ELSEVIER

Physica A 241 (1997) 249–258

PHYSICA A

Nonlinear optics of fractal nanomaterials: Small-particle composites and self-affine thin films

Vladimir M. Shalaev[a,*], E.Y. Poliakov[a], V.A. Markel[a], R. Botet[b]

[a] *Department of Physics, New Mexico State University, Las Cruces, New Mexico 88003, USA*
[b] *Laboratoire de Physique des Solides, Centre d'Orsay, 91405 Orsay, France*

Abstract

Fractal nanostructured materials, such as nanocomposites and self-affine thin films, are shown to possess giant optical nonlinearities. The enhancement results from the sub-wavelength localization of dipolar modes and strong local field fluctuations.

PACS: 78.90.+t; 42.65.An; 61.43.Hv; 42.70.Nq; 42.65.Hw
Keywords: Optics; Fractals; Composites; Films

Optical phenomena experience giant enhancements in metal nanocomposites and rough thin films consisting of small nm-sized particles and roughness features, respectively. The enhancement is associated with excitation of surface plasmons which are collective modes and depend strongly on the morphology (geometrical structure) of the material. Fractal structures are prevalent in composites and cold-deposited thin films. The emergence of fractal geometry was a significant breakthrough in the description of irregularity. Fractal objects do not possess translational invariance and, therefore, cannot transmit running waves. Accordingly, collective excitations, such as surface plasmons, tend to be localized in fractals [1]. Formally, this is a consequence of the fact that plane running waves are not eigenfunctions of the operator of dilation symmetry characterizing fractals.

Fractal aggregates of small particles embedded in a three-dimensional host are self-similar (scale-invariant), within a certain interval of sizes. Unlike fractal assembles of particles, a self-affine surface reveals a scale-invariance if different scaling factors are applied in the (x, y)-plane of the surface and in the normal, z-direction. We studied

* Corresponding author. Tel: (505) 646-1932; fax: (505) 646-1934; e-mail: vshalaev@nmsu.edu.

0378-4371/97/$17.00 Copyright © 1997 Elsevier Science B.V. All rights reserved
PII S0378-4371(97)00092-7

nonlinear optical properties of small-particle composites and rough thin films characterized by various random morphology. In the following, we first consider small-particle composites and then self-affine films.

Nonlinear electrical and optical properties of nanostructured composites have attracted much attention in recent years [1–15], partly, because they have much larger nonlinear susceptibilities than those of ordinary bulk materials.

As is well known, there is only one dipolar mode that can be excited by a homogeneous field in a spherical object. For a 3D collection of small particles, such as randomly close-packed spheres (CPS) in a spherical volume and random gas of particles (RGP), the absorption spectra are still peaked near the relatively narrow resonance of the individual particles, i.e., all eigenmodes of the collection of particles are located in a small spectral interval [1].

In contrast to conventional (non-fractal) 3D systems, the dipolar interactions in low-dimensional fractals are not long range; this results in localization of the corresponding eigenmodes at various random locations in a fractal cluster. These modes form a broad optical spectrum of fractal aggregates which is characterized by strong inhomogeneous broadening. It is important that despite asymptotically zero density of particles in a fractal cluster, there is always a high probability of finding a number of particles in close proximity to any given one (in fractals embedded in d-dimensional space, the pair correlation $g \propto r^{D-d}$, where D $(<d)$ is the fractal dimension; accordingly, g becomes large at small r). Therefore, there are strong interactions between neighboring particles, which lead to the formation of eigenmodes covering a broad spectral range. The large variety of different local configurations in a fractal cluster leads to the wide spectral interval covered by the eigenmodes. We emphasize that this behavior is different from nonfractal composites (such as RGP and CPS) where dipolar eigenmodes are not localized and typically occupy a narrow spectral interval. Thus in objects with fractal morphology, the density–density correlation, $g(r) \propto r^{D-d}$, results in unusual combination of properties: whereas the volume fraction filled by N particles in a fractal is very small, $\propto N^{1-d/D} \to 0$, there are strong interactions between neighboring particles [1].

Localization of eigenmodes in fractals leads to a patchwork-like distribution of local fields associated with "hot" and "cold" zones [16]. This brings about large spatial fluctuations of local fields in fractal composites and giant enhancement of various optical effects [1].

In fractals formed by metal particles, the dipole eigenmodes cover the visible and infra-red parts of the spectrum; the mode quality factors increase with the wavelength, i.e., the local fields are especially large in the long wavelength part of the spectrum [1].

