section $\sim 4 \times 10^{-16}\,\text{cm}^2$, taken per volume occupied by metallic nanoparticle with the diameter ~ 10 nm (typical size of nanoparticles used in or experiments [35]) causes local gain of the order of $10^3\,\text{cm}^{-1}$. If the number of adsorbed R6G

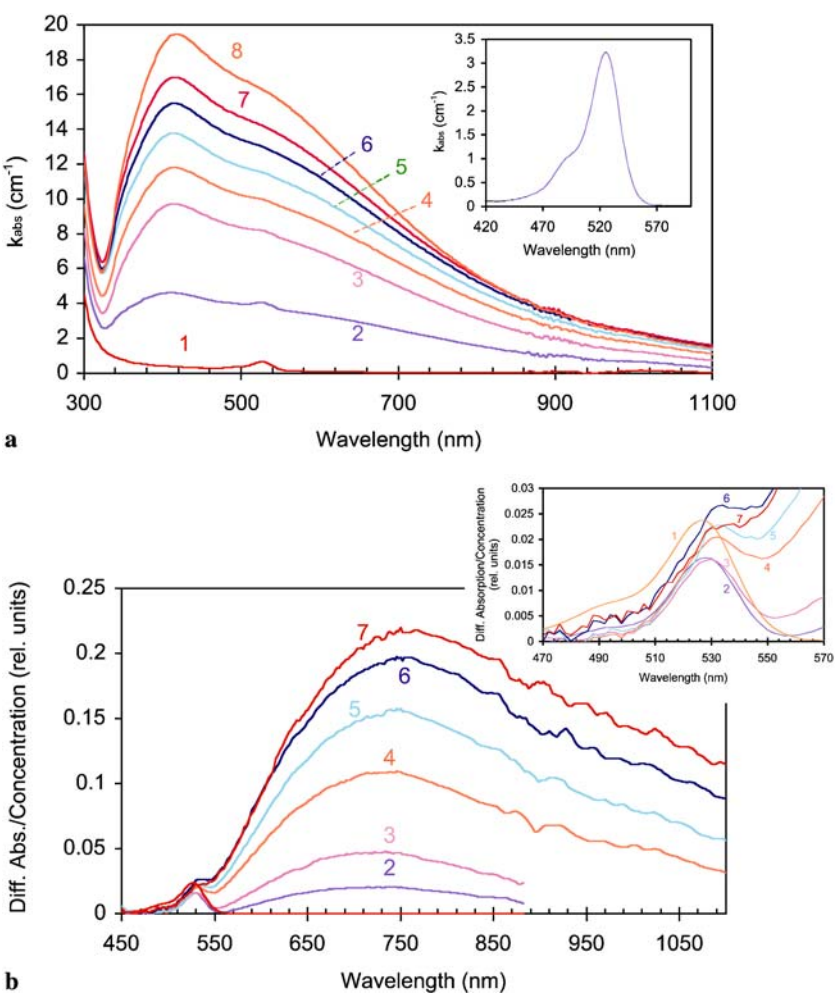

FIGURE 1 (**a**) Trace 1 – absorption spectrum of pure R6G dye solution (2.1×10^{-6} M); trace 8 – absorption spectrum of pure Ag aggregate solution ($8.8 \times 10^{13}\,\text{cm}^{-3}$); traces 2–7 – absorption spectra of R6G-Ag aggregate mixtures. The ratio of Ag aggregate solution to R6G solution in the mixture is equal to 27.1/72.9 (2), 57.3/42.7 (3), 66.5/33.5 (4), 74.8/25.2 (5), 80.8/19.2 (6), and 86.8/13.2 (7). *Inset*: Absorption spectrum of pure R6G dye solution (1.25×10^{-5} M). (**b**) Difference absorption spectra (absorption spectrum of the mixture minus scaled spectrum of the aggregate, normalized to the concentration of R6G dye in the mixture). The traces in figure (**b**) correspond to the spectra with similar numbers in figure (**a**). *Inset*: Enlarged fragment of the main frame. Trace 1 corresponds to pure R6G dye

molecules per metallic nanoparticle exceeds one, the effective local gain can be even higher.

