Fractals in Microcavities: Giant Coupled, Multiplicative Enhancement of Optical Responses

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A novel class of optical materials, microcavities doped with nanostructured fractal aggregates, was studied. Fractal aggregate optical excitations may be concentrated in regions smaller than the diffraction limit of conventional optics, resulting in large local fields. Seeding the aggregates into microcavities further increases the local fields because of light trapping by microcavity resonance modes. These microcomposites possess unique optical properties, including very large probabilities of radiative processes. In our experiments, lasing at extremely low pump intensities, below 1 mW, and strongly enhanced Raman scattering was observed in fractal-microcavity-dye composites. [S0031-9007(99)09367-9]

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The giant enhancement of the optical response in metal nanocomposites and thin metallic films containing nanoscale surface features has been intensively studied in recent years [1–4]. This enhancement is associated with the excitation of surface plasmons, collective electromagnetic modes whose characteristics are strongly dependent on the geometrical structure of the metallic component of the medium.

Nanocomposites often are scale invariant and their structure is characterized by fractal geometry. Collective optical excitations, such as surface plasmons, are often spatially localized in fractals [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, and nonlinear absorption and refraction [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 [5]. These resonances, which may have very high quality factors ($Q = 10^5$ to 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 a dye-doped cylindrical or spherical microcavity occurs when either the laser pump or the fluorescence (or both) couple to microcavity MDR's [6]. Moreover, the increased feedback produced by MDR's is sufficient to obtain laser emission from a dye-doped microdroplet under both cw and pulsed laser excitation [7], with the threshold cw pump intensity 3 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 Rayleigh-wing scattering and four-wave parametric oscillation under moderate intensity cw excitation [8].

Strong existing evidence suggests 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. We find that doping of a dye solution inside a microcavity containing silver fractal aggregates results in a giant enhancement of the efficiency of lasing and nonlinear Raman scattering. Note that, although Ag colloid aggregates introduce absorption and, hence, linear losses inside the microresonator, at the same time they increase the efficiency of dye excitation and emission. We believe that results discussed in this paper demonstrate the unique potential of such devices in the development of ultralow threshold microlasers, nonlinear optical devices for photonics, as well as new opportunities of microanalysis, including spectroscopy of single molecules.

Silver colloid solutions were prepared by reduction of silver nitrate by sodium citrate in an aqueous solution [9]. 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., $0.03M$ saturated fumaric acid) to the monomer solution promotes the aggregation of colloidal nanoparticles into fractal clusters, containing, typically, 10^3 monomers. Electron microscopic analysis of the aggregates reveals that they possess a fractal structure with the fractal dimension $D \simeq 1.8$ characteristic of the cluster-cluster aggregation of monomer particles.

Extinction spectra of nonaggregated silver colloids in the visible region of the spectrum exhibit a single resonance feature centered at 420 nm and width 80 nm; this peak is due to the surface plasmon excitation in single Ag nanoparticles. Aggregation leads to the appearance of a broad wing extending toward the long-wavelength part of the spectrum. Enhanced extinction in the long- wavelength region (see Fig. 1c) is a consequence of induced high-Q optical modes in metal fractal aggregates [2] independent of the presence of dye.

Lasing experiments were done with rhodamine 6G (R6G) dye. A small amount of a parent solution of $10^{-4}M$ R6G in methanol was added to the Ag colloid solution, and the resulting dye concentrations ranged from $10^{-8}M$ to $10^{-5}M$. Cylindrical microcavities were fabricated from quartz tubes (inner diameter is 700 μm and outer diameter is 1000 μm), with the colloidal-dye solution placed within the tube.

A 10 mW cw Ar-ion laser ($\lambda = 514.5$ nm) and a 0.75 mW cw green He-Ne laser ($\lambda = 543.5$ 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 and 35 μm for Ar and He-Ne lasers, respectively. Pump beam polarization was vertical (along the axis of the tube), and output radiation was collected at 90 degrees to the incident radiation as shown in Fig. 1; configuration 1a (1b) 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 per mm grating provided an instrumental spectral resolution of 0.028 nm (full width at half maximum, FWHM).