We consider a system of N polarizable particles (monomers) with the dipole–dipole interactions between them at the optical frequency. The monomers are positioned at the points $\mathbf{r}_i$ $(i=1,\ldots,N)$ and assumed to be much smaller than the wavelength, λ, of the incident wave. For the sake of simplicity, we restrict our consideration to the quasi-static limit (i.e., assume that $R_c \ll \lambda$, where R_c is the size of a cluster). Then, the interaction operator has the form $W_{\alpha\beta}^{ij} \equiv (i\alpha|W|j\beta) = [\delta_{\alpha\beta} - 3n_\alpha^{(ij)} n_\beta^{(ij)}] r_{ij}^{-3}$ where Greek

indices stand for Cartesian components, (the summation over repeated Greek indices is implied), $\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$, and $\mathbf{n}^{(ij)} \equiv \mathbf{r}_{ij}/r_{ij}$.

The enhancement of optical processes in a small-particle composite occurs because local fields exhibit strong fluctuations that significantly exceed the applied field. The local field, $\mathbf{E}_i$, acting on the ith particle (monomer) in a cluster is given by: $E_{i\alpha} = \alpha_0^{-1}\alpha_{i,\alpha\beta} E_\beta^{(0)}$, where $\mathbf{E}^{(0)}$ is the applied field, α_0 is the polarizability of the individual monomer and $\alpha_{i,\alpha\beta}$ is the local polarizability of a monomer in a cluster which is related to the local dipole moment $d_{i\alpha}$ induced on the ith particle via the formula $d_{i\alpha} = \alpha_{i,\alpha\beta} E_\beta^{(0)}$. Note that since we restrict our consideration to the quasi-static approximation, by $\mathbf{E}^{(0)}$, $\mathbf{E}_i$, and $\mathbf{d}_i$ we mean the amplitudes of the fields and dipoles, i.e., the spatial- and time-varying factors are omitted.

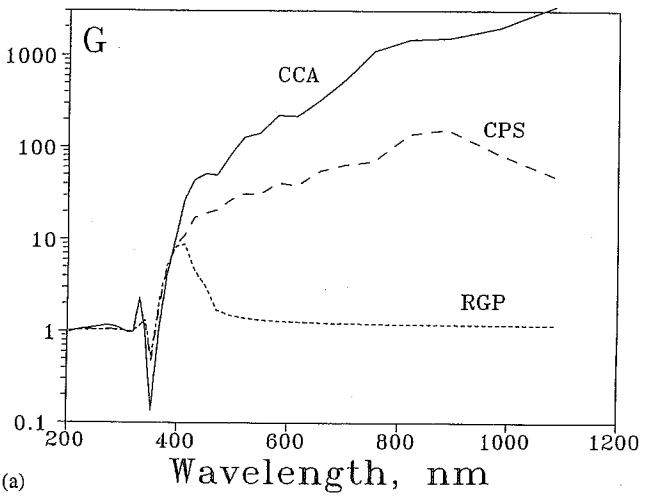
By solving the coupled-dipole equations (CDE) in the quasi-static approximation, $d_{i\alpha} = \alpha_0[E_\alpha^{(0)} + \sum_j W_{\alpha\beta}^{ij} d_{j\beta}]$, we obtain [1]: $\alpha_{i,\alpha\beta} = \sum_{nj} (i\alpha|n)(n|j\beta)[(w_n - X) - \mathrm{i}\delta]^{-1}$, where $X \equiv -\mathrm{Re}[\alpha_0^{-1}]$, $\delta \equiv -\mathrm{Im}[\alpha_0^{-1}]$, and w_n and $|n)$ are the eigennumbers and eigenvectors of the interaction operator: $(n|W|m) = w_n \delta_{nm}$. Thus $(i\alpha|n)$ are the components of the vector $|n)$ in the orthogonal basis $|i\alpha)$. With given coordinates of particles (dipoles), we can find eigenfunctions and eigenvalues of the interaction operator, W, and then, using the above formulas, to determine local dipoles, d_i, and fields, E_i.