3 Experimental samples

We studied absorption, emission, and Rayleigh scattering in the mixtures of R6G dye (Rhodamine 590 Chloride from Exciton) and aggregated silver nanoparticles. The starting solutions of R6G in methanol had concentrations of dye molecules in the range 1×10^{-6}–2.1×10^{-4} M. Poly(vinylpyrrolidone)-passivated Ag aggregate suspended in ethanol was prepared using the routine described in [36]. The estimated concentration of Ag nanoparticles in the original aggregate suspension was $8.8 \times 10^{13}\,\mathrm{cm}^{-3}$. In many particular experiments, we diluted Ag aggregate before mixing it with dye. The absorption spectrum of Ag aggregate is characterized by a broad band covering the whole visible range and extending to near-infrared, Fig. 1 trace 8. The major absorption band of R6G peaks at ≈ 528 nm, Fig. 1a trace 1 and inset of Fig. 1a. The emission band of dye has a maximum at 558 nm.

4 Enhancement of surface plasmon by optical gain: demonstration and discussion

In the Rayleigh scattering experiment, mixtures of aggregated silver nanoparticles and rhodamine 6G dye were pumped with 10 ns pulses of a second harmonic Nd:YAG laser, $\lambda = 532$ nm. A part of the pumping beam was used to excite the R6G laser operating at the maximum of the gain spectrum, $\lambda \sim 558$ nm (inset of Fig. 2). The beam of the R6G laser, which Rayleigh scattering was studied, was aligned with the pumping beam and directed to the sample through a small (0.5 mm) pinhole. The pump and probe beams were collinear and their diameters were larger than size of the pinhole.

The probe light scattered by Ag aggregate ($\lambda = 558$ nm) was collected by an optical fiber together with the scattered pumping light ($\lambda = 532$ nm) and the emission of dye. The fiber was positioned at the angles ranging from $\sim 45°$ to $\sim 135°$ relative the direction of the beam propagation, within several millimeters from the cuvette. Using a monochromator, we recorded the spectrum of light collected by the fiber between 540 and 650 nm. The scattered probe light was seen