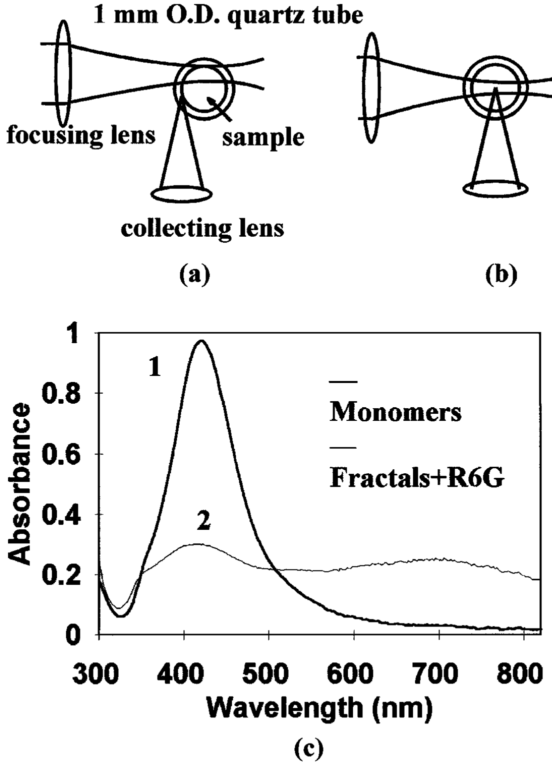

FIG. 1. Schematic diagram of the experimental configurations: (a) Microcavity MDR's efficiently excited. (b) MDR's effectively unexcited. (c) Absorption spectra of silver colloidal particles (1) and their fractal aggregates (2) in 1 mm path length cell.

Elastic scattering of a laser beam passed through the outer edge of the empty cylindrical tube exhibited a well-defined, MDR angular structure consistent with a cylindrical microcavity with an outer diameter of 1000 μm; alternatively, when the beam is passed through the inner edge of the empty tube (see Fig. 1a), 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; most of our experiments were performed using this illumination geometry (see Fig. 1a). Our observations imply that elastic scattering from fractal aggregates and monomers 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 $Q^{-1} = Q_{\mathrm{a}}^{-1} + Q_{\mathrm{sv}}^{-1} + Q_{\mathrm{ss}}^{-1}$, where Q_{a}^{-1}, Q_{sv}^{-1}, and Q_{ss}^{-1} are losses due to absorption, volume scattering, and surface scattering, respectively [5]. (Diffraction losses are negligible in our case.) If colloidal aggregates are present in the microcavity, the volume absorption is an important loss mechanism. The measured absorption coefficient for the aggregated colloidal solution is $\alpha = 5\ \mathrm{cm}^{-1}$ at $\lambda = 543.5$ nm, so that $Q_{\mathrm{a}} = 2\pi n/\alpha\lambda_L = 3.4 \times 10^4$, where $n = 1.46$ is the refractive index. The measured scattering loss, $Q_{\mathrm{sv}}^{-1} + Q_{\mathrm{ss}}^{-1}$, is smaller than Q_{a}^{-1} by, at least, 1 order of magnitude.

Figure 2 contrasts the luminescent spectrum of a $5 \times 10^{-7}M$ aqueous dye solution in a microcavity with and without the presence of Ag fractal aggregates [in the former case, neutral density (OD = 5) filters were

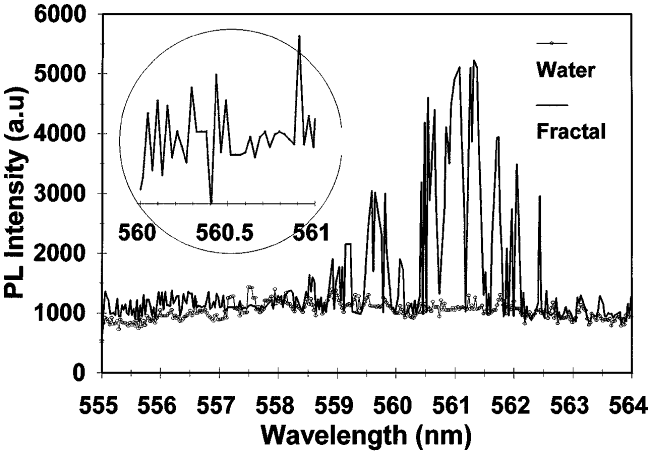

FIG. 2. Luminescence spectrum of $5 \times 10^{-7}M$ R6G dye solution in microcavity, with [heavy line, neutral density (OD = 5) filters are used] and without (circles, dashed line) fractals, for $\lambda_L = 514.5$ nm, cw Ar laser excitation. Inset gives detail of spectrum without fractals showing typical mode structure.

