Spectral Dependence of Selective Photomodification in Fractal Aggregates of Colloidal Particles

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Localization of optical excitations and selective photomodification are studied experimentally in fractal aggregates of silver colloidal nanoparticles. The localized optical excitations of the fractal colloids cover a broad spectral range, from the visible to the infrared. We show that the absorbed laser energy is localized in an increasingly smaller number of particles with increasing the laser wavelength from 355 to 1900 nm. The size of the photomodified regions can be as small as 20 nm. The observed modification is explained by optically induced sintering (coalescence) of colloidal nanoparticles. [S0031-9007(97)05209-5]

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Localization of vibrational and optical excitations in disordered media and, in particular, in fractal systems has been studied intensively (see, for example, [1–4]). Generally, the localization of dynamic excitations in fractal objects results from the fact that plane running waves are not eigenfunctions of the operator of dilatation symmetry.

Irradiation of metal nanocomposites by a laser pulse with energy above threshold leads to "photoburning" of dichroic holes in the absorption spectrum near the laser wavelength [5]. Selective photomodification of the geometrical structure and photoburning of spectral holes have been observed in silver and gold colloids, polymers doped with metal aggregates, and films produced by laser evaporation of a silver target [5,6]. This phenomenon originates from the localization of optical excitations in fractal structures that are prevalent in random nanocomposites. The localized optical modes of silver fractal aggregates were directly imaged by means of photon scanning tunneling microscopy [7]. The localization in fractals arises because of the scale-invariant distribution of highly polarizable particles (monomers). As a result, various small groups of particles having different local configurations interact with the light independently and resonate at different frequencies, as was first theoretically predicted in [8] and indirectly demonstrated in experiments [5]. The scaling theory of localized optical modes in fractals was developed in [2]. Optical eigenmodes formed by the interactions between monomers in fractals are localized in domains much smaller than both the optical wavelength and the cluster size, and their frequencies span a spectral range much broader than the monomer absorption bandwidth associated with the surface plasmon resonance [2–4]. Photomodification of resonance complexes of monomers that contribute to the absorption at a wavelength λ results in appearance of a hole in the absorption spectrum near λ [5,6].

In the present paper, we demonstrate experimentally that photomodification of Ag fractal aggregates occurs within domains as small as $24 \times 24 \times 48$ nm^3 that corresponds to localization of optical excitations on as few as two monomers. Spectral and electron microscope investigation of selective photomodification of Ag fractal colloids, as well as numerical simulations, confirm that the energy absorbed by the fractal medium is localized in a progressively smaller number of monomers as the laser wavelength increases from 355 to 1900 nm. Thus, one of the main theoretical conjectures, namely, that the localization, on average, becomes stronger toward the longer wavelengths [2,3] is experimentally verified.

In our experiments we used an optical parametric oscillator (Spectra-Physics MOPO 730), tunable from 440 up to 1900 nm, with a pulse duration ≈ 4 and 7 ns pulses of the third harmonic of Nd:YAG laser. A Cary-14 spectrophotometer and JEM-100 CX and Hitachi H-7000 transmission electron microscopes were used for sample characterization. For both spectrophotometric and electron microscopy studies, our samples were provided with spatial markers which allowed us to identify a given aggregate before and after laser irradiation. This is equivalent to carrying out the measurements *in situ* both in the spectrophotometer and in the electron microscope.

Aggregate samples were prepared from silver colloidal solutions. As well known, aggregation of colloidal particles results in fractal structures with fractal dimension $D \approx 1.8$ [9]. We obtained the same D for the colloidal aggregates used in our experiments. After aggregation, we added 1% by weight of gelatin to the solution, after which it was poured onto a glass substrate. The samples, dried for a week at room temperature, formed a gelatin film of thickness $l \approx 25$ μm doped with Ag fractal aggregates, consisting of several thousand monomers each. The size of the aggregates was $1-4$ μm, and the distances between their boundaries had the same value so that the aggregates were spatially separated. Thinner samples, $l \approx 1$ μm, were prepared by the spin-cover method. The average monomer diameter was 24 or 14 nm, depending on whether colloid preparation method [10] or [11] was used.