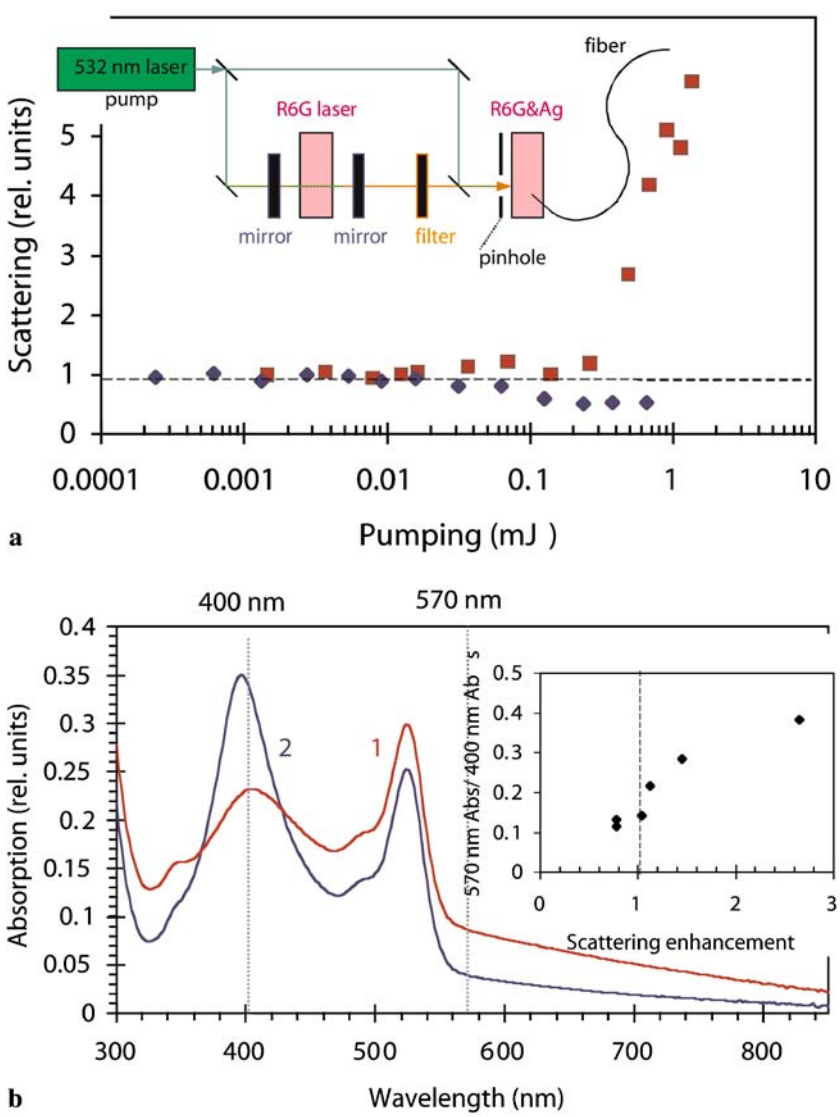

FIGURE 2 (**a**) Intensity of the Rayleigh scattering as the function of the pumping energy. (**b**) Absorption spectra of the dye-Ag aggregate mixtures; R6G – 2.1×10^{-5} M, Ag aggregate – $8.7 \times 10^{13}\,\mathrm{cm}^{-3}$. *Squares* in figure (**a**) and trace 1 in figure (**b**) correspond to one mixture, and *diamonds* in figure (**a**) and trace 2 in figure (**b**) correspond to another mixture. *Inset* of figure (**a**): Pump-probe experimental setup for the Rayleigh scattering measurements. *Inset* of figure (**b**): The ratio of the absorption coefficients of the dye-Ag aggregate mixtures at 570 nm and 400 nm plotted versus the enhancement of the Rayleigh scattering measured at 0.46 mJ

in the spectrum as a relatively narrow line centered at 558 nm on the top of a much broader emission band. Thus, it could be easily separated from the dye emission and the scattered pumping light.

In the experiment, the energy of the probe light was kept constant (at low fluence that could not significantly depopulate excited dye molecules) and the intensity of scattered probe light was measured as a function of the pumping energy. The sixfold increase of the Rayleigh scattering with the increase of pumping is shown in Fig. 2a, squares. This is a clear experimental demonstration of the compensation of loss in metal and enhancement of the quality factor of surface plasmon resonance by optical gain.

The mixtures of Ag aggregate and rhodamine 6G dye were studied in a 1 mm thick cuvette. At the dye concentration 2.1×10^{-5} M, which we used in the majority of our experiments, the optical amplification at $\lambda = 558$ nm did not exceed $\sim 7\%$ at 1 mm length. (Note that low average gain is not inconsistent with the existence of high local gain in the vicinity of nanoparticles, which enhances the surface plasmon resonance 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 elongation of the photon paths in the pumped volume due to scattering was insignificantly small. Thus, an increase of the intensity of scattered light in our experiment was due to an enhancement of the Rayleigh scattering cross section of (aggregated) silver nanoparticles rather than an amplification of scattered light in a medium with gain.

Experimentally, no noticeable enhancement of scattering was observed in pure R6G dye solution or pure Ag aggregate suspension. The results of the surface plasmon enhancement measurements did not depend (within experimental accuracy) on the orientation of the fiber collecting light. We also did not see evidence of photo-modification that could lead to enhanced scattering at 558 nm.

Depending on the shape of the absorption spectrum of the Ag aggregate-dye mixture (Fig. 2b) the intensity of the Rayleigh scattering could increase or decrease with the increase of pumping (Fig. 2a). Inset of Fig. 2b shows a monotonic dependence of the scattering enhancement measured at 0.46 mJ pumping energy versus the ratio of the absorption coefficients of the mixture at 570 and 400 nm. One can see that the relatively strong absorption of the mixture at 570 nm, which is a signature of aggregated Ag nanoparticles, helps to observe an enhanced Rayleigh scattering. Although physical properties of the mixtures were chiefly determined by the concentrations of ingredients, such factors as the regime of steering, steps by which one ingredient was added to another, time, etc. could make absorption spectra of two nominally identical mixtures different. (Experimental data corresponding to two mixtures with identical concentrations of components and different properties are shown in Fig. 2.) Even if we do not precisely understand the relationship between the absorption spectra and the physical properties of the mixtures, which govern the results of the scattering experiments, the correlation exists with no doubts.