used]. Without aggregates, a weak, broad luminescence band is observed with a maximum at $\lambda = 560$ nm and a FWHM of 30 nm for $\lambda_L = 514.5$ nm excitation; the lower trace in Fig. 2 shows the central portion of this spectrum and the inset provides an expanded view. In the inset, representative groupings of small amplitude peaks may be seen corresponding to luminescence emission coupled to microcavity MDR's. The measured intermode spacing between these peaks, $\Delta\lambda \approx 0.066$ nm, closely approximates the theoretical intermode spacing of $\Delta\lambda = (\lambda^2/2\pi a)[(n^2 - 1)^{-1/2}\tan^{-1}(n^2 - 1)^{1/2}] \approx 0.076$ nm, calculated for a quartz microcavity of outer radius $a = 0.5$ mm and refractive index $n \approx 1.46$ of the quartz tube and air refractive index 1. This result gives additional evidence that the feedback provided by the microcavity results from total internal reflections from the outer surface of the quartz tube. The spectral widths of the peaks are limited by our instrumental resolution.

In the presence of fractal aggregates, the luminescence intensity and spectrum are changed dramatically. (Note that enhanced luminescence of R6G molecules adsorbed onto island Ag films was reported in [10].) Figure 2 illustrates the huge increase in MDR peak intensities within a narrow spectral region centered near $\lambda = 561$ nm with a bandwidth of approximately 3 nm for the tube containing the Ag-R6G composite. Closely spaced but spectrally distinct modes in this region are found to have intermode spacings essentially identical to those for the aggregate-free spectra discussed above. The measured value of a single peak FWHM, $\delta\lambda = 0.04$ nm (it is close to our instrumental width), allows us to estimate a lower bound for the quality factors, $Q \approx \lambda/\delta\lambda = 1.5 \times 10^4$. This lower bound value is consistent with the previous estimate of $Q \cong 3.4 \times 10^4$. Photoluminescence enhancement resulting from fractal aggregates was 10^5 to 10^6 so that, with the additional multiplicative enhancement provided by the microcavity, the resultant enhancement of photoluminescence is estimated as 10^9 to 10^{11}.

Analogous enhanced emission spectra from a dye/fractal/microcavity system are observed under He-Ne laser excitation. Huge MDR peaks are centered near $\lambda = 610$ nm in this case. The narrowing of the emission spectrum (from 30 to 3 nm) is characteristic of laser action. To test this point, we studied the emission intensity of different spectral components as a function of the pump intensity; Fig. 3 presents our results. It was found that this dependence is linear for low excitation intensities for all components (for example, in spectral regions *A* and *B* in Fig. 3). However, when the pump intensity exceeds a certain critical value in the range between 20 and 50 W/cm^2, some peaks (*C* and *D*) grow dramatically, exhibiting a lasing threshold dependence. The threshold power for $\lambda_L = 543.5$ nm He-Ne laser excitation is as small as 2×10^{-4} W.

The enhanced emission was found to be confined within an approximately 50 μm region of the tube in a vertical direction, which contained the incident pump light; moreover, emission from this region exhibits angular patterns characteristic of microcavity MDR's.

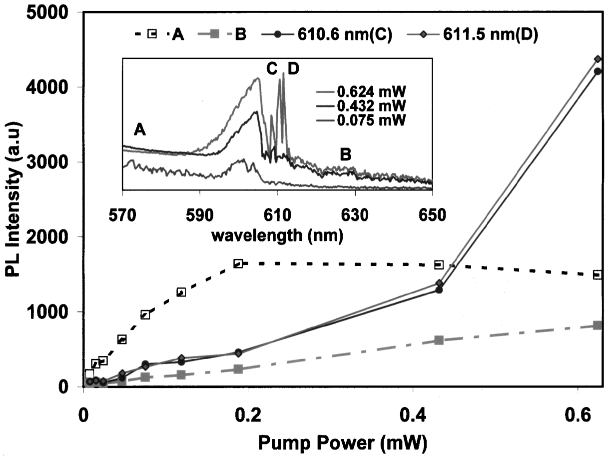

FIG. 3. Nonlinear dependence of luminescence peak intensity of dye/fractal/microcavity system on 543.5 nm HeNe pump power; spectral locations and pump powers shown in inset. Locations *A*, *B* exhibit linear dependence on pump power while features *C*, *D* exhibit nonlinear threshold behavior with pump power.

Thus, the spectral, threshold, and spatial dependencies confirm the laser nature of the observed emission. It is noteworthy that the R6G concentration was only $5 \times 10^{-7} M$ in these experiments, 3 orders of magnitude lower than that for conventional dye lasers with an external cavity and for a microdroplet laser without Ag aggregates [7]. 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 Ag 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 compared with $5 \times 10^{-7} M$ concentration; the additional dye concentration is apparently not adsorbed onto the Ag particles, but remains in solution as free molecules, where it does not effectively contribute to the enhanced lasing effect. We conclude that, for our composites, the effect of increasing local pump and luminescence field is stronger than emitted field losses, connected with optical absorption by fractals and nonradiative quenching of excitation.

