Surface-Plasmon-Enhanced Radiation Effects in Confined Photonic Systems

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Abstract— **Combined action of a resonant cavity and metal nanocomposites is shown to result in dramatic enhancement of spontaneous emisson rate in the optical spectral range. The cavity leads to modification of the optical density of states (Purcell effect), whereas the metal nanoparticles lead to giant local-field effects in spontaneous emission occuring because of surface-plasmon-enhanced vacuum field fluctuations. It is also shown that the surface-plasmon resonances may result in a full photonic gap in a metal-dielectric composite, even for a completely random structure of the composite. In our experiments, lasing at extremely low pump intensities, below 1 mW was observed for a novel class of optical materials, microcavities doped with fractal aggreates of metal nanoparticles.**

I. Introduction

GIANT enhancements of optical responses, linear and nonlinear, in metal nanocomposites and thin metallic films containing nanoscale surface features have been intensively studied in recent years [1]–[4]. These enhancements are associated with excitation of surface plasmons, collective electromagnetic modes whose characteristics are strongly dependent on the geometric structure of the metallic component of the medium.

Nanocomposites often look similar at different spatial scales, i.e., they are scale-invariant and their structure is characterized by fractal geometry. Since fractal objects do not possess translational invariance, they cannot transmit the running waves that are characteristic of homogeneous media. Rather, collective optical excitations in fractals, such as surface plasmons, tend to be spatially localized [2]. This localization leads to the presence of nanometer-scale spatial regions of high local electric fields,"hot" spots, and accordingly, to significant enhancement for a variety of optical processes, such as Raman scattering, four-wave mixing (FWM), quadratic electro-optical effect, and nonlinear absorption and refraction [2]–[4].

The presence of hot spots associated with localized optical modes in fractals is of special importance in nonlinear optical excitations, since the nonlinear optical emission primarily originates in the regions of the hot spots where the local enhancement may exceed the average by many orders of magnitude. For Raman scattering, for example, enhancement in the hot spots can be as large as 10^{10} to 10^{15}, as shown in recent theoretical [2], [5] and experimental [6], [7] studies, whereas the average enhancement for Raman scattering in fractals is 10^6 [2]. These results foreshadow fascinating possibilities for linear and nonlinear local spectroscopy of single molecules and nanoparticles in fractals [2]–[4].

An alternative approach for achieving large enhancement of the optical response involves the excitation of morphology-dependent resonances (MDR's) in dielectric microcavities [8]. These resonances, which may have extremely high quality factors ($Q = 10^5 - 10^9$), result from confinement of the radiation within the microcavity by total internal reflection. Light emitted or scattered in the microcavity may couple to the high-Q MDR's lying within its spectral bandwidth, leading to enhancement of both spontaneous and stimulated optical emissions. For example, enhanced fluorescence emission from an organic dye-doped cylindrical or spherical microcavity occurs when either the laser pump or the fluorescence (or both) couple to microcavity MDR's [9]. Moreover, the increased feedback produced by MDR's is sufficient to obtain laser emission from a dye-doped microdroplet under both continuous wave (CW) [10] and pulsed [11] laser excitation, with the threshold cw pump intensity three orders of magnitude lower than that of a conventional dye laser in an external cavity.

The existence of high-Q microcavity modes is also responsible for numerous stimulated nonlinear effects including: Stimulated Raman and Raleigh-wing scattering and four-wave parametric oscillation under moderate intensity cw excitation [12]; A large (>100) quantum electrodynamics (QED) enhancement [10], [12] arising from MDR-induced changes in the density of states; Optical bistability connected with the thermal nonlinearity of fused silica microspheres under low power (10^{-5} W) cw excitation [13]; Lasing emission from a microcavity doped with two fluorescent species (a dye-doped sol and liquid dye) via enhanced radiative (MDR) and nonradiative (Forster) energy-transfer [14], [15].

Strong existing evidence is seen to suggest that fractal nanocomposites and microcavity resonators individually result in large enhancements of optical emissions. In the present paper, we demonstrate that huge, multiplicative enhancement factors are obtained under the simultaneous, combined action of these two resonant processes when the emitting species is adsorbed onto metal fractal aggregates contained within high-Q microcavities.

Another cavity effect arises from the possibility of enhancing the spontaneous emission (SE) rate [16] of an emitter placed in a cavity (Purcell effect). Originally formulated for a

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localized dipole in resonance with a single cavity mode with quality-factor Q, the SE rate in the cavity mode referenced to the SE rate in a homogeneous medium, is given by the Purcell figure of merit $F_p \sim Q\lambda^3/V$ where V is the effective cavity volume. By placing a fractal aggregate in a microcavity of volume $\sim\lambda^3$ further enhancement of the zero-point fields (and thus of the SE rate) can be achieved because of the high-quality factors of the aggregate's optical excitations and their localization in subwavelength regions of space. Microcavities of very high resonance quality can be also formed by introducing a point defect in a photonic band crystal [16].