Figures 1(a) and 1(c) are electron micrographs of samples obtained by methods [10] and [11], respectively. Figures 1(b) and 1(d) show the corresponding aggregates after irradiation by laser pulses at two different wavelengths, where in each case the pulse energy per unit area exceeds the threshold value, W_{th}, that results in local photomodification of the aggregates.

Comparison of electron micrographs of the cluster before and after irradiation at $\lambda_L = 1079$ nm [Figs. 1(a) and 1(b), respectively] shows that the structure of the cluster as a whole remains the same after the irradiation, but monomers within small nm-sized domains change their size, shape, and local arrangement. The minimal number of monomers in the regions of modification is 2–3. Thus, a resonance domain at $\lambda_L = 1079$ nm can have a size as small as $\lambda_L/25$. Although there are fluctuations in both shape and size of the modified domains, Fig. 1(b) reveals that the "hot" zones associated with resonant excitations are highly localized, in accordance with the theoretical predictions [2,8]. Moreover, we found from analysis of the electron micrographs that the total number of monomers in the photomodified domains at $\lambda_L = 1079$ nm and $W/W_{th} = 1.5$ comprises only $\approx 10\%$ of the total number of monomers in the aggregate.

Theory [2] predicts that localization of optical excitations in a fractal aggregate becomes, on average, weaker toward shorter wavelengths, and at the resonance of an individual monomer (≈ 450 nm, for Ag monomers in gelatin) most of the collective excitations are delocalized.

Our experiments support this prediction: at $\lambda_L = 532$ nm, a larger fraction of monomers, $\approx 30\%$, are in the photomodified domains (not shown), and at the wavelength close to the monomer absorption peak, $\lambda_L = 450$ nm, about 70% of the monomers are modified after irradiation [see Figs. 1(c) and 1(d)]. Thus, the electron microscope studies clearly indicate that the number of monomers effectively interacting with light significantly decreases with λ_L, i.e., localization of the optical excitations in fractals becomes stronger.

We also performed spectroscopic studies of the spectral hole photoburning that are correlated with local changes in the structure of irradiated clusters. In Fig. 2(a), we show the absorption spectrum of a sample obtained from a colloid prepared by the method [10]. The long wavelength tail in the spectrum is due to the aggregation of colloidal particles into fractal clusters [3,4]; the spectrum is well described by theory [3]. Irradiation of the sample by sufficiently intense pump pulses at the wavelength λ_L results in formation of a persistent spectral hole in the absorption spectrum near λ_L for a probe field with the same polarization as the pump, as shown in Fig. 2(b) (two different λ_L were used). The holes appear because of the photomodification of those local monomer configurations in a fractal that resonate at λ_L. For a constant pulse duration, the spectral hole occurs when the laser pulse energy

FIG. 1. Electron micrographs of silver colloid aggregates before (a),(c) and after (b),(d) irradiation by laser pulses at $\lambda_L = 1079$ nm, $W = 11$ mJ/cm^2 (b), and $\lambda_L = 450$ nm, $W = 20$ mJ/cm^2 (d). The circles in (b) are an aid to the eye.
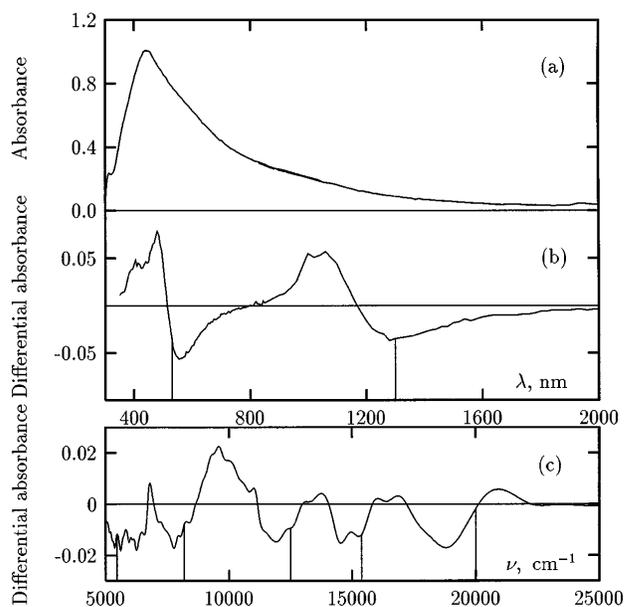
FIG. 2. (a) Absorption spectrum of silver aggregates in a gelatin film. (b) Difference in the absorbance of the silver-gelatin film before and after irradiation by pulses at $\lambda_L = 532$ nm, $W = 24$ mJ/cm^2 and at $\lambda_L = 1300$ nm, $W = 11$ mJ/cm^2. (c) An example of five spectral holes recorded at the same area and with laser pulses of the same linear polarization. The vertical bars denote laser frequencies. $W/W_{th} = 1.1-1.3$; the number of pulses increases from 5 in the visible to 30 in the IR range to obtain the holes of the same depth.

