Photostimulated aggregation of ultradispersoidal silver particles into fractal clusters

V V Slabko†, S V Karpov†, V I Zaitsev†, Guo Zhenhua†§, A K Popov‡∥,
Li Zaiguang‡, Lu Dongsheng‡, Fan Yongchang‡ and An Chengwu‡

† Institute of Physics, Russian Academy of Sciences, and Krasnoyarsk University,
Krasnoyarsk University, Krasnoyarsk 660036, Russia
‡ National Laboratory of Laser Technology, Huazhong University of Science and Technology,
Wuhan, Hubei 430074, People's Republic of China

Abstract. In this paper, studies of the photostimulated aggregation of ultradispersoidal silver particles into fractal clusters observed in colloidal solutions irradiated by different types of pulsed and continuous-wave lasers and by non-monochromatic light are described. A photoaggregation mechanism is suggested, on the basis of mutual opposite charging of different-sized particles due to the equalization of their size-dependent Fermi energies in a conducting medium.

1. Introduction

Clusters play an important role in physical chemistry, and material and surface sciences. A comprehensive study (Cohen and Knight 1990) is available of the main physical properties of simple clusters, whereas fractal clusters (fractals) have been much less studied but are attracting increasing attention.

Fractals are aggregates of monomers with an asymptotically zero density of monomers (Butenko *et al* 1990). The number of monomers in a fractal cluster of radius R grows as $N \sim R^D$. D is the most important physical fractal (Hausdorff) parameter, which is a non-integer and smaller than the dimensionality d of space ($d = 3$ for a volume, and $d = 2$ for a surface). For example, clusters in aggregated hydrosols of noble metals are typical fractals with $D = 1.7$.

A theory of optical properties of fractal clusters has been given by Shalaev and Stockman (1987, 1988) and Butenko *et al* (1988a, b). As is known, the absorption spectra of isolated metallic balls (monomers) having a size of the order of 10 nm are determined by the presence of a surface plasma resonance with a FWHM of about 100 nm (Heard *et al* 1983, Butenko *et al* 1990). For silver hydrosols, this resonance occurs in the vicinity of 400 nm. Aggregation of monomers into fractal clusters results in an inhomogeneous spectral broadening covering the entire visible and part of the IR ranges. The frequency shift of eigenresonances in monomers is caused by the dipole–dipole interaction of light-induced oscillating dipole moments of each monomer with its nearest environment. The fractal cluster apparently contains a statistical set of configurations of interacting monomers, differing in the position

§ On leave from the National Laboratory of Laser Technology, Huazhong University of Science and Technology, Wuhan, Hubei 430074, People's Republic of China.

∥ On leave from the Institute of Physics, Russian Academy of Sciences and Krasnoyarsk University, Krasnoyarsk 660036, Russia.

of interacting particles with respect to each other. The larger the size of a cluster, the greater is the variety of environmental realizations and hence the more extended is the long-wavelength wing of the spectrum.

A conclusion about the inhomogeneous nature of the absorption spectrum of fractal clusters has been experimentally proved in our previous work (Karpov *et al* 1988), where we report the observation of the effect of photomodification of clusters. The effect was observed in the form of dichroic dips appearing in the absorption spectrum of weak probe radiation absorbed by fractals near the wavelength range of strong laser radiation used to pre-irradiate the cluster medium. This effect is due to evaporation of resonant monomers in the fractal.

However, when irradiated with $\lambda = 540$ nm laser pulses, the hydrosols with the incomplete aggregation process exhibited not only a spectral dip but also an enhanced absorption in the long-wavelength spectral wing. In terms of the above considerations, this effect can also be interpreted as a simultaneous observation of the effect of photomodification and of photostimulated aggregation of free monomers into fractal clusters, resulting in further complication of their structure.

The objective of this paper is to study the effect of photostimulated aggregation of metal clusters and to show the potential feasibilities of using optical radiation to control the rate of aggregation and properties of silver fractal clusters. Both the experimental evidence and the first theoretical interpretation of the phenomenon of photostimulated aggregation are presented. Experimental data important for the further development of the theory are obtained.

The problems addressed here apply to colloidal chemistry as well. Thus the mechanisms of photostimulated aggregation considered in this paper can occur in any processes, leading to light-induced coagulation of monomers. In particular, they can account for coagulation of colloidal particles irradiated by UV and x-ray radiation, as discussed by Voyutsky (1976). The indicated processes can result in the formation of not only fractal structures but also dense colloidal structures.