The light frequency, ω, enters in the above equations implicitly via the complex variable $Z = \alpha_0^{-1}(\omega) \equiv -[X + \mathrm{i}\delta]$. Material and geometrical properties of monomers affect the problem only via the parameter Z. The real part, $X = X(\omega)$, plays the role of a spectral variable instead of ω, and the imaginary part, $\delta > 0$, describes dissipation in a monomer; in general, δ can also depend on ω. The quantity $q = \delta^{-1}$ defines a resonance quality-factor. The dependences of X and δ on ω for silver are specified in [1].

A parameter characterizing enhancements of the local-filed intensities is defined as $G = \langle |E_i|^2 \rangle / |E^{(0)}|^2$, where the symbol $\langle \cdots \rangle$ denotes an average over an ensemble of random clusters. The enhancement G is related to the cluster absorption, $\mathrm{Im}\,\alpha(X) = (1/3)\,\mathrm{Im}\langle \alpha_{i,\alpha\alpha} \rangle$, as follows [17]: $G = \delta[1 + X^2/\delta^2]\mathrm{Im}\,\alpha(X)$.

In Fig. 1(a), we show the enhancement of the intensities of local fields, $G = \langle |E_i|^2 \rangle / |E^{(0)}|^2$, in silver cluster-cluster aggregates (for CCA, the fractal dimension $D \approx 1.78$), and nonfractal silver RGP and CPS, with $D = d = 3$. As seen in the figure, the local-field enhancements in fractal CCA are much larger than in non-fractal RGP and CPS. In Fig. 1b, we also show an electron micrograph of a typical silver cluster–cluster aggregate.

High local fields result in giant optical nonlinearities for optical processes in small-particle composites. In particular, the Kerr nonlinear susceptibility can be very large in particle aggregates. The Kerr polarizability has, in general, the form $\chi_{\alpha\beta\gamma\delta}^{(3)}(\omega; \omega, \omega, -\omega)$, and determines nonlinear corrections ($\propto$ the field intensity) to the refractive index and absorption. We consider the enhancement of the Kerr susceptibility due to the clustering of small particles embedded in a linear host material. Rough estimation for the enhancement can be found from the relation $G_K \sim \langle E_i^3 E_i^* \rangle / [E^{(0)}]^3 E^{(0)*}$. The enhancement factor is, in general, complex: $G_K \equiv G_K' + \mathrm{i}G_K''$. If the original nonlinear susceptibility



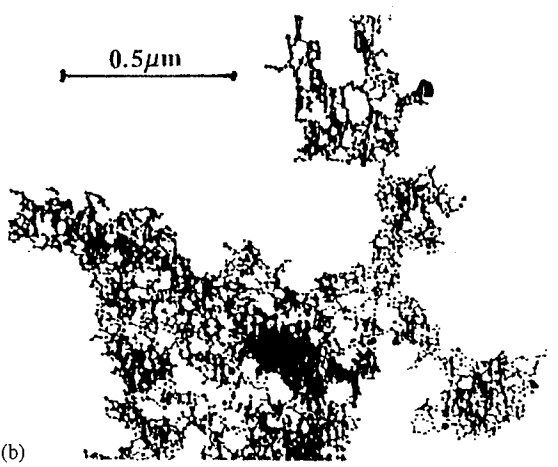


Fig. 1. (a) Enhancement factors, G, of local field intensities plotted against λ for particle aggregates: fractal cluster–cluster aggregates, CCA (solid line), a random gas of particles (RGP) with the same as for CCA volume fraction of metal (short-dashed line), and a close-packed spheres, CPS (long-dashed line). (b) Electron micrograph of a silver CCA.

of monomers composing a cluster, $\chi^{(3)}_{\text{monomer}}$, (which can be associated with a monomer itself or an adsorbant molecule on it) is real, then, the real part, G'_K, and the imaginary part, G''_K, determine, respectively, the enhancement for the nonlinear refraction and for the nonlinear correction to absorption of a particle aggregate.

We found that G'_K is, on average, larger than G''_K and can be approximated by the formula $G'_K \approx C[X^4/\delta^3]\mathrm{Im}\,\alpha(X)$, where C is a constant and $\mathrm{Im}\,\alpha(X)$ describes a linear absorption by composite material. In Fig. 2, we present plots of G'_K (a) and G''_K (b) for $X<0$ (the calculations for $X>0$ give similar results). The calculations