The paper is organized as follows. In Section II we discuss local field effects in fractals; their role in spontaneous emission is considered in Section III. Our experimental studies of lasing from microcavity/fractals composites are discussed in Section IV. In Section V, we consider the role of surface-plasmon resonance in photonic gap materials; Section VI concludes the paper.

II. Local Field Effects in Fractals

Dipolar eigenmodes in fractal composites are substantially different from those in other media. For example, there is only one dipolar eigenstate that can be excited by a homogeneous field in a dielectric sphere; the total dipole moment of all other eigenstates is zero and, therefore, they can be excited only by inhomogeneous field. In contrast, fractal aggregates possess a variety of dipolar eigenmodes, distributed over a wide spectral range, which can be excited by a homogeneous field. In the case of continuous media, dipolar eigenstates (polaritons) are running plane waves that are eigenfunctions of the operator of translational symmetry. This also holds in most cases for microscopically disordered media that are, on average, homogeneous. Dipolar modes, in this case, are typically delocalized over large areas, and all monomers absorb light energy, with approximately equal rate, in regions that significantly exceed the wavelength. In contrast, fractal composites have eigenstates that are often localized in subwavelength regions. Absorption by monomers in these "hot zones" is much higher than by other monomers in a fractal composite. This is a consequence of the already mentioned fact that fractals do not posses translational symmetry; instead, they are symmetrical with respect to scale transformation.

Localization of excitations in fractals [17] was first predicted for acoustic excitations and demonstrated in an ingenious experiment by Sapoval *et al.* on a fractal drum-head [17]; for optical excitations the localization was predicted by Shalaev and Stockman and later observed experimentally [18]. Recently, Stockman *et al.* [19], showed that localization in fractals is inhomogeneous in the sense that eigenmodes with very different coherence radii can coexist at the same wavelength; at frequencies close to the resonance of individual particles even chaotic behavior of the eigenmodes can occur.

What all of this means is that for a fractal object the optically excited distribution of the resonant electrical polarization will not be homogeneous on the fractal but concentrated in "hot spots" much smaller in size than the size of the fractal and often much smaller than the wavelength. When sufficiently concentrated, the large electromagnetic fields in the hot spots can result in very large enhancements of optical nonlinearities and in other effects, such as photochemistry that is usually associated with high fields.

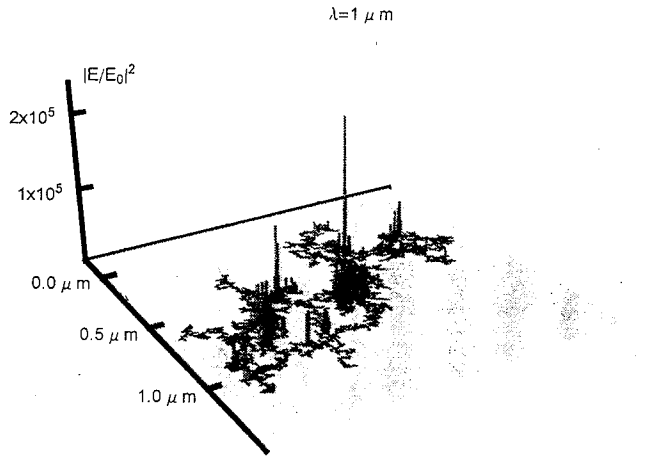


Fig. 1. Local field distribution on a fractal aggregate of silver particles, $\lambda = 1$ μ m.

When the constituent particles of a fractal cluster are irradiated by light, oscillating dipole moments are induced in them which interact strongly through dipolar forces leading to the formation of collective optical modes. Under such circumstances, the local field distribution can be calculated to an acceptable level of approximation by solving the coupled-dipole equation (CDE) $\mathbf{d}_i = \alpha_0(\mathbf{E}_0 + \Sigma_{j\neq i}\,\hat{W}_{ij}\mathbf{d}_j)$, where $\mathbf{d}_i$ is the local dipole induced on the ith particle (related to the local field $\mathbf{E}_i \equiv E(\mathbf{r})$ by $\mathbf{d}_i = \alpha_0\mathbf{E}_i$), α_0 is the polarizability of the individual particles composing the cluster, $\mathbf{E}_0$ is the incident electromagnetic wave, and $\hat{W}_{ij}$ is the operator describing the coupling between the induced dipoles on particles i and j. Hence, the second term in the brackets represents the contribution to the local field $\mathbf{E}_i$ due to the dipole moments induced on all of the particles in the cluster.

The local field distribution $g(\mathbf{r}) = |E(\mathbf{r})/E_0|^2$ excited by light of wavelength $\lambda = 1$ μm at the surface of a simulated fractal aggregate of silver nanoparticles is shown in Fig. 1. The largest fields are extremely localized; and the local field intensity in the hot spots can exceed the applied field by up to 10^5, while the average enhancement $G = \langle|E(\mathbf{r})/E_0|^2\rangle$ is only $\sim 10^2$ to 10^3.

