OPTICAL PROPERTIES OF FRACTAL NANOCOMPOSITES

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ABSTRACT

Optical prossesses in nanostructured fractal composites are shown to be strongly enhanced. The enhancement occurs because of a localization of dipolar eigenmodes in subwavelength areas.

Composite materials constituted of tens-of-nanometer-sized particles possess fascinating electromagnetic properties and they are likely to become ever more important with the miniaturization of electronic components. Fractal structures are very prevelant in composites. The emergence of fractal geometry was a significant breakthrough in the description of irregularity [1]. Fractal objects (fractals) do not possess translational invariance and, therefore, cannot transmit ordinary waves [2,3]. Accordingly, dynamical excitations such as vibrational modes, known as fractons, tend to be localized in fractals [3]. Formally, this is a consequence of the fact that plane running waves are not eigenfunctions of the operator of dilatation symmetry (scale-invariance) characterizing fractals. The efficiency of fractal structures in damping running waves is probably the key to a "self-stabilization" of many of the fractals found in nature [2].

The localization of optical eigenmodes can lead to a dramatic enhancement of many optical effects in fractals [4-6]. The theory of optical excitations in fractal clusters and percolation systems has been intensively developing during the last decade, in particular, by Berry [7], Stroud [8], Bergman [9], Fuchs and Claro [10], Devaty [11], Brouers [12], Niklasson [13], and by Stockman, Markel and Shalaev [4-6, 14-23]. One of the most fascinating optical properties of fractals is a strong localization (in regions smaller than the wavelength λ) of the dipolar eigenmodes [6, 8, 12, 14-17, 24]. Localized modes concentrate electromagnetic energy in areas smaller than the diffraction limit of conventional optics ($\sim \lambda$) acting, to some extent, as antennas or as the "near-field lenses". Such modes produce high-local-field zones resulting in strong enhancement of optical processes (especially, nonlinear ones which are proportional to the local field strengths to a high power). In fractal aggregates composed of metal nanoparticles and in rough self-affine films the modes are associated with localized surface plasmon (LSP) oscillations. Direct experimental observation of the strongly localized optical modes in fractal silver aggregates has been recently reported [24].

As shown previously [4-6, 15-23], resonant excitation of strongly localized optical modes in fractals results in a huge enhancement of resonant Rayleigh [16], Raman [18] and, especially, nonlinear light scattering [21-23]. We have also predicted recently that, in addition to localization of light-induced dipole excitations, fractality can result in Anderson localization (trapping) of the light itself within a range of the order of a wavelength [19].

An important property of the interaction of light with fractals is the very strong frequency and polarization dependence of the spatial location of light-induced dipole modes [6, 22, 24]. Such frequency-spatial and polarization-spatial selectivity of the interaction can find applications in the recording and processing of optical information. This selectivity arises because the fractal morphology provides localization of optical modes on different sections of an object with random local structure and because of the tensor character of the dipole (or, multipole, in a general case) interactions between particles forming the fractal object.

A well-known example of a fractal aggregate of particles is a metal colloid cluster. In particular, fractal aggregates of silver colloid particles can be produced from a silver sol generated by reducing silver nitrate with sodium borohydride. Addition of an adsorbate (e.g., phthalazine) promotes aggregation and fractal colloid clusters form. This aggregation can be described as follows. A large number of initially isolated silver nanoparticles execute random walks in the solution. Encounters with other nanoparticles result in their sticking together, first to form small groups, which then aggregate into larger formations, and so on. This is the so called cluster-cluster aggregation model, which results in clusters having fractal dimension $D \approx 1.78$. Cluster-cluster aggregation can be

Mat. Res. Soc. Symp. Proc. Vol. 367 © 1995 Materials Research Society

easily modeled in a computer, which provides excellent simulation of the empirically observed structures.