per unit area W exceeds a certain threshold value W_{th}. Our measurements showed that the maximum hole depth (that can be observed at $W/W_{th} = 10$) corresponds to $\Delta\alpha/\alpha_0 \approx 0.5$, where α_0 is the nonperturbed absorption coefficient and $\Delta\alpha$ is the change in the absorption coefficient due to the photomodification. The value of W_{th} strongly decreases with λ_L, e.g., $W_{th} = 28$ mJ/cm^2 at $\lambda_L = 355$ nm and $W_{th} = 7.1$ mJ/cm^2 at $\lambda_L = 1440$ nm.

The phenomenon of frequency-, polarization-, and space-selective photomodification is of interest not only because it provides the information concerning localization of optical excitations and restructuring of nanoparticles, but also because of its possible application to dense optical data recording. The possibility of recording several spectral holes on the same spot of a fractal film is demonstrated in Fig. 2(c). This suggests that by using different λ's and a laser beam focused on a spot of the size $\sim\lambda$, many bits of information corresponding to the different λ's and polarizations can be optically recorded inside λ-sized regions of a fractal sample at room temperature. In contrast with the focusing of energy in conventional optics, where the focal region scales in size with λ, the localization range is $\ll\lambda$ in this case, and decreases with λ. It is also noteworthy that the photoburning effect allows one to record data in analog form, since the hole depth increases with intensity. When the sample is heated to 175 °C, the spectral holes retain their principle features, although their shapes change. Thermal stability of the sample and polarization selectivity may be regarded as an advantage in comparison with the recording of narrower spectral holes at helium temperatures. In accordance with theoretical predictions [3,4], the widths of the spectral holes decrease from 3000 to 2000 cm^{-1} when λ_L changes from 500 to 1400 nm. The presence of spectral holes in the IR implies that broadening of the absorption spectrum of silver fractal clusters remains inhomogeneous, at least, up to 2000 nm.

As seen in Fig. 2, irradiation at a given pump wavelength λ_L also results in a region of increased absorbance shifted to shorter wavelengths with respect to the spectral hole. This can be explained by the fact that photomodification changes the geometrical structure of resonance groups of monomers so that the modified parts of a sample absorb the probe radiation at a wavelength different from λ_L. In the red and IR regions, typical resonance groups have an elongated form with a high aspect ratio; photomodification tends to decrease this aspect ratio, and, therefore, shifts the absorption peak of the modified groups toward shorter wavelengths. For example, sintering (see below) of two neighboring spherical monomers can transform them into a single almost spherical monomer with a larger radius [12].

Further insight concerning the interaction of metal fractal clusters with light can be obtained from the spectral dependence of the energy absorbed per unit volume, Q, in the layer where photomodification occurs. This series of experiments was performed at a laser pulse energy near

threshold (defined by the requirement of a fixed spectral hole depth, $\Delta\alpha/\alpha_0 = 10^{-2}$, after irradiation by 10 laser pulses). In this case, the spectral dependence of Q is given by $Q(\lambda_L) \approx \alpha_0(\lambda_L)W_{th}(\lambda_L)$. Figure 3 shows that Q significantly decreases as λ_L changes from 355 to 2000 nm.