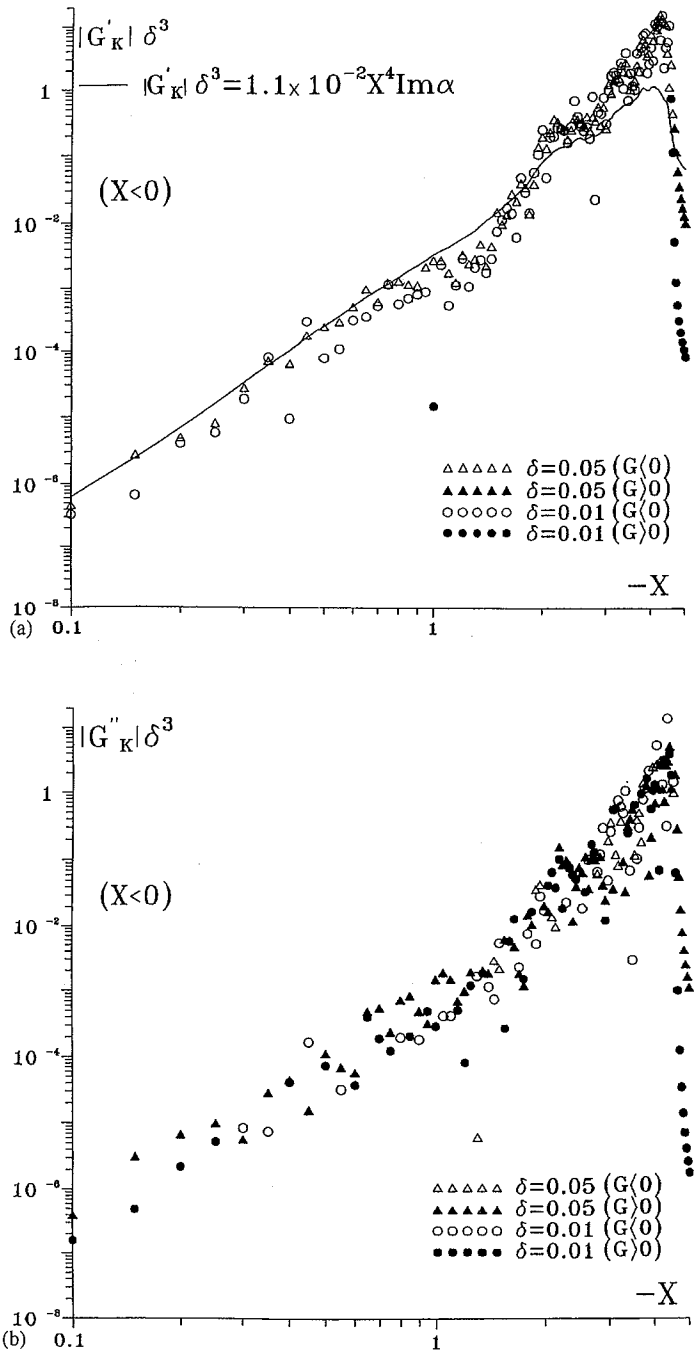


Fig. 2. The enhancement of the Kerr optical susceptibility, $\chi^{(3)}$, in CCA: (a) the real part, G'_K, and (b) the imaginary part, G''_K.

were made for fractal CCA. The solid line in Fig. 2(a) represents the calculations based on the above formula, with the C chosen so that $|G'_K\delta^3|=1$ in its maxima at $X\approx -4$. As follows from the figure, both real and imaginary parts of the enhancement are approximately proportional to the third power of the eigenmode quality factors, $q^3(\sim\delta^{-3})$. In the maxima, $G'_K\sim\delta^{-3}$ (G''_K is several times smaller than G'_K). For metal particles, in particular, the decay parameter varies from $\delta=0.01$ to $\delta=0.1$ in the infrared and visible parts of the spectrum; accordingly, the enhancement ranges from $|G_K|\sim 10^3$ to $|G_K|\sim 10^6$ in this spectral range. It also follows from Fig. 2 that the real part G'_K is negative for most of the resonant modes, i.e., a nonlinear correction to the refractive index, Δn, is negative, if $\chi^{(3)}_{\text{monomer}}>0$, and positive, if $\chi^{(3)}_{\text{monomer}}<0$ (leading to self-defocusing and self-focusing of the light beam, respectively). Interestingly, the imaginary part, G''_K, changes its sign as a function of X very rapidly. Thus, a nonlinear correction to the absorption coefficient (given by G''_K for real $\chi^{(3)}_{\text{monomer}}$) is a very strong function of the laser frequency and can be both positive and negative. The fact that the nonlinear contribution to the absorption can have a different sign is not surprising: there are nonlinear optical processes (associated with the Kerr-type nonlinearity) leading to both positive and negative nonlinear contributions to absorption [18].