The number of particles, N, in a fractal aggregate is given by $N = (R_c/R_0)^D$, where R_c is the radius of gyration of the cluster and R_0 is a typical separation between neighbor monomers. For silver colloid fractal clusters one typically has $R_0 \sim 10nm$, $R_c \sim 1\mu m$ and $D \approx 1.78$. Note that each section of a fractal composite contains holes comparable in size to the section itself. Such a structure is statistically self-similar, i.e., it posseses a scale-invariance property. The positions of particles in a cluster are correlated so that the pair correlation function has a power-law dependence: $g(r) \propto r^{D-d}$, where d is the dimension of the embedding space ($d = 3$ in the case under consideration). The mean density of a fractal cluster $\rho \sim N/R_c^d \propto R_c^{D-d} \to 0$ when $R_c \to \infty$ since $D < d$. Thus, the larger a fractal cluster, the smaller its mean density. This is because holes in a fractal composite are presented in all scales from the minimum ($\sim R_0$) to the maximum ($\sim R_c$).

Metallic particles constituting a nanocomposite are polarizable and possess an optical resonance with high quality-factor $Q : Q \gg 1$. This resonance is associated with plasmon oscillations within the spherical particles. Light-induced dipole-dipole interactions between the polarizable particles in the aggregate are determined by the complex polarizability χ_0 of an isolated monomer. For a spherical monomer (in vacuum) $\chi_0 = R_m^3(\epsilon - 1)/(\epsilon + 2)$, where R_m is the monomer radius, and $\epsilon = \epsilon' + i\epsilon''$ is the dielectric constant of the metal. Defining $X \equiv -Re[\chi_0^{-1}]$, and $\delta \equiv -Im[\chi_0^{-1}]$, X plays the role of a spectral variable and δ expresses the dielectric losses. At the resonant frequency ω_0 one has $\epsilon'(\omega_0) = -2$ and $X(\omega_0) = 0$. In the vicinity of the localized surface plasmon (LSP) resonance, $X \propto \omega - \omega_0$ where ω is the frequency of light. The quality factor is determined by $Q = (R_0^3\delta)^{-1} = (R_0/R_m)^3|\epsilon - 1|^2/3\epsilon'' \sim |\epsilon - 1|^2/3\epsilon''$.

An external optical field induces transitional dipole moments on the particles, and strong dipole interactions lead to a renormalization of the problem, from one of N dipoles in a cluster to one of $3N$ collective dipolar eigenmodes. These modes in the case of silver fractal nanocomposites cover a wide spectral range, from approximately 340 nm to 1000 nm, i.e., the visible and near-infrared parts of the spectrum. Thus, while the LSP resonance of an isolated silver particle peaks (in water) at 400 nm, a fractal nanostuctured aggregate resonates at an almost continuous set of frequencies in a broad spectral range and, accordingly, can provide enhancement at all these frequencies. These resonances are shifted mostly to the red-wavelenght part of the spectrum where the quality-factor Q for metal nanocomposites is significantly larger than that at the near uv resonance of an isolated spherical particle. (For silver, $Q \sim 10$ at the uv resonance of an isolated particle, and $Q \sim 10^2$ at the collective plasmon resonances of a fractal nanocomposite in the visible and ir ranges [18]).

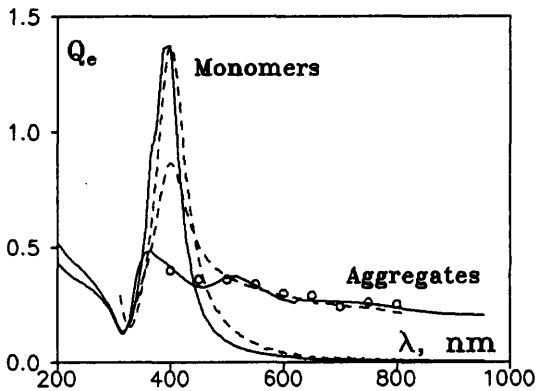

Fig. 1: Extinction spectrum of silver colloid fractal aggregates (dashed lines - experiment; cirlces and solid lines - simulations).

In Fig. 1 we present the results of our numerical simulations of the extinction spectrum of isolated silver monomers and their fractal aggregates compared with experimental data. Clearly, the aggregation results in a large tail in the red and near infra-red part of the spectrum. In the case of fractal composites the simulations have been performed for 10 clusters of 500 particles each (the solid line with a large wing) and for 4 clusters of 10,000 partiles each (circles). As follows from the figure the simulations discribe well the experimental data in the wing of the absorption spectrum asocciated with localized optical modes of fractal nanocomposites. The discreapancy in the central part of the spectrum (which is mostly due to delocalized modes) occurs because in the experiments a number of particles remained nonaggregated in solution and led to additional (not related to fractal aggregates) absorption at 400 nm.