Locally intense fields of this magnitude suggest a large number of unusual local optical and photochemical effects, among them, single-molecule spectroscopy. Specifically, because for surface-enhanced Raman scattering (SERS) the local enhancement-factor $\propto |E|^4$ [2], it can reach magnitudes of 10^{10} or greater, making Raman spectroscopy of single molecules possible.

Direct imaging of hot spots in fractal aggregates by near-field scanning optical microscopy (NSOM) has already been reported for fractal aggregates of colloidal silver particles prepared in solution, then gravitationally deposited onto a glass substrate (as the one shown in Fig. 1) [18]. The images exhibit the expected spatially localized hot spots that change

their positions with both the wavelength and polarization of the incident light. Near-field excitation spectra of colloidal silver aggregates have also been collected [18] by parking the NSOM tip at various points above the surface and varying the excitation wavelength. The tip "collects" light from regions of the aggregate several tens of nanometers in size. The near-field spectra observed consist of several resonances whose spectral components depend on the sample site probed. These resonances can only be observed in the near-field. The far-field images and spectra are composed of contributions from large areas of the cluster leading, in general, to averaging of the hot spots and the spectral resonances.

With sufficient laser intensity, the fields created in the hot spots can be so high that they cause structural modification of the aggregate either by fusing some of the constituent particles or locally fragmenting the aggregate [3]. This will, in turn, modify the hot-spot pattern, and other optical properties of the aggregate, such as its absorption spectrum. Specifically, a laser beam of a given wavelength should create spectral holes in the absorption at that wavelength. Electron micrographs taken before and after irradiation show that the structure of the colloidal cluster remains globally unchanged; however, a few particles within domains the size of the hot spots (a few nanometers) change their size, shape, and local arrangement. Modifications as small as two or three particles were observed when clusters were irradiated with $\lambda_L = 1079$ nm, implying that at this wavelength the resonance domains can be as small as $\lambda_L/25$ [3].

III. Surface-Enhanced Purcell Effect

Spontaneous emissions (SE) of a particle in vacuum and in resonators are substantially different (Purcell effect). This is because the density of photon states is modified by a resonator, inhibiting the SE rate for nonresonant modes and enhancing it for the resonant frequencies. The SE enhancement factor (Purcell factor) at frequency ω is given by $Q(\lambda/L)^3$, where $Q = \omega/2\gamma$ is the resonance quality-factor, (γ is the resonance width), λ is the wavelength, and L is a characteristic dimension of the resonator. Below we show that surface-plasmon-enhanced local fields can result in further, multiplicative enhancement of spontaneous emission.

The SE rate Γ for reaction $i \to f + p$ (where i and f are the initial and final states of a particle, and p corresponds to the emitted photon) can be found from Fermi's "Golden Rule" (see, for example, [8])

$$\Gamma = \frac{2\pi}{\hbar} \sum |(f,p|\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}|i,0)|^2 \delta(\hbar\omega - E_f + E_i) \propto |(f|\hat{\mathbf{d}}|i)|^2 |(1|\hat{\mathbf{E}}|0)|^2 \rho(\omega) \propto |(f|\hat{\mathbf{d}}|i)|^2 \rho(\omega) \quad (1)$$

where $\hat{\mathbf{E}}$ and $\hat{\mathbf{d}}$ are the field and dipole moment operators, and $\rho(\omega)$ is the photon density of states.

The dipole moment of a particle $(f|\hat{\mathbf{d}}|i) = \mathbf{d}$ can be found in the quasiclassical approximation as $\mathbf{d} = \alpha_0 \mathbf{E}$, where α_0 is the particle polarizability and $\mathbf{E} = \mathbf{E}(\mathbf{r})$ is the local field acting on the particle. The enhancement factor for spontaneous emission in a resonant cavity compared to the emission in vacuum (Purcell factor F_p) is given, as mentioned, by

$$F_p = \frac{\Gamma}{\Gamma_0} = \frac{\rho(\omega)}{\rho_0(\omega)} \sim Q\left(\frac{\lambda}{L}\right)^3 \quad (2)$$

where $\rho_0(\omega) = V\omega^2/\pi^2 c^3$ is the vacuum density of states; we also take into account that, for an intermode spacing larger than γ, the cavity mode density $\rho(\omega)$ is estimated as $\rho(\omega) \sim 1/\gamma$.

Now we assume that molecules that sponataneoulsy emit are placed on a metal surface that can sustain plasmon oscillations. As shown previously [2], a particular strong enhancement of optical processes can be achieved in fractal aggregates of metal nanoparticles; this is because of localization of plasmon modes in fractals leading to extremely high local fields in the areas of localization, "hot spots." In this case, an additional source of amplification for spontaneous emission occurs because of the fractal-surface-enhanced local fields, including the zero-point em fields. Such enhancement of local fields in fractals occurs in a very wide spectral range [2], including the visible and infrared parts of the spectrum. If the molecules are adsorbed on a surface of a fractal which, in turn, is placed inside of a microcavity, then the combined effect of a microcavity ("conventional" Purcell effect) and the local-field enhancement of zero-point fluctuations due to the plasmon modes can result in a dramatic modification of the spontaneous emission rate.

