Observation of a wavelength- and polarization-selective photomodification of silver clusters

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It has been observed that a long-lived hole is burnt out of the absorption spectrum of fractal clusters of silver when they are illuminated by a laser pulse. The hole appears in the absorption spectrum of only that linear polarization which is the same as the polarization of the laser pulse. The observed effect is linked with a photomodification of the clusters as they locally absorb light of a given frequency and polarization.

Research on the interaction of fractal clusters (fractals) with electromagnetic radiation is becoming progressively more important since it is now becoming clear that these fractals have unique optical properties,[1–3] particularly nonlinear properties.[2,3] Fractals are aggregates with an asymptotically zero averge density which consist of particles (monomers) connected by bonds. In particular, some typical fractals with a Hausdorff dimensionality $D \approx 1.7$ are particles in clustered hydrosols of noble metals.[4] Rautian *et al.*[3] have observed a huge (10^6-fold) intensification of degenerate four-wave mixing during the aggregation of silver particles into clusters. Akimov *et al.*[5] have observed a 10^3-fold intensitifcation of the light at the second-harmonic frequency upon the formation of silver clusters. The results of Refs. 3 and 5 have attracted particular interest to research on this medium.

In the present letter we report the observation of a nonlinear laser photomodification of silver clusters which is selective in terms of the frequency and polarization of the light.

We studied three cluster media: 1) clustered silver hydrosols prepared by dissolv-

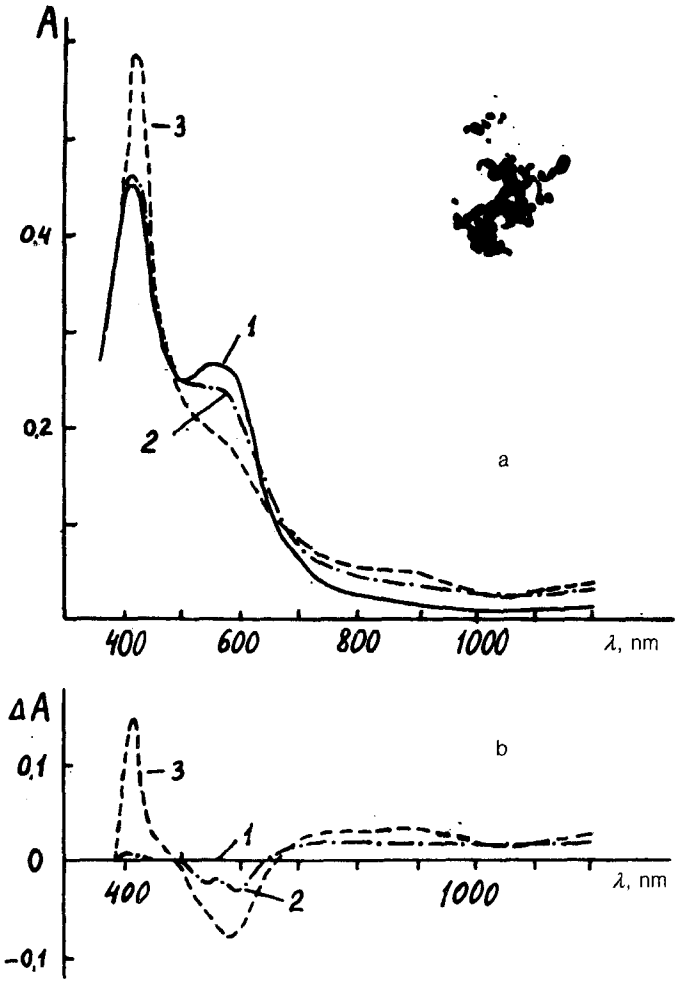

FIG. 1. Extinction spectra (a) and differential spectra (b) of illuminated (lines 2, 3) and unilluminated (1) silver hydrosols. 2—30 min after illumination at $\lambda = 532$ nm in a dose of 0.3 J/cm^3 ($W = 60$ mJ/cm^2); 3—15 h after an additional illumination at $\lambda = 532$ nm in a dose of 0.4 J/cm^3 ($W = 60$ mJ/cm^2) and at $\lambda = 1064$ nm in a dose of 5 J/cm^3 ($W = 0.3$ J·cm^2). The inset is an electron micrograph of a silver cluster.

ing a collargol sample and then adding NaOH (Ref. 3); 2) Ag clusters in gelatin; 3) Ag clusters in the gelatin layer of a photographic emulsion, prepared by the method of Ref. 5. According to electron micrographs, the hydrosol consists of clusters 0.1–1 μm in size, which are formed from monomers with a radius $R \approx 10$ nm (the inset in Fig. 1 shows a typical cluster). Comparing the number of monomers with the sizes of the clusters on the micrographs, we found an estimate of the fractal dimensionality: $D \approx 1.7$. The absorption spectrum of the Ag monomers which have not aggregated has a high-contrast peak at $\lambda \approx 400$ nm. The clusters are characterized by the appearance of a broad absorption band in the visible and near-IR regions. The spectra were re-