The strong localization of the eigenmodes results in accumulation of electromagnetic energy in areas smaller than the wavelength. These "hot zones" are characterized by very high local fields. Note that these local fields are strongly fluctuating in space so that $\langle |E_{loc}|^2 \rangle \gg \langle |E_{loc}| \rangle^2$ [6, 14] ($\langle ... \rangle$ denotes averaging over the ensemble of clusters).

The localization of the eigenmodes is characterized by a coherence length L_X of the eigenmodes defined by [14, 17]

$$L_X^2 = \frac{\langle \sum_n \delta(X - w_n) \{ \sum_i (i\alpha \mid n)^2 r_i^2 - [\sum_i (i\alpha \mid n)^2 \vec{r}_i]^2 \} \rangle}{\langle \sum_n \delta(X - w_n) \rangle}$$

where $(i\alpha|n)$ and w_n are the eigenfunctions and eigenvalues of the dipole-dipole interaction operator, $\hat{W}$, between particles in a cluster. This definition has a clear quantum-mechanical analogy with $(i\alpha \mid n)$ as the wave function. In Fig. 2 we plot L_X against X. According to the figure, the localization increases for larger values of $|X|$, i.e., for larger detuning from the resonance of an isolated particle given by $X = 0$. The most localized modes have linear dimensions which are of the order of the particle size.

The increase of the localization with increasing $|X|$ leads to the higher local intensity associated with the modes and, as a result, to larger enhancements. As shown in previous papers, the enhancement of optical processes, such as Raman scattering and DWFM, significantly increases towards larger values of $|X|$ [6, 18, 23]. Note also that fluctuations are very strong and increase toward the center $X = 0$. These are long-range fluctuations near the critical point, $X = 0$, which ultimately provide the scaling of optical excitations similar to a phase transition [14, 15]. Thus, the point $X = 0$ plays a role similar to the phase transition point in phase transition theory.

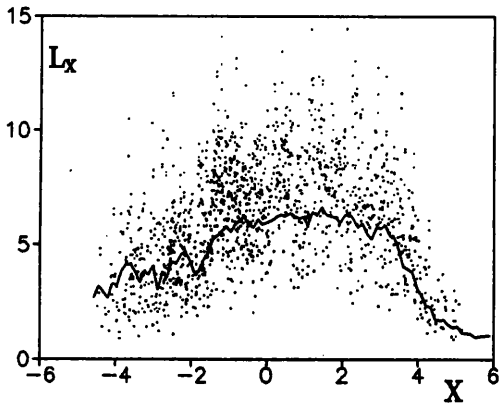

Figure 2: The localization length L_X of eigenmodes versus their eigenvalue a^3X for the cluster-cluster aggregate, CCA, with $N = 500$ particles. (The diameter of a particle, a, is equal to unity). The dependence L_X averaged over an interval of $a^3\Delta X = 0.02$ for ten CCAs is shown by the solid line.

The property of fractal nanocomposites to produce high-field areas can be utilized for controling some optical characteristics, such as light absorption and scattering, of various optical materials. This can be achieved by adding into a material a certain amount of metal nanocomposites and thereby improving its optical sensitivity. The same property is of importance in high resolution spectroscopy also and, especially, in the nonlinear case. The huge enhancement of a number of linear and nonlinear optical effects observed in metal colloid clusters and on rough surfaces is in a large part due to the high-field zones.

As already mentioned, spatial locations of the regions of high local field strongly depend on the frequency and polarization of light. The ability to distinguish optical frequencies and polarizations is one of the most interesting, and potentially useful, properties of fractal nanocomposites. We envision applications in optical signal processing and optical data storage based on this unique property. For example, one may wish to demultiplex, i.e., to spatially separate and detect, a set of optical communication channels which are distinct from each other only by their carrier frequency. Another possibility, in the realm of optical data storages, is to photomodify the absorption spectrum of a small region of a cluster, thereby creating a frequency- or polarization-addressable optical data bit. Our preliminary experiments on frequency- and polarization-selective photomodification of fractal clusters [22] support these expectations.