For simplicity, we assume that the concentration of fractals in a cavity is low so that the cavity modes are not purturbed much by the presence of fractals. In this case, the surface-enhanced Purcell factor F^{SE} for a molecule/fractal/microcavity composite is a product of F_p and the local-field factor $G = \langle |E(\mathbf{r})|^2 \rangle / |E_0|^2$

$$F^{SE} = \frac{\Gamma}{\Gamma_0} = \frac{\langle |(f|\hat{\mathbf{d}}|i)|^2 \rangle}{|(f_0|\hat{\mathbf{d}}|i_0)|^2} \frac{\rho(\omega)}{\rho_0(\omega)} = \frac{\langle |\mathbf{d}| \rangle^2}{|\mathbf{d}_0|^2} \frac{\rho(\omega)}{\rho_0(\omega)} \sim GF_p \sim GQ\left(\frac{\lambda}{L}\right)^3 \quad (3)$$

where we have the averaged $\langle \ldots \rangle$ over the random positions of metal particles. It can be shown that for an arbitrary random ensemble of particles, $G \equiv \langle |E(\mathbf{r})/E_0|^2 \rangle = [(X^2 + \delta^2)/\delta] \langle \mathrm{Im}[\alpha] \rangle$, where $\langle \mathrm{Im}[\alpha] \rangle \equiv \mathrm{Im}[\alpha(X)]$ is the average imaginary part of the polarizability describing the absorption, and $X(\omega)$ and $\delta(\omega)$ are defined through the polarizability of individual particles as $\alpha_0^{-1} = -(X + i\delta)$ [21]. The local-field factor G can achieve magnitudes of the order of 10^2 to 10^3 for a fractal aggregate of silver nanoparticles in the visible spectral range and up to 10^5 in the near and mid-infrared parts of the spectrum. The local enhancement in the hot spots can be even larger (see Fig. 1).

We note that formula (3) is valid when $F_p > 1$; otherwise the enhancement factor is entirely due to the local-field factor for zero-point fluctuations enhanced by plasmon oscillations, i.e., $F^{SE} \sim G$. This case occurs for large cavities or free space, with little or no modification of the density of photon states. We note here that the local field enhancement of spontaneous emission in dielectrics was also considered in [22]. In contrast to dielectrics, the local-field factor in metals can be dramatically enhanced due to surface plasmons.

The same result for enhancement of spontaneous emission can be also obtained semiclassically, by using the idea that the optical theorem, i.e. the equivalence of the amount of light taken out of the incident wave (extinction) and the amount of light redistributed over all angles (scattering) may be viewed as a microscopic analog of the Einstein's thermodynamic arguments relating extinction (and absorption), stimulated, and spontaneous emission [22]. Then, semiclassically, spontaneous emission can be thought of as a process that balances "absorption" of vacuum field fluctuations (zero-point fluctuations), if they were considered classically. The intensity of the vacuum field fluctuations can be formally introduced through the relation $|E|^2/(4\pi) = \hbar\omega(n + 1/2)V^{-1}$ by setting $n = 0$.

IV. Lasing from Fractals in Microcavities

Below we discuss our experimental studies of optical properties of novel materials, microcavities doped with fractal aggregates of metal nanoparticles. In our experiments we used a cylindrical microcavity of the inner diameter 700 microns and outer diameter 1 mm. Such a microcavity is obviously too large to observe the conventional Purcell effect; still, spontaneous emission can be enhanced due to the local-field effect associated with plasmon resonances of metal fractal aggregates. In our experiments we studied lasing from microcavity/fractals composites. The performed experiments clearly indicate that surface-plasmon-enhanced radiation effects in confined photonic systems can find many exciting applications. We note, however, that since the lasing effect depends not only on the spontaneous emission rate but also on the enhancement experienced by both the pump and generated beams, we cannot extract from our experiments a factor characterizing the predicted modification of spontaneous emission due to plasmon modes in fractals.

In our experiments, we found that lasing emission from Rhodamine 6G (R6G) dye molecules adsorbed onto silver colloidal aggregates inside a cylindrical microcavity could be obtained for dye molarities approximately three orders of magnitude lower than for the corresponding microcavity dye laser in the absence of colloidal aggregates, and for a threshold pump intensity approximately three orders of magnitude less than for a conventional dye laser. We believe that these, and other, results discussed in this paper, demonstrate the unique potential of such materials in the development of ultra-low threshold microlasers, nonlinear-optical devices for photonics, as well as new opportunities of micro-analysis, including spectroscopy of single molecules.

Silver colloid solutions were prepared by reduction of silver nitrate by sodium citrate in an aqueous solution [20]. Boiling this solution results in the formation of silver nanoparticles (monomers) with an average diameter of 25 nm. Addition of an organic acid (e.g., 0.03 M saturated fumaric acid) to the monomer solution promotes the aggregation of colloidal nanoparticles into fractal clusters, containing, typically, 10^3 to 10^4 monomers. Electron microscopic analysis of the aggregates reveal that they possess a fractal structure with the fractal dimension $D \simeq 1.8$ characteristic of the cluster-cluster aggregation of monomer particles [23].