A plausible explanation for different scattering properties of different mixtures could be in line with the theoretical model developed in recent [37], in which a three-component system consisting of metallic nanoparticle, shell of adsorbed onto it molecules with optical gain, and surrounding dielectric (solvent) has been studied. In particular, it has been shown that depending on the thickness of an amplifying shell, the absorption of the complex can increase or decrease with the increase of the gain in dye [37]. Similarly, we can speculate that in our experiments, in different mixtures we had different numbers of adsorbed molecules per metallic nanoparticle, which determined the enhancement or the reduction of the Rayleigh scattering. The explanation above is qualitative. The extension of the theory developed in [37] to aggregates of nanoparticles is yet to be done.

5 Damping of surface plasmon by absorption in surrounding dielectric

Using the same line of arguments as was used in [29], one can infer that by embedding metallic nanoparticle in a dielectric medium with absorption, one can further increase the imaginary part of the denominator in the field enhancement factor $\propto [\varepsilon_m - \varepsilon_d]/[\varepsilon_d + p(\varepsilon_m - \varepsilon_d)]$ and, correspondingly, reduce the quality factor of the plasmon resonance and the peak absorption cross section. This effect should always accompany the effect of the SP enhancement by gain and be observed in the same dye-Ag aggregate mixtures. The absorption coefficient of the dielectric medium, which is comparable to the critical value of gain $\sim 10^3\ \mathrm{cm}^{-1}$, should be adequate for the observation of a significant damping of a SP resonance.

In order to study the damping of the SP plasmon by absorption, we added Ag aggregate solution to the dye solution by small amounts and recorded absorption spectra of the mixtures (Fig. 1a, traces 2–7). In different particular experiments, the 'step' size varied between 1% and 25% of the maximal Ag concentration. We then scaled the absorption spectrum of pure Ag aggregate to fit each of the spectra of the mixtures at ≤ 450 nm and calculated the difference spectra {mixture–aggregate}. The differential spectra obtained this way, normalized to the concentration of the R6G dye in the mixture, reveal the regular absorption band of R6G dye, at $\sim 0.53\ \mu$m, and a much broader new absorption band centered at 0.72–0.75 μm (Fig. 1b). The latter broad band can be due to hybrid states formed by R6G molecules chemisorbed onto silver nanoparticles in the presence of Cl^- [38]. The possible effect of chloride ions known in the literature includes an increased R6G adsorption caused by the co-adsorption with anions, orientation of the adsorbed molecules, and changes in the aggregates structure [38, 39]. The latter may also cause the changes in the absorption spectra of the particle aggregates.

As one can see in Fig. 1b, with the increase of Ag aggregate in the mixture, the strength of the absorption band of R6G (calculated using the procedure described above) decreased, with the rate exceeding the rate of the reduction of the R6G concentration. (According to [35], the observed reduction of the R6G absorption is due to Ag aggregate but not a solvent without Ag.)

Spontaneous emission spectra of the dye-Ag aggregate mixtures were studied in the setup schematically shown in the inset of Fig. 3, when the dye or a mixture of dye with Ag aggregate was placed in a 1 mm cuvette. The samples were

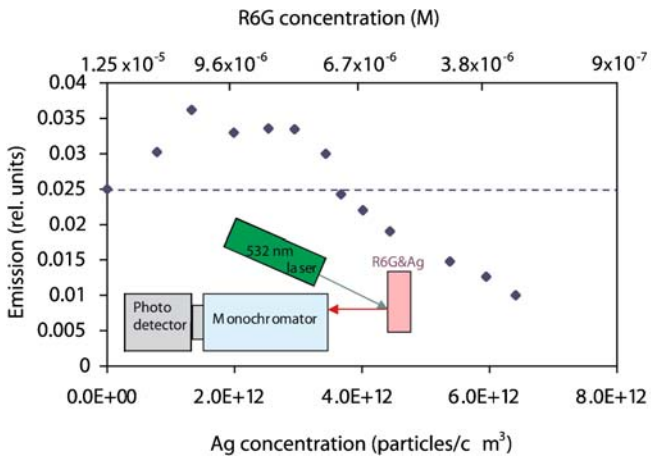

FIGURE 3 Emission intensity recorded at the addition of Ag aggregate to R6G dye. The starting concentrations of R6G and Ag aggregate are, respectively, 1.25×10^{-5} M and 8.7×10^{12} cm^{-3} The emission intensity corresponds to "as is" detected signal that has not been a subject to any normalization. *Inset*: Schematic of the experimental setup used at the emission intensity measurement