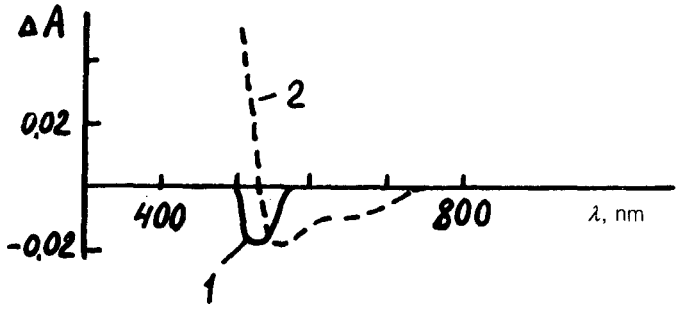

FIG. 2. Differential extinction spectra of a photographic emulsion illuminated with a single pulse ($\lambda = 532$ nm, $t = 10$ ns, $W = 20$ mJ/cm^2) and of an emulsion which has not been illuminated. 1—5 min after illumination; 2—3 h after illumination.

corded on an SF-20 or SF-26 spectrophotometer with a cell 10 mm long.

The clusters were illuminated with the beams from Nd:YAG and Nd:$YAlO_3$ lasers, second-harmonic pulses ($\lambda = 532$ and 540 nm), and pulses of stimulated Raman scattering in acetone ($\lambda = 641$ nm). We used Q-switched pulses ($t \approx 10$ ns, ultrashort pulses ($t = 30$ ps), and quasi-cw beams ($t = 0.1$ ms).

It was found that when the clusters are illuminated with pulses which interact with their long-wave absorption band, holes appear near the laser wavelengths in the absorption spectrum (Figs. 1–3). The width and shape of a hole depend on the method by which the clusters are prepared, the nature of the buffer medium, and the time interval between the illumination and the recording of the spectrum. The extinction spectrum of the illuminated hydrosols in Fig. 1 also reveals an increase in the absorption on the short- and long-wave sides of the hole. The width of the hole (3500 cm^{-1}) is approximately the same as the width of the absorption line of the monomers in the unaggregated hydrosl (5000 cm^{-1}) (Ref. 3). It constitutes only a small fraction of the absorption band of the clusters (20 000 cm^{-1}). The narrowest holes (1800 cm^{-1}) are detected in the spectrum of the clusters in a PÉ-1 holographic emulsion (line 1 in Fig. 2). As time elapses (on the order of an hour) after the illumination, however, the hole shifts toward a longer wavelength and becomes broader; the absorption on the short-wave side increases (line 2). Similar relaxation processes occur in the hydrosols. The measurements revealed that in a liquid they occur in a time on the order of 1 min. The minimum of the hole in Fig. 1b is therefore shifted in the long-wave direction from $\lambda = 532$ nm.

Holes which were stable—for at least a month—in the absorption spectrum were observed in the case of the clusters fixed in gelatin (Fig. 3). The pronounced slowing of the relaxation can be explained on the basis that the mobility of the particles is lower than that in a liquid and that the silver concentration is lower (by factor of 10^3) than that in the emulsion. The depth and width of the hole increase with increasing number of illuminating pulses and with increasing pulse energy.

It is important to note that a hole appears only in the absorption spectrum of the