The enhancement for four-wave-mixing (FWM) process can be expressed in terms of G_K according to the formula $G_{\text{FWM}}=|G_K|^2\approx C^2[X^8/\delta^6][\text{Im}\,\alpha(X)]^2$. Since $G_{\text{FWM}}\propto\delta^{-6}$, the enhancement can be very large for small δ (i.e., high quality factors). A million-fold enhancement of degenerate FWM due to the clustering of initially isolated silver particles in a colloidal solution was experimentally obtained in Ref. [4]. Our calculations give roughly the same enhancement. The experimentally obtained value for the nonlinear susceptibility in silver fractal composites is $\bar{\chi}^{(3)}\sim p\times 10^{-5}$ esu at $\lambda=532$ nm. Even for a very small Ag volume fraction used in the experiment, $p\sim 10^{-5}$, this gives $\bar{\chi}^{(3)}\sim 10^{-10}$ esu (cf., a typical value of $\chi^{(3)}$ in crystals is $\sim 10^{-15}$ esu). Moreover, p is a variable quantity and can be increased. We can assign the value 10^{-5} esu to the nonlinear susceptibility, $\chi^{(3c)}$, of silver fractal clusters. Note that the obtained value $\chi^{(3c)}\sim 10^{-5}$ esu for Ag fractals is three orders of magnitude larger than the $\chi^{(3)}$ measured for non-aggregated Ag particles [8]. The huge nonlinearity, $\chi^{(3c)}\sim 10^{-5}$ esu, with a time of the nonlinear response lying in the ps-scale, makes metal fractal aggregates very attractive for many potential applications.

We also found the enhancements associated with particle clustering for third-harmonic generation (THG) and Raman scattering. It is shown that the susceptibility of a composite material consisting of random small-particle clusters is proportional to q^3 for Raman scattering and to q^4 for THG, where as above $q\sim\delta^{-1}$ is a quality factor for the eigenmodes [1]. Our calculations for Raman scattering are in good agreement with experiments [1].

We also studied optical properties of self-affine thin films. Such films are formed by condensing atomic beams onto a low temperature substrate. To simulate a self-affine surface, we used the restricted solid-on-solid (RSS) model which generates surfaces with fractal dimension $D=2.6$ and well approximates cold-deposited metal (in particular, silver) films [19] (see Fig. 3(a)).