It is worth comparing fractal nanocompsites with other inhomogeneous media and, specifically, with a medium having the same volume fraction of metal particles which, however, are randomly distributed in a three-dimensional space. This is, of course, different from a fractal nanocomposite where the positions of particles are correlated, so that $g(r) \propto r^{D-d}$ with $D < d$. The volume fraction p of particles in a fractal cluster is very small, $p \ll 1$, (in fact, $p \to 0$ at $R_c \to \infty$). For a random inhomogeneous media with $p \ll 1$ and $D = d$ (we refer it as "gas" of particles), one can apply the well-known Maxwell-Garnett theory [9] which predicts only one resonant frequency close to the resonance of an isolated particle at $X(\omega) = 0$. In fractals, however, in spite of the fact that the mean density is asymptotically zero, there is a high probability of finding a number of particles close to any particular one. (The pair correlation finction, $g(r) \propto r^{D-d}$, increases with the decrease of a distance r between the particles). Thus, in fractals there is always a strong interaction of a particle with others distributed in its random neighborhood. As a result, there exist localized eigenmodes which are oriented spatially in different parts of a cluster, with the location depending on the eigenfrequency and polarization characteristics of the mode. As mentioned above, some of these modes are significantly shifted to the red part of the spectrum and therefore their quality factors are much larger than at $X(\omega) = 0$, for a non-interacting particle. (As follows from the Drude formula, $Q \propto \lambda$ in the infrared part of the spectrum [18]). Thus, the dipole-dipole interaction of particles composed into a fractal cluster "generates" a wide spectral range of resonant modes with improved quality-factors and with spatial locations which are very sensitive to the frequency and polarization of the excited field.

The other medium with which to compare fractal composites is a close-packed 3-dimensional aggregate of metal nanoparticles (the volume fraction occupied by metal particles in this case is $p \sim 1$). Since the dipole-dipole interaction for 3-dimensional structures is long-range, one expects that eigenmodes in this case are delocalized over the whole sample. Accordingly, fluctuations of local fields ($\propto 1/\sqrt{N}$) are much smaller than in the case of localized dipolar modes in a fractal aggregate. Because the strong fluctuations of local fields are primarily responsible for high values of optical nonlinear response, the nonlinear susceptibilities of a random close-packed aggregate are significantly smaller than those of a fractal aggregate. Thus in both considered cases of non-fractal composites, a "gas" of particles and a close-packed aggregate, the enhancement of optical processes is expected to be much smaller than for a fractal nanocomposite.

In Fig. 3, we present the results of numerical simulations for the enhancement of local field intensities, $G = \langle E^2 \rangle / (E^{(0)})^2$ (E and $E^{(0)}$ are the local random field and the external driving field, respectively). Clearly, the enhancement of local fields in fractal composites (cluster-cluster aggregates, CCA) achieves much larger values than for the case of non-fractal silver composites (either a "gas" of silver particles with the same, as in the CCA, p or a close-packed random aggregate of silver spherules). Note also that for fractal composites G strongly increases with increasing wavelngth λ. This occurs because of two basic reasons: first, localization of eigenmodes in fractals increases with λ and, second, the mode quality-factor ($Q \sim |\epsilon - 1|^2 / 3\epsilon''$) also increases

for the eigenmodes located towards the red part of the spectrum.

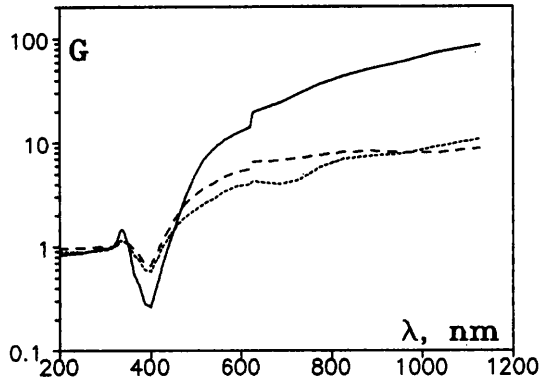

Fig. 3: Enhancement factors, G, of the local field intensities plotted against λ for the fractal composite (solid line), "gas" of particles with the same as for the fractal aggregate volume fraction of metal (short-dashed line), and the close-packed aggregate of particles (long-dashed line). The local intensites in all cases were averaged over ensemble of random aggregates with $N \approx 500$ in each cluster.