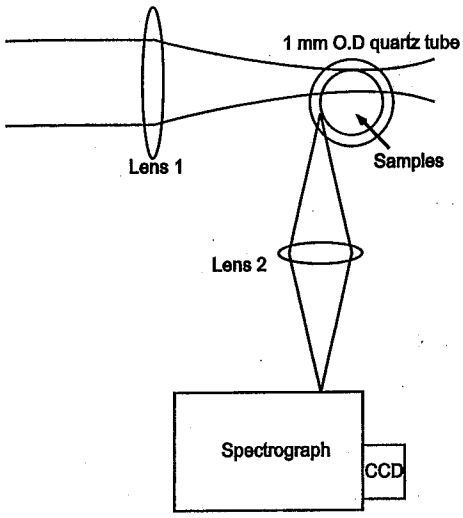
Lasing experiments were done with R6G dye. A small amount of a parent solution of 10^{-4} M R6G in methanol was added to the silver colloid solution; the resulting dye concentration in the samples studied ranged from 10^{-8} to 10^{-5} M. Cylindrical microcavities were fabricated from cylindrical quartz tubes, with the dye/colloidal solution placed within the tube. Note that the addition of R6G to the colloid solution resulted in increased aggregation.

A 10 mW cw Argon-ion laser ($\lambda_L = 514.5$ nm) and a 0.75 mW cw green He-Ne laser ($\lambda_L = 543.5$ nm) were used as pumping sources. The pump beam (approximately 2 mm in diameter) was focused into the tube by a 75 mm focal length lens; focal plane beam diameters were 70 μm and 35 μm for an Argon and a He-Ne lasers, respectively. Pump beam polarization was vertical (along the axis of the tube), and the output radiation was collected at 90° to the incident radiation. This configuration 2a(b) was used when MDR's were (were not) excited in the cylindrical microcavity. Spectroscopic measurements were performed using a CCD camera mounted to a SpectraPro-300i spectrograph; an 1800 groove per millimeter grating provided an instrumental spectral resolution of 0.028 nm (full-width at half-maximum, FWHM).

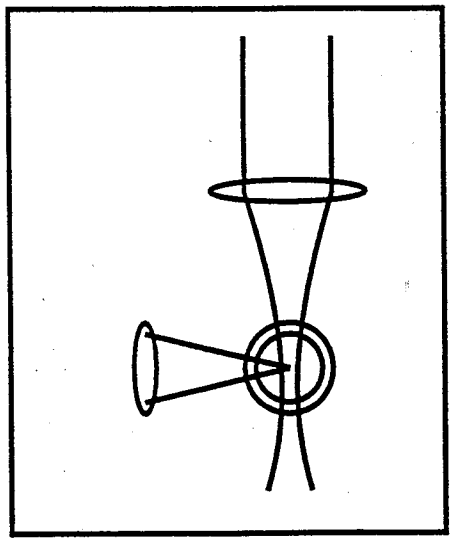
Elastic scattering of a laser beam passed through the outer edge of the empty cylindrical tube exhibited a well-defined, MDR angular structure; alternatively, when the beam is passed through the inner edge of the empty tube [see Fig. 2(a)], the intensity of the MDR peaks is significantly reduced. However, filling the tube with a colloidal solution again resulted in strong elastic scattering with a clearly resolved MDR angular structure; this observation implies that light scattering by colloidal particles facilitates trapping of the radiation in the MDR cavity modes. For this reason, most of our experiments were performed using this illumination geometry (see Fig. 2(a)), because it provides both the effective optical excitation of fractals within the microcavity and the coupling of this light to the microcavity MDR's.

Elastic scattering by fractal aggregates and monomers also contributes to output-coupling of radiation from microcavity MDR's. Scattering, together with absorption, decreases the quality-factor Q of the cavity modes according to $Q^{-1} = Q_a^{-1} + Q_{sv}^{-1} + Q_{ss}^{-1}$, where Q_a^{-1}, Q_{sv}^{-1}, and Q_{ss}^{-1} are losses due to absorption, volume scattering, respectively, [8]. If colloidal aggregates are present in the microcavity, the volume absorption is the most important loss mechanism. The measured absorption coefficient at $\lambda_L = 543.5$ nm is $\alpha = 5$ cm^{-1}, so that $Q_a = 2\pi n/\alpha\lambda_L = 3.4 \times 10^4$, where $n = 1.46$ is the refractive index. The measured scattering loss, $Q_{sv}^{-1} + Q_{ss}^{-1}$, is smaller than Q_a^{-1} by, at least, one order of magnitude, implying that scattering may be regarded in our experiments primarily as an output-coupling mechanism for microcavity radiation. An alternative output-coupling mechanism, which is based on a resonator with a deformed cross section [24], is more appropriate for active cavity media with high reflectivity.