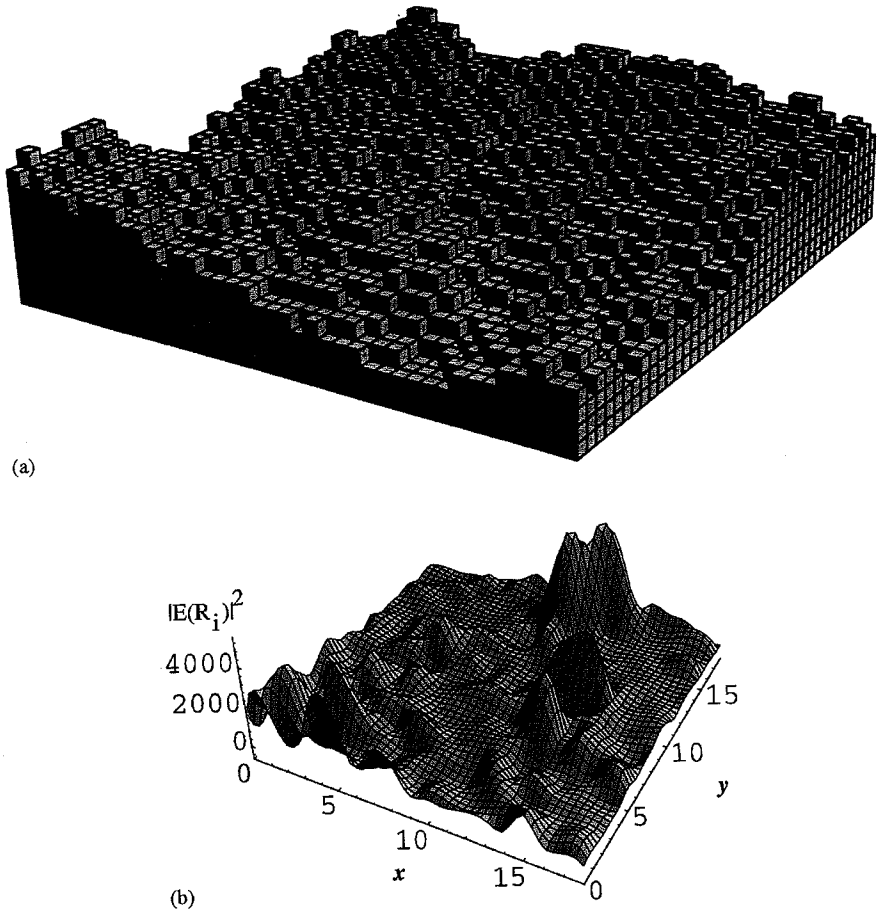


Fig. 3. (a) The self-affine film obtained in the restricted solid-on-solid model ($D=2.6$). (b) Local field distributions on the Ag self-affine film ($X=-3$, s-polarization of light).

To calculate optical excitations of a self-affine thin film by an incident wave, we used the "discrete-dipole approximation" (DDA) [20]. In the DDA, one replaces an odd-shaped object (such as a rough thin film) by an array of point dipoles, with the spacing between the dipoles small compared to the wavelength and sizes of spatial inhomogeneities. Each dipole has an oscillating polarization in response to both an incident wave and the electric fields due to all of the dipoles in the array. Assuming that the size of a sample is much smaller than the wavelength (so that the quasi-static approximation is valid), the self-consistent solutions for the dipole polarizations (oscillating at frequency ω) can be obtained as the solutions to a set of the coupled-dipole equations (CDE).

We observed that the eigenmodes of a self-affine surface manifests strongly inhomogeneous spatial distributions characterized by various degree of localization. On a metal self-affine film, the intensities in areas of high local fields ("hot" zones) exceed

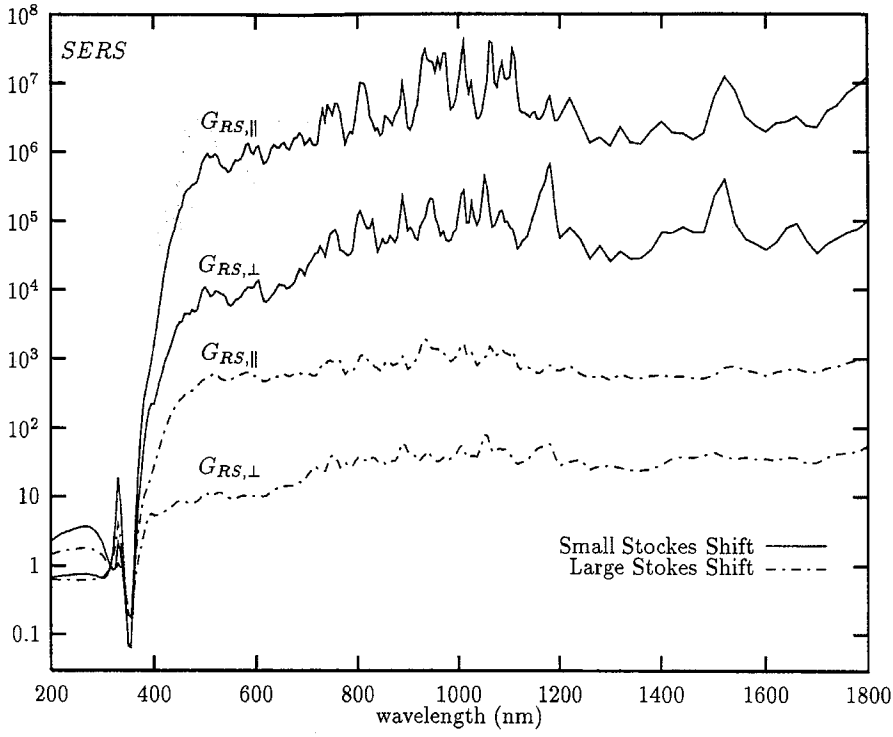


Fig. 4. The enhancements of Raman scattering on silver self-affine films, $G_{RS,\|}$ and $G_{RS,\perp}$, for the light polarized in the (x, y)-plane and normal to it, respectively.

the applied field intensity by approximately three orders of magnitude. The spatial locations of the "hot" zones are very strong functions of the frequency and polarization of the incident light.