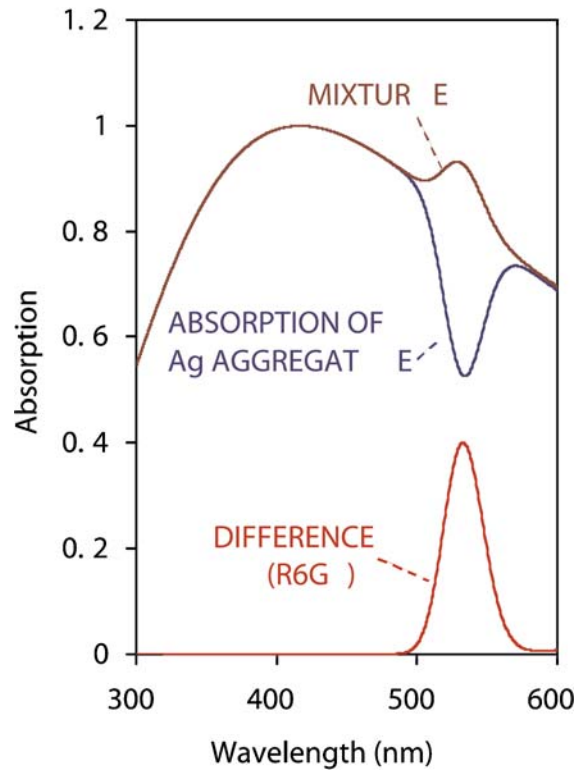

FIGURE 4 Schematic of the proposed decomposition of the absorption spectrum of the mixture into the absorption spectra of the components

pumped and the luminescence was collected nearly normally to the surface of the cuvette. We found that while the shape of the emission band was practically unaffected by the presence of Ag aggregate in the mixture, its intensity changed significantly. At the starting concentrations of R6G and Ag aggregate, equal to R6G $= 1.25 \times 10^{-5}$ M, Ag $= 8.7 \times 10^{12}$ cm^{-3}, the emission intensity of the dye (measured in the maximum at ~ 558 nm) increased up to 45% at the addition of small amounts of aggregated silver nanoparticles (Fig. 3). At the further increase of the concentration of Ag aggregate in the mixture, the emission intensity decreased. However, its relative decrease was much smaller than the relative reduction of the R6G absorption determined as it was described above.

According to [40, 41], the quantum yield of spontaneous emission of low concentrated R6G dye is $\sim 95\%$. Thus, the experimentally observed emission enhancement cannot be due to the increase of the quantum yield. An enhancement of emission can be explained by increased absorption of R6G in the presence of Ag aggregate. However, at first glance, this explanation contradicts the experimental observation: a seeming reduction of the R6G absorption with the increase of Ag aggregate concentration, inset of Fig. 1b.

We argue that the commonly accepted procedure of the decomposition of an absorption spectrum into its components, which we used to treat data of Fig. 1, is not applicable to the mixture of two substances (dye and aggregated Ag nanoparticles) which affect each other, and that the paradox above has a clear physical explanation.

The absorption spectrum of a fractal aggregate is comprised of a continuum of homogeneous bands corresponding to metallic nanostructures with different effective form factors. The homogeneous widths of individual bands are comparable to the characteristic widths of the absorption and emission bands of R6G dye. Following our prediction of the suppression of the SP resonance by the absorption in a dielectric, we speculate that the absorption band of R6G "burns" a hole in the absorption spectrum of the aggregate in the frequency range corresponding to the absorption of dye. Thus, the conventional method that we used to extract the absorption band of R6G from the absorption spectrum of the mixture was not applicable to our system. Instead, the absorption spectrum of the mixture should be decomposed according to the method schematically shown in Fig. 4. This explanation suggests that we have experimentally observed the predicted suppression of the SP resonance by absorption in the surrounding dielectric medium. The experimental observation of this effect provides additional support to our claim above of the enhancement of the SP by gain.

6 Summary

We have demonstrated six-fold enhancement of the SP resonance in the mixture of Ag aggregate and R6G dye. This paves the way for numerous applications of nanoplasmonics, which currently suffer from strong damping caused by absorption loss in metal. We have also predicted and experimentally observed the counterpart of the phenomenon above, namely, the suppression of the SP in metallic nanostructure embedded in a dielectric medium with absorption.

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