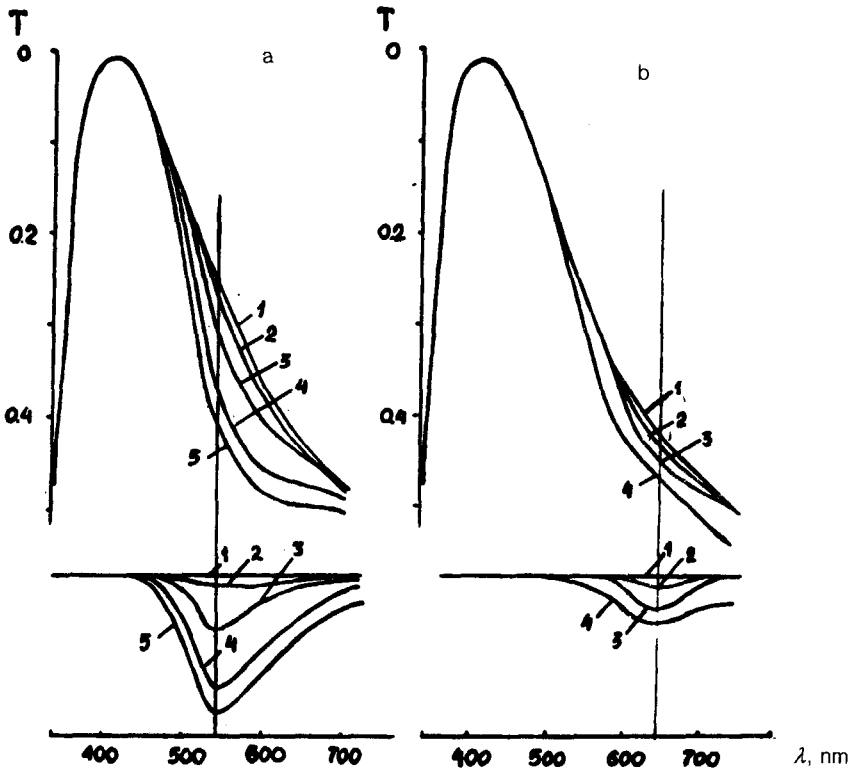

FIG. 3. Transmission spectrum (top) and differential spectrum (bottom) of silver clusters in gelatin which have and have not (lines 1) been illuminated with picosecond light pulses. a) $\lambda = 540$ nm. 2, 3, 4, 5—1, 20, 80, and 230 pulses with $W = 1.5$ mJ/cm^2. b) $\lambda = 641$ nm. 2, 3,—20 and 120 pulses with $W = 2$ mJ/cm^2; 4—with $W = 8$ mJ/cm^2.

same linear polarization as that of the laser pulse. There is no hole in the absorption spectrum of the orthogonal polarization.

Hole burning requires a threshold value of the pulse energy (or is a highly nonlinear function of this energy). In the hydrosol (Fig. 1), at $t = 10$ ns, a hole is observed at $\lambda = 532$ nm at an energy density $W \gtrsim 10$ mJ/cm^2. In the picosecond regime, the threshold energy is lower by a factor of several units than in the nanosecond regime, and at $t = 0.1$ ms and $W = 0.1$ J/cm^2 no hole burning is detected.

We attribute the observed changes in the spectrum to a frequency-selective photomodification of fractal clusters of silver. Different local configurations of monomers which have moved close to each other in a fractal absorb light at different wavelengths.[1] The long-wave absorption band of a cluster results from local anisotropic density fluctuations with a long axis running parallel to the electric vector of the light wave. These local configurations are burnt out by the light.

According to estimates, each "resonant" monomer of a cluster at $W = 1.5$ mJ/cm^2 and at a monomer concentration of 10^{12} cm^{-3} absorbs about 3×10^5 photons in

one pulse. This number corresponds to the energy required to evaporate a silver particle with $R = 10$ nm. With $t = 30$ ps, the size of the energy localization region, $d \sim \sqrt{t}$, corresponds to a single monomer, while with $t = 10$ ns it spans several monomers. These results explain the large value of the threshold energy and the partial loss of the frequency and polarization selectivity with increasing pulse length which is seen experimentally.

In the experiments we studied the time evolution of the degenerate four-wave mixing with Ag clusters. We used picosecond pulses, applying the readout pulse after a delay. It was found that in addition to the instantaneous response, due to the electron nonlinearity, there is also a scattering by a lattice which appears because of the photomodification of the clusters. This scattering occurs if the pulse energy is above a threshold. The measured rise time of this photomodification is 100 ps.

In summary, it has been established experimentally that the broadening of the absorption line of fractals is a nonuniform process. The width of the burnt-out hole is approximately the same as the width of the absorption line of the monomers. The polarization effect points unambiguously toward an anisotropy of the broadening of the spectrum of clusters and thus a local nature of the modification. These properties agree qualitatively with the theory of Ref. 1. Nonequilibrium structures in the spectrum and thus in the structure of the clusters undergo relaxation over times ranging from several minutes (in a liquid) to several months (in gels).

The frequency-selective photomodification of clusters is interesting from the standpoint of increasing the density of optical data storage. The photomodifcation of the clusters occurs at room temperature and exhibits a polarization selectivity, although the widths of the holes are considerably greater than in Ref. 6.

[1]V. M. Shalaev and M. I. Shtokman, Zh. Eksp. Teor. Fiz. **92**, 509 (1987) [Sov. Phys. JETP **65**, 287 (1987)].
[2]A. V. Butenko, V. M. Shalaev, and M. I. Shtokman, Zh. Eksp. Teor. Fiz. **94**, 109 (1988) (Sic).
[3]S. G. Rautian, V. P. Safonov, P. A. Chubakov *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 200 (1988) [JETP Lett. **47**, 243 (1988)]; Preprint No. 466F, Siberian Branch, Academy of Sciences of the USSR, Krasnoyarsk, 1987.
[4]D. A. Weitz and M. Oliveria, Phys. Rev. Lett. **52**, 1433 (1984).
[5]I. A. Akimov, A. V. Baranov, V. M. Dubkov *et al.*, Opt. Spektrosk. **63**, 1276 (1988) [Opt. Spectrosc. (USSR) **63**, 756 (1987)].
[6]R. A. Avarmaa and K. K. Rebane, Usp. Fiz. Nauk **154**, 433 (1988) [Sov. Phys. Usp. **31**, 225 (1988)].

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