The field distribution on Ag self-affine film for $X = -3$ ($\lambda \sim 500$) and s-polarized light is shown in Fig. 3(b). As seen in the figure, the field in the hot zones is much larger than the applied field, $E^{(0)} = 1$.

Our simulations also showed that a change of the wavelength or/and the polarization strongly affects the field distribution. A similar strong dependence on frequency and polarization of the applied field was obtained in experiments on near-field scanning optical microscopy of localized optical modes in Ag fractal aggregates deposited onto a surface [16].

We also studied enhanced Raman scattering from self-affine thin films. In Fig. 4, we show the averaged enhancement of Raman scattering, for both small and large Stokes shifts, on silver self-affine films generated in the RSS model. As seen in the figure, the enhancement increases toward the long-wavelength part of the spectrum and reaches very large values, $\sim 10^7$; this agrees well with experimental observations of SERS on cold-deposited thin films [21].

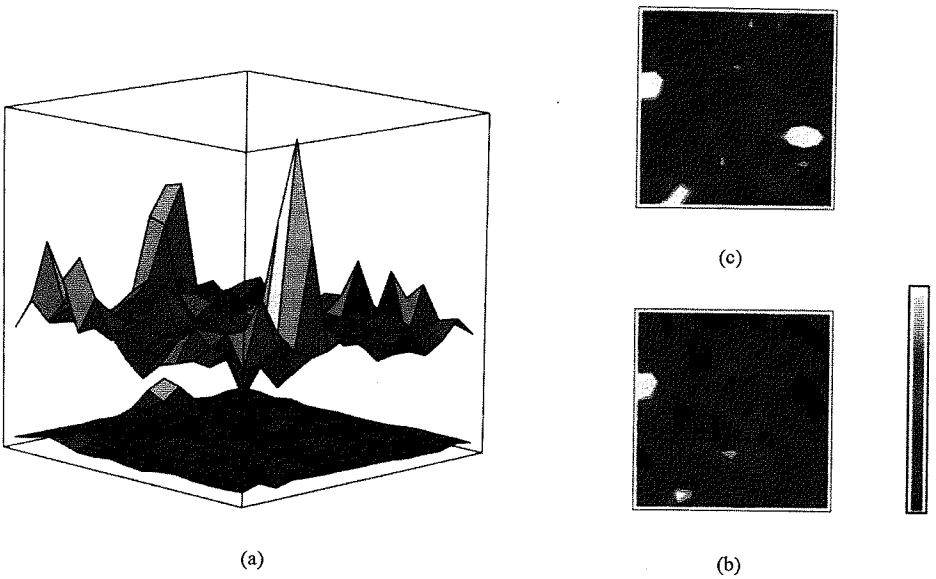


Fig. 5. (a) The spatial distributions for the local fields at the fundamental frequency, $\lambda = 550\,\text{nm}$, (bottom; the field distribution is magnified by factor of 3) and for the Stokes fields, $\lambda_s = 600\,\text{nm}$, (top). (The applied field is linearly polarized in the plane of the film.) (b) and (c) The contour-plots for the field distributions shown on (a).

In Fig. 5, the field spatial distributions at the fundamental and Stokes frequencies are shown. As seen in the figure, the distributions contain "hot" spots, where the fields are very high. The spatial positions of these spots are strong functions of frequency and polarization of the applied field [19]. Although the Stokes signal is proportional to the local field at the fundamental frequency, ω, the generated Stokes field, with frequency ω_s, excites, in general, other eigenmodes. Hence the field spatial distributions produced by the applied field and by the Raman signal can be different, as clearly seen in the figure.

The observed picture is expected to be typical for various optical processes in strongly disordered fractal systems, such as self-affine thin films. Specifically, hot spots associated with fields at different frequencies and polarizations can be localized in spatially separated nm-sized areas. These novel nano-optical effects can be obtained with NSOM providing a sub-wavelength resolution.

We also calculated enhancement for second harmonic generation (SHG) from self-affine silver films. The obtained enhancement is very high, $\sim 10^6$.

To summarize, dipole–dipole interactions in fractals are not long-range (as they are in conventional 3D media) and many of the collective eigenmodes are strongly localized in different parts of a fractal object with various random structures. This ultimately leads to strong spatial fluctuations of the fields. Optical nonlinearities emphasize the role of fluctuations leading to giant enhancements.

This research was supported by NSF under grant DMR-9500258 and by NATO under grant CRG 950097.