We studied the emission intensity of different spectral components as a function of the pump intensity. It was found that this dependence is linear for low excitation intensities for all components. However, when the pump intensity exceeds some critical value in the range between 20 and 50 W/cm^2,

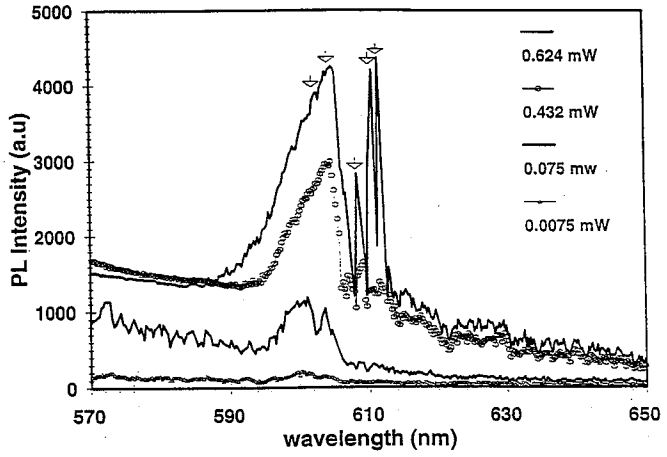


(a)

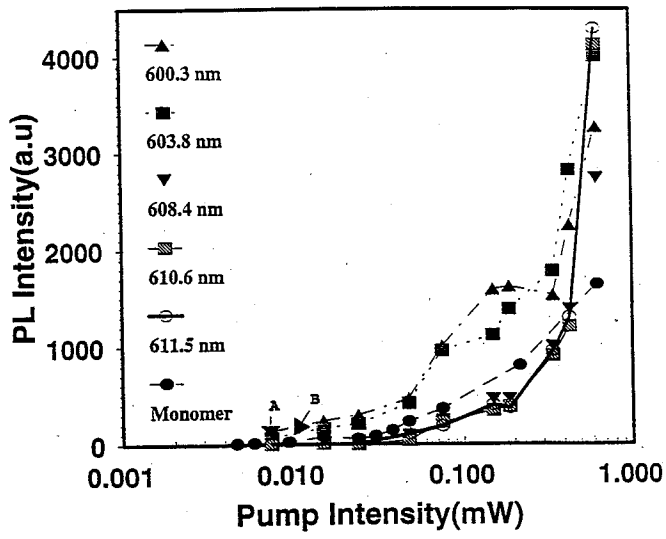


(b)

Fig. 2. Schematic diagram of the experimental configurations. (a) Microcavity MDR's efficiently excited and (b) MDR's effectively unexcited. Lens 1, focal length 75 mm; lens 2 used for f/number matching into spectrograph. Quartz cylinder inner diameter is 0.7 mm.



(a)



(b)

Fig. 3. (a) Photoluminescence spectra of 5×10^{-7} M R6G dye/fractal aggregate solution in a microcavity for $\lambda_L = 543.5$ nm HeNe laser excitation at different pump powers. (b) Lasing threshold effect for selected spectral components [shown by arrows in Fig. 3(a)]. For comparison, the pump-power dependence of the luminescence spectrum of a dye-doped, nonaggregated monomer solution at 611.5 nm is also shown; the intensity has been increased by a factor of 10^2 for which the intensities of points a and b are five and ten units.

some peaks grow dramatically, exhibiting a lasing threshold dependence (Fig. 3). The threshold power for $\lambda_L = 543.5$ nm He-Ne laser excitation is as small as 2×10^{-4}W. It is noteworthy that the R6G concentration was only 5×10^{-7} M in these experiments, three orders of magnitude lower than for conventional dye lasers with an external cavity and three orders of magnitude lower than for a microdroplet laser without silver fractal aggregates [10]. In our experiments, the minimum R6G concentration that results in lasing can be as low as 10^{-8} M. These findings suggest that the lasing effect is due to dye molecules adsorbed on the surface of silver aggregates. This conclusion is also supported by the fact that increasing the R6G concentration to 10^{-5} M does not result in additional growth of the lasing peak intensities; the additional dye concentration is apparently not adsorbed onto the silver particles, but remains in solution as free molecules, where it does not effectively contribute to the enhanced lasing effect.

Our experiments show that placing R6G dye in a microcavity leads to enhancement of dye photoluminescence by a factor between 10^3 and 10^5. By adding nonaggregated silver colloidal particles to the dye solution in a microcavity, further multiplicative enhancement is obtained, varying between 10^2 and 10^3. Finally, aggregation of the colloidal particles in the microcavity into fractals results in a final multiplicative enhancement factor which varies between 10^3 and 10^4. Combining these multiplicative enhancement factors, the overall emission enhancement provided by fractal/microcavity composite media can be enormously large, varying in our experiment between 10^{10} and 10^{12}.