To complement the experimental observations, we also performed numerical calculations for the fraction of most absorbing resonant monomers, n_r, contributing 50% to the total absorption. We assume that the resonant monomers contribute up to 50% to the total absorption, with the rest being due to nonresonant particles; this conclusion is supported by the fact that the depth of the largest spectral holes observed in our experiments is about half of the initial absorption. Since photomodification occurs in the most absorbing monomers, it is plausible to assume that $W_{th} \propto n_r$. To compare with the experimental data for $\alpha_0 W_{th}$, we plot results of our theoretical calculations for the product αn_r in Fig. 3 (solid line). In these calculations (similar to those in [3]), ten fractal aggregates of 1000 particles each were generated using the model of diffusion-limited cluster-cluster aggregation that results in aggregates simulating the experimental colloidal aggregates very well [9]. The quantities n_r and α were calculated by solving the coupled dipole equations (which couple the dipole moments of particles to each other and to the external wave via dipole fields) by the standard Jacobi diagonalization and using the known data for the optical constants of silver [3]. It was shown that the near-zone terms in the dipole radiation field play the prevailing role in fractal aggregates of colloidal particles with $D \approx 1.8$ [3,13]. This allowed us to use the quasistatic approximation in our calculations. The effect of higher multipole interactions was phenomenologically taken into account by introducing the effective particles with geometrical intersection of nearest neighbors as suggested in [3]. It was shown that this method provides satisfactory description of the optical properties of fractals [3].

As seen in Fig. 3, the theoretical calculations agree well with the experimental observations for almost all wavelengths (poor agreement near $\lambda \sim 400$ nm is probably due
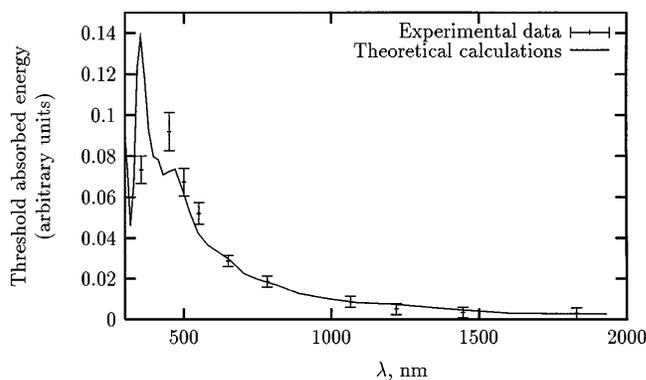
FIG. 3. Spectral dependence of the threshold absorbed energy per unit volume, $\alpha_0 W_{th}$ (see the text for details).

to the presence of nonaggregated particles in the sample). According to the results obtained, the absorption is almost equally distributed over all monomers in a cluster for λ close to the monomer absorption peak ~ 450 nm [cf. Fig. 1(d)]. However, it becomes progressively more localized as λ increases towards the infrared region, and only about 5% of monomers provide 50% of the total absorption for $\lambda \approx 2$ μm [cf. Fig. 1(b)]. [To extract these numbers from Fig. 3, we took into account the $\alpha(\lambda)$ dependence.] This means that at longer wavelengths there are small resonance domains in a fractal that account for a large fraction of the total absorption. Consequently, the threshold photomodification energy tends to decrease with λ. This can be interpreted as an effective "focusing" of the incident light in resonance domains whose sizes are much smaller than λ.