References

[1] V.M. Shalaev, Phys. Rep. 272 (1996) 61; V.A. Markel, V.M. Shalaev, E.B. Stechel, W. Kim and R.L. Armstrong, Phys. Rev. B 53 (1996) 2425; V.M. Shalaev, E.Y. Poliakov and V.A. Markel, Phys. Rev. B 53 (1996) 2437.
[2] D. Stroud and P.M. Hui, Phys. Rev. B 37 (1988) 8719.
[3] A.V. Butenko, V.M. Shalaev and M.I. Stockman, Z. Phys. D 10 (1988) 81.
[4] S.G. Rautian, V.P. Safonov, P.A. Chubakov, V.M. Shalaev and M.I. Stockman, Pis'ma Zh. Eksp. Teor. Fiz. 47 (1988) 243 [JETP Lett. 47 (1988) 243]; A.V. Butenko et al., Z. Phys. D 17 (1990) 283.
[5] V.M. Shalaev, M.I. Stockman and R. Botet, Physica A 185 (1992) 181.
[6] V.M. Shalaev, V.A. Markel and V.P. Safonov, Fractals 2 (1994) 201; V.M. Shalaev, R. Botet, D.P. Tsai, J. Kovacs and M. Moskovits, Physica A 207 (1994) 197.
[7] D.J. Bergman and D. Stroud, Physical properties of macroscopically inhomogeneous media. in: solid state physics, Vol. 46, (Academic Press, New York, 1992), p. 147; D.J. Bergman, Phys. Rev. B 39 (1989) 4598.
[8] C. Flytzanis, Prog. Opt. 29 (1992) 2539; D. Ricard. Ph. Roussignol and C. Flytzanis, Opt. Let. 10 (1985) 511; F. Hache, D. Ricard, C. Flytzanis and U. Kreibig, Appl. Phys. A 47 (1988) 347.
[9] K.W. Yu, Y.C. Wang, P.M. Hui and G.Q. Gu, Phys. Rev. B 47 (1993) 1782; K.W. Yu. P.M. Hui and D. Stroud, Phys. Rev. B 47 (1993) 14 150.
[10] J.E. Sipe and R.W. Boyd, Phys. Rev. B 46 (1992) 1614.
[11] P.M. Hui and D. Stroud, Phys. Rev B 49 (1994) 11 729.
[12] K.W. Yu, Phys. Rev. B 49 (1994) 9989.
[13] D. Stroud and X. Zhang, Physica A 207 (1994) 55; X. Zhang and D. Stroud, Phys. Rev. B 49 (1994) 944.
[14] P.M. Hui, Phys. Rev. B 49 (1994) 15 344; K.W. Yu, Y.C. Chu and Eliza M.Y. Chan, Phys. Rev. B 50 (1994) 7984.
[15] O. Levy, D.J. Bergman and D.G. Stroud Phys. Rev. E 52 (1995) 3184; D. Bergman, O. Levy and D. Stroud, Phys. Rev. B 49 (1994) 129; O. Levy and D. Bergman, Physica A 207 (1994) 157.
[16] D.P. Tsai, J. Kovacs, Z. Wang, M. Moskovits, V.M. Shalaev, J. Suh and R. Botet, Phys. Rev. Lett. 72 (1994) 4149; V.M. Shalaev and M. Moskovits, Phys. Rev. Lett. 75 (1995) 2451.
[17] V.A. Markel, L.S. Muratov, M.I. Stockman and T.F. George, Phys. Rev. B 43 (1991) 8183; M.I. Stockman, L.N. Pandey, L.S. Muratov and T.F. George, Phys. Rev. Lett. 72 (1994) 2486; M.I. Stockman, L.N. Pandey, L.S. Muratov and T.F. George, Phys. Rev. B 51 (1995) 185; M.I. Stockman, L.N. Pandey and T.F. George, Phys. Rev. B 53 (1996) 2183.
[18] R.W. Boyd, Nonlinear Optics (Academic Press, New York, 1992).
[19] V.M. Shalaev, R. Botet, J. Mercer and E.B. Stechel, Phys. Rev. B 54 (1996) 8235.
[20] E.M. Purcell and C.R. Pennypacker, Astrophys. J. 186 (1973) 705; B.T. Draine, Astrophys. J. 333 (1988) 848.
[21] R.K. Chang and T.E. Furtak eds. Surface Enhanced Raman Scattering (Plenum Press, New York, 1982).