Clearly, the enhancement of nonlinear optical processes will be especially strong since the generated intensity in this case is proportional to a high power of the local field. The enhancement factor G for an optical process $\propto E^n$ can be estimated as [7]: $G \sim \langle |E/E^{(0)}|^n \rangle \sim [Q(\lambda)]^{n-1} F(\lambda)$, where $F(\lambda)$ is a smooth function of the wavelength which is of the order of unity. In particular, for degenerate four-wave mixing, DFWM, (when the generated amplitude is enhanced as well as the driving field) the theory predicts the giant enhancement $G \propto Q^6$ [23]. The nonlinear polarization P_{NL} for DFWM of waves with amplitudes $E^{(0)}$ and $E_1^{(0)}$ can be presented as $P_{NL} = p\chi_{FC}^{(3)}[E^{(0)}]^2 E_1^{(0)*}$ where $\chi_{FC}^{(3)} = \chi^{(3)} G^{1/2}$ is the effective nonlinear susceptibility of a fractal composite ($\chi^{(3)}$ is the nonlinear susceptibility of nonaggregated particles).

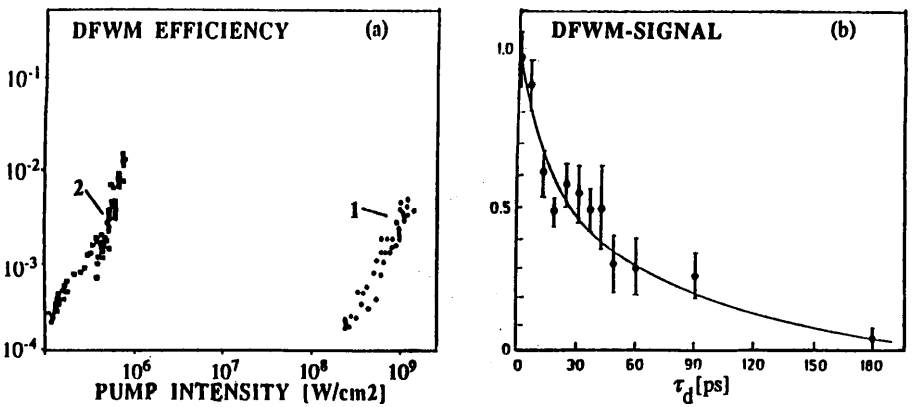

Fig. 4: a) DFWM efficiency vs pump intensity for silver particles which are isolated (1) and aggregated into fractal composites (2) ($\lambda = 532$ nm); b) DFWM signal vs the time delay of one of the pumps ($\lambda = 540$ nm; pulse duration is $\tau \approx 30$ps). Taken from [21] and [22].

In Fig. 4a we plot the experimental data for conversion efficiency $\eta = I_s/I_1 \propto I_0^2$ (I_s, I_1 and I_0 are the intensities of the DFWM signal, probe beam and pump beam, respectively). The conventional scheme for observation of optical phase conjugation (OPC), with two opositely directed pump beams and a probe beam directed at small angle with respect to the pumps, was used in the experiment. As follows from the figure, similar values of η can be obtained in silver particles aggregated into fractals at pump intensities $\sim 10^3$ less than in the case of non-aggregated, isolated, particles. Since $\eta \propto I_0^2$ the enhancement factor for silver fractal composites is $G \sim 10^6$. The measured value of the nonlinear susceptibility is very large $\chi_{FC}^{(3)}(-\omega,\omega,\omega;-\omega) \sim 10^{-5}$ e.s.u.

Rapid nonlinear response of fractal nanocomposites was tested in the OPC scheme when one of the input pulses was delayed by moving the mirror that reflected the input beam back to the sample. As follows from Fig. 4b the DFWM signal is twice decreased with the time delay τ_d increasing up to 30 ps, which coincides with the pulse duration. Hence, the relaxation time of the nonlinear response does not exceed 10^{-11} s. Such a large nonlinear susceptibility $\chi_{FC}^{(3)} \sim 10^{-5} e.s.u$ with the time of nonlinear response $\leq 30ps$ is, to our knowledge, a world record and it indicates that fractal metal nanocomposites possess high potential in various applications (e.g., as optical switches).

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