An extremely pronounced time-dependent effect was also observed in our experiments when a dye solution, initially containing nonaggregated colloidal silver particles, was irradiated with a CW pump laser (Fig. 4). This time dependence

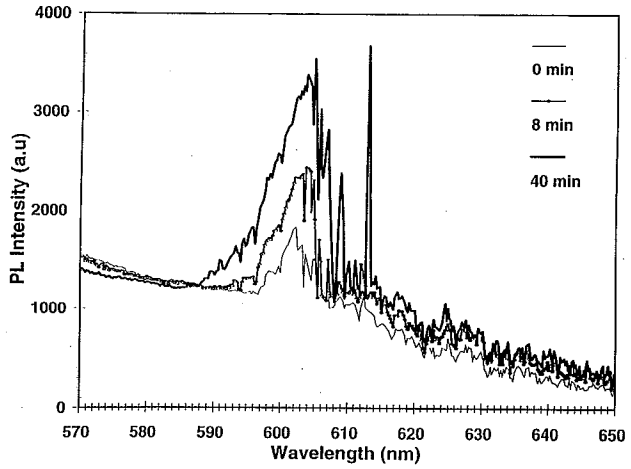


Fig. 4. Photostimulated aggregation of colloidal particles at increasing irradiation times using $\lambda = 543.5$ nm HeNe laser excitation (maximum power, 0.75 mW).

is likely due to photostimulated aggregation, which has been conjectured to be induced by surface-enhanced ionization of the metal monomers. Another possible contribution to the observed time-dependent lasing is the pulling of fractal aggregates into the high-field area associated with the whispering gallery modes due to the gradient forces. In either case, the amount of fractal aggregates in the MDR areas increases with irradiation time until resonant enhancement is sufficient to lower the lasing threshold to the level provided by the HeNe pump laser, at which point the overall enhancement of the light emission due to the combined effects of the microcavity and the fractal resonances reaches 10^{10} to 10^{12}.

V. Photonic Stop-Bands in Metal-Dielectric Composites

In this Section we show that surface-plasmon resonances can result in photonic gaps (more exactly, stop bands) in metal-dielectric composites.

First we note that a microcavity with high Q can be constructed with the help of photonic band crystals [16]. This can be done by introducing a defect in an ideal photonic band crystal, that can lead to the appearance of localized photon states.

One can also use metal (instead of dielectric) particles as one of the two components of a photonic crystal. Metal particles can sustain plasmon resonances; as a result, at some frequencies, the effective dielectric permittivity of such a material, basically random metal-dielectric composite, can become negative. The negative dielectric constant means that the propagating modes cannot occur, in other words, there is a photonic gap, in this case. This effect can be also used for creating localized states, similar to the case conventional photonic crystals. It is important to emphasize that the dielectric function can become negative, leading to photonic gaps, even in completely random metal-dielectric composites.

In the simplest case, the Maxwell–Garnett approximation can be used to obtain the dispersion relations in composite materials, including translationally invariant metal-dielectric crystals. To calculate the dispersion relations, we need to know the effective dielectric permittivity of the medium, which in the Maxwell–Garnett approximation can be found from the following formula:

$$\frac{\varepsilon_{eff} - \varepsilon_2}{\varepsilon_{eff} + (d-1)\varepsilon_2} = p_1 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + (d-1)\varepsilon_2} \tag{4}$$

where d is the dimension of space, ε_1 and ε_2 are the dielectric constants of the two components forming a composite (or crystal), and ε_{eff} is the effective dielectric permittivity of the material. We note that this formula can be equally used for periodic crystals and random composites. In both cases, in the vicinity of plasmon resonances the effective dielectric constant can become negative leading to nonpropagating modes ("photonic gaps"). For lattice parameters used in our calculations, the metal concentration $p_1 \simeq 0.06 \ll 1$, so that there is no need to use the more accurate Bruggemann formula, which can be also used at $p \sim 1$.

Materials sustaining surface plasmon resonances are characterized by a huge variation of the dielectric permittivity near the resonant frequencies, making it possible to change the effective dielectric permittivity in a wide range, including the negative values that correspond to the gap states. Even in the first approximation, without consideration of more subtle effects, such as Bragg reflections in periodic structures, composite materials, sustaining plasmon modes, may possess a full band gap in the photon dispersion relations. By introducing defects in such composite material, one can also obtain localized photonic states.

We also performed more elaborated calculations for a metal-dielectric crystal in the visible spectral range and obtained excellent agreement with the Maxwell–Garnett approximation, as described below.

The dispersion relations $\omega(\mathbf{k})$ ($\mathbf{k}$ are the wavevector coordinates in the first Brillouin zone) can be found from formula [25]

$$\left\| \alpha_0(\omega)^{-1} \frac{c_0^2}{\omega^2} \mathbf{I} + \sum_{\mathbf{x}_i \neq 0} e^{-i\mathbf{k}\cdot\mathbf{x}_i} \mathbf{G}_0(\omega, \mathbf{x}_i) \right\| = 0 \tag{5}$$

where $\mathbf{I}$ is the 3×3 identity matrix, $\mathbf{\Delta}_\mathbf{k} = \mathbf{I} - \mathbf{e}_\mathbf{k}\mathbf{e}_\mathbf{k}$, with $\mathbf{e}_\mathbf{k} = \mathbf{k}/k$ being the transverse projection operator, and $\mathbf{G}_0(\omega, \mathbf{x}_i)$ is a free-space Green function of the Helmholtz equation.