Below we briefly discuss a possible mechanism for the observed photomodification. We made an estimate of the laser heating of silver nanospheres in gelatin for an exponential pulse shape. We used the adiabatic approximation (i.e., the pulse duration was assumed to be much larger than all characteristic times of the system) and neglected the temperature dependence of all thermodynamic constants. From the thermal conductivity equation for an isolated spherical silver nanoparticle in gelatin, with the heat source homogeneously distributed inside the particle, we estimate the increase in the particle temperature as

$$T_p - T_0 \approx 3\sigma W \{4\pi R^3 c_1 \varrho_1 [1 + \sqrt{\Gamma t_p} (\sqrt{\Gamma t_p} + a)]\}^{-1},$$

where $a = \sqrt{3c_2\varrho_2/c_1\varrho_1}$, $\Gamma = \kappa_2/c_1\varrho_1 R^2$, c_1, c_2, and ϱ_1, ϱ_2 are the specific heats and mass densities of silver and gelatin, κ_2 is the thermal conductivity of gelatin, R is the radius of silver particles, σ is the absorption cross section per monomer, t_p is the pulse duration, and $T_0 = 300$ K is the initial temperature. With the known values of the thermodynamic constants, and the measured absorption cross section, the above formula yields $T_p \approx 600$ K at the threshold energy $W_{\text{th}} = 11.6$ mJ/cm^2 for $\lambda_L = 550$ nm.

According to [12], sintering of metal nanoparticles starts as early as the temperature exceeds half the melting point T_m (for Ag, $T_m \approx 1234$ K), and the characteristic time of this process is 100 ps. Thus, the above temperature T_p is sufficient to initiate sintering in silver colloids at the threshold pulse energy W_{th}. Note that enlargement of Ag nanoparticles by approximately a factor of 2 was also observed in island Ag films after thermal heating to 570 K [14].

In conclusion, the present study of the spectral dependence of selective photomodification of fractal colloidal aggregates shows that in accordance with theoretical predictions, the number of monomers strongly interacting with the incident light decreases substantially toward the IR. The localization of optical excitations in fractal clusters permits optical recording of data on nm scales.

[1] S. Alexander and R. Orbach, J. Phys. (Paris), Lett. **43**, L625 (1982); A. Petri and L. Pietronero, Phys. Rev. B **45**, 12 864 (1992); B. Sapoval, T. Gobron, and A. Margolina, Phys. Rev. Lett. **67**, 2974 (1991).

[2] V. A. Markel, L. S. Muratov, M. I. Stockman, and T. F. George, Phys. Rev. B **43**, 8183 (1991); M. I. Stockman, L. N. Pandey, and T. F. George, Phys. Rev. B **53**, 2183 (1996).

[3] V. A. Markel, V. M. Shalaev, E. B. Stechel, W. Kim, and R. L. Armstrong, Phys. Rev. B **53**, 2425 (1996).

[4] V. M. Shalaev, Phys. Rep. **272**, 61 (1996).

[5] A. V. Karpov et al., JETP Lett. **48**, 571 (1988).

[6] Y. E. Danilova, A. I. Plekhanov, and V. P. Safonov, Physica (Amsterdam) **185A**, 61 (1992).

[7] D. P. Tsai et al., Phys. Rev. Lett. **72**, 4149 (1994); V. M. Shalaev and M. Moskovits, Phys. Rev. Lett. **75**, 2451 (1995).

[8] V. M. Shalaev and M. I. Stockman, Sov. Phys. JETP **65**, 287 (1987); A. V. Butenko, V. M. Shalaev, and M. I. Stockman, Sov. Phys. JETP **67**, 60 (1988).

[9] D. Weitz and M. Oliveria, Phys. Rev. Lett. **52**, 1433 (1984); R. Jullien and R. Botet, Aggregation and Fractal Aggregates (World Scientific, Singapore, 1987).

[10] S. M. Heard, F. Griezer, C. G. Barrachough, and J. V. Sandera, J. Colloid Interface Sci. **93**, 545 (1983).

[11] P. C. Lee and D. Meisel, J. Phys. Chem. **86**, 3391 (1982).

[12] H. Zhu and R. S. Averback, Philos. Mag. Lett. **73**, 27 (1996).

[13] V. M. Shalaev, R. Botet, and R. Jullien, Phys. Rev. B **44**, 12 216 (1991).

[14] K. Baba, K. Yamaki, and M. Miyagi, in Chemistry and Physics of Small-Scale Structures, Technical Digest Series Vol. 2 (OSA, Santa Fe, New Mexico, 1997), pp. 52–54.