Microcavity surface-enhanced Raman scattering (SERS) was also investigated. SERS spectra from sodium citrate molecules adsorbed on Ag aggregates in a microcavity were obtained under conditions where MDR's either were, or were not, excited (see Figs. 1a and 1b). We found that SERS is 10^3 to 10^5 times more intense when MDR's are excited. However, of greater interest is the coupled, multiplicative enhancement factor caused by both fractal aggregates and microcavities. By comparing Raman signal levels from sodium citrate

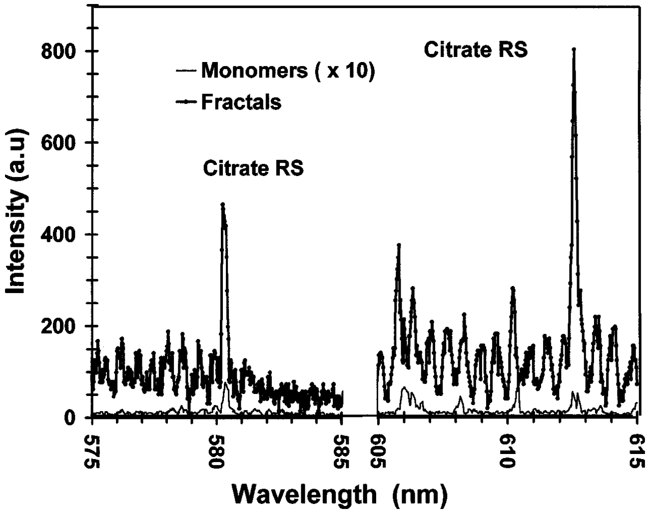

FIG. 4. Inelastic scattering spectra of nonaggregated silver monomers without dye (thin line, lower trace) and fractal aggregated monomers with $5 \times 10^{-7} M$ dye solution (thick line, upper trace) in microcavity for $\lambda_L = 543.5$ nm, cw He-Ne laser (maximum power is 0.75 mW).

adsorbed on Ag colloid aggregates and from a high-concentration sodium citrate solution without colloidal particles, we found that SERS enhancement resulting from fractal aggregation of colloidal silver is 10^5 to 10^6, which is consistent with the data of Ref. [11]. Thus, with the additional, multiplicative enhancement provided by the microcavity, the resultant average SERS enhancement by fractals in a microcavity is estimated to be in the range 10^8 to 10^{11}. Since the optical excitations are localized in small nanometer-size hot spots, and the local enhancement in these spots can exceed the average one by 5 to 6 orders of magnitude [4], we estimate the resultant local SERS enhancement to be 10^{13} to 10^{17}. These enhancement factors exceed the local SERS enhancements for single molecule SERS (10^{12} to 10^{15}) reported in [12]. We expect that placing fractal nanostructures in a microcavity will facilitate new possibilities for optical microanalysis and studies of lasing and nonlinear optical effects in single molecules.

This is illustrated in Fig. 4 which contrasts microcavity spectra of nonaggregated Ag monomers without R6G dye (lower trace) with fractal aggregates containing a $5 \times 10^{-7} M$ dye solution (upper trace) under $\lambda_L = 543.5$ nm HeNe excitation. Two spectral fragments are shown between $\lambda = 575$ and 615 nm. One can see a set of luminescence peaks whose minimal spacing is approximately equal to the intermode spacing of our cylindrical microcavity. In addition, two large amplitude peaks distinguish themselves in the observed spectra. We have provisionally identified the largest peak at 612.6 nm with the combination Raman mode $(1310 + 780)\ \mathrm{cm}^{-1}$ of sodium citrate, used to grow silver monomers and present in minute ($3 \times 10^{-4} M$) concentrations in our monomer solutions; the other peak at 580 nm corresponds to the $1160\ \mathrm{cm}^{-1}$ fundamental Raman mode of the citrate molecule. These peaks exhibit a nonlinear dependence on pump intensity and may be regarded as surface-enhanced stimulated Raman scattering in a microcavity, notably, excited by a 0.75 mW cw pump laser.

In summary, results reported in the present paper promise an advance in the design of micro- and/or nanolasers, operating on a small number of, or even on individual, molecules adsorbed on metal nanostructures within a micro- and/or nanocavity, as well as offering the possibility of combining surface-enhanced radiative processes and high-Q morphology-dependent resonances in microcavities.

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