A simple cubic crystal lattice for silver particles in a dielectric host with $\varepsilon_d = 1$ was used in our calculations. The dielectric permittivity or silver can be well described by the Drude formula:

$$\varepsilon_m = \varepsilon_b - \left(\frac{\omega_p}{\omega}\right)^2 \frac{1}{1 + i\omega_\tau/\omega} \tag{6}$$

with the parameters $\varepsilon_b = 5.0$, $\omega_p = 9.1$ eV, and $\omega_\tau = 0.021$ eV. For the polarizability of silver particles we used the formula

$$\alpha_0(\omega) = \frac{4\pi}{3} R^3 \frac{\varepsilon_m - 1}{\varepsilon_m + 2} \tag{7}$$

where $R = 5$ nm are the particle radii. The lattice constant is 20 nm. Results of the numerical calculations compared with those based on the simple Maxwell–Garnett formula are shown

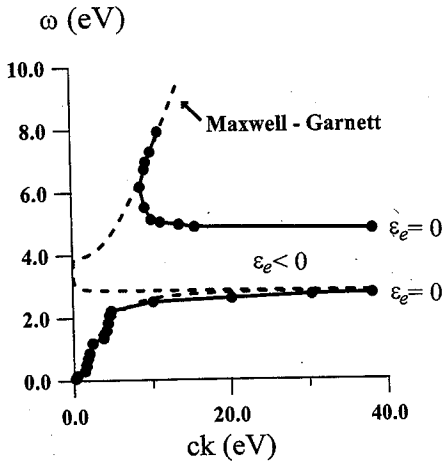


Fig. 5. Dispersion relation for a simple cubic silver-dielectric plasmonic crystal ($\Gamma - X$ direction). Lattice unit is 20 nm, dimension of silver spheres is 5 nm.

in Fig. 5. (The dispersion relations in Fig. 5 are shown for the $\Gamma - X$ direction.) As seen in Fig. 5, the numerical simulations are well described by the Maxwell–Garnett formula; both approaches clearly indicate the presence of a stop band. Since the Maxwell–Garnett formula does not require any periodicity, we can conclude that the same stop band can be obtained in a random metal-dielectric composite.

We want to emphasize that the presence of the stop band is simply due to expelling the em field by a composite material which inlcudes a metal component with the negative effective dielectric function. In this sense, it is a more robust effect since it is not based on the delicate interfence phenomena in the Bragg reflection, requiring the high periodicity as in photonic crystals. In a composite material, where the resonant plasmon oscillations can be excited, the sign and magnitude of the effective dielectric function can be easily controled by varying the metal filling factor and the frequency. It is important that near the plasmon resonance of a metal-dielectric composite light can be expelled even at low metal concentrations when losses are not significant; this is the case, for example, for fractal composites which have asymptotically zero density.

VI. Conclusions

In this paper we considered the role of surface-plasmon excitations in various radiation effects. In particular, we showed that the local-field effects due to surface plasmons can lead to the surface-enhanced Purcell effect, with the multiplicative enhancement resulting from modification of the photon state density in a resonant cavity and surface-plasmon enhanced vacuum field fluctuations. Local-field enhancement is particularly strong in fractal aggregates of metal nanoparticles because of localization of surface plasmon excitations in fractals.

Combining the energy-concentrating effects due to localization of optical excitations in fractals with light trapping by microcavity resonance modes can lead to especially strong enhancement of radiation effects. In our experiments, lasing at extremely low pump intensities, below 1 mW, was observed in microcavity/fractal composites.

In our experiments we have also obtained dramatic enhancement of Raman scattering, up to 10^{12}, on average, and up to 10^{18} in the hot spots, in the microcavity/fractal composites (to be published elsewhere).

A large variety of optical processes can be enhanced or otherwise modified by incorporating fractal clusters in the media or by ensuring that aggregation results in fractals. For example, fractals can be utilized to improve the performance of random lasers, such as powder lasers and laser paints [26], where lasing emissions can take place as a result of coherent multiple light-scattering in a disordered dielectric (or semiconductor) with appropriate structural elements. The notion of creating a "ring" laser cavity in a random medium through a sequence of multiple coherent scattering events along a closed path is itself, a fascinating, and almost counter-intuitive prospect. Scattering is normally considered detrimental to lasing; since, in a conventional laser cavity, it tends to remove photons from the lasing mode. In a properly constructed random medium, however, strong multiple scattering could return photons to the amplification region resulting in mode amplification [26]. By doping the laser powder or paint medium with fractal aggregates, or by imparting a fractal character to the medium as a whole, one could significantly decrease the pump power needed to effect lasing, in other words, one could decrease the lasing threshold.

We also showed that surface plasmon oscillations can be used for designing materials with large photonic gaps. It is important that such materials, with the negative effective dielectric function, can be made even from random metal-dielectric composites, i.e., they do not require periodicity needed for conventional dielectric photonic crystals.

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