2. Experimental details

The purpose of the experiments was to study the process of photostimulated growth of fractal clusters in silver hydrosols, and to propose, analyse and verify the possible mechanisms of the phenomenon.

According to electron micrographs, the hydrosol under study consists of fractal clusters about 0.1–1 μm in size, each of them consisting of monomers 3–20 nm in size (see, e.g., figure 2 in the paper by Butenko *et al* (1990)). As has been mentioned, the absorption spectrum of non-aggregated monomers of Ag takes the shape of a pronounced peak at $\lambda_1 = 400$ nm. The appearance of a broad absorption band in the visible and near-IR ranges is an indication of the process of aggregation into clusters. The spectra were recorded with a spectrometer, the cell length being 2 mm.

A non-aggregated hydrosol can be prepared by numerous techniques, one of which is to use a preparation called Collargol (Butenko *et al* 1990). The experimental curves shown in figures 1 and 2 were obtained with identical samples of this type of hydrosol. Colloids prepared by two other techniques (Creighton *et al* 1979, Heard *et al* 1983) exhibited similar qualitative dependences.
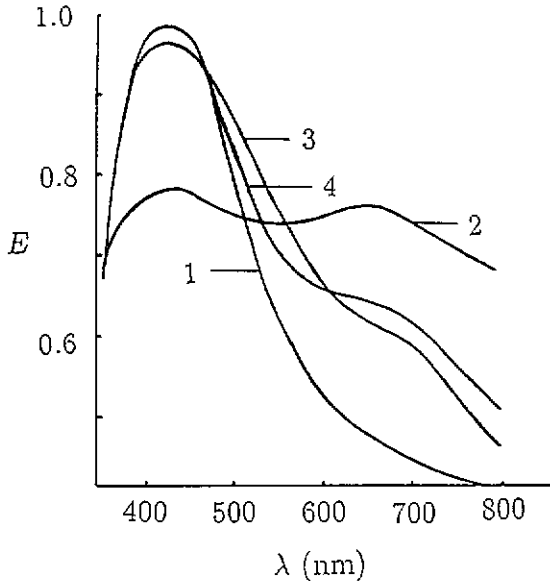
Figure 1. Absorption spectra of silver hydrosols: curve 1, isolated monomers; curve 2, developed aggregation of monomers; curves 3 and 4, changes in the absorption spectrum of a silver hydrosol with incomplete aggregation process (curve 3, before irradiation; curve 4, after irradiation) showing the coexistence of the two effects photomodification and photoaggregation. The changes are due to a single pulse of YAlO$_3$:Nd laser: $\lambda = 540$ nm; $\tau = 30$ ps; $J = 3$ mJ cm^{-2}.

2.1. Pulsed-laser experiments

As has already been mentioned in this paper, investigation of the effect of photoaggregation was encouraged by the experimental results on illumination of silver hydrosols with incomplete aggregation. Second-harmonic single pulses ($\tau \simeq 30$ ps) of a YAlO$_3$:Nd laser were used in the experiments in the approximate intensity range $(0.3-1) \times 10^{10}$ W cm^{-2}. Figure 1 shows the absorption spectra of the irradiated and unirradiated medium. From the figure, one can see a characteristic difference between the spectra: the increase in absorption in the long-wavelength wing of the spectrum and simultaneous formation of a spectral dip. It is important to emphasize that the solution changes its colour instantly after each pulse action. However, visual observation of the dynamics of the process appears impossible, since it apparently develops within fractions of a second.

Hydrosols irradiated by first-harmonic radiation ($\lambda = 1.08$ μm) did not show any spectral changes.

Spectral changes typical of the process of aggregation were also observed in weak aggregated hydrosols irradiated with ruby laser pulses ($\lambda = 694$ nm) with a pulse duration $\tau \simeq 50$ ns and an intensity of about 10^8 W cm^{-2}.

Of particular interest were the experimental results obtained for silver hydrosols at the initial stage of aggregation irradiated by an excimer laser, because its wavelength lies outside the inhomogeneous wing of the absorption spectrum of clusters and thus cannot induce their selective photomodification.

The excimer laser parameters were as follows: single pulse energy, 115 mJ; irradiation energy density, 115 mJ cm^{-2}; wavelength, 308 nm; pulse duration, about 50 ns; variable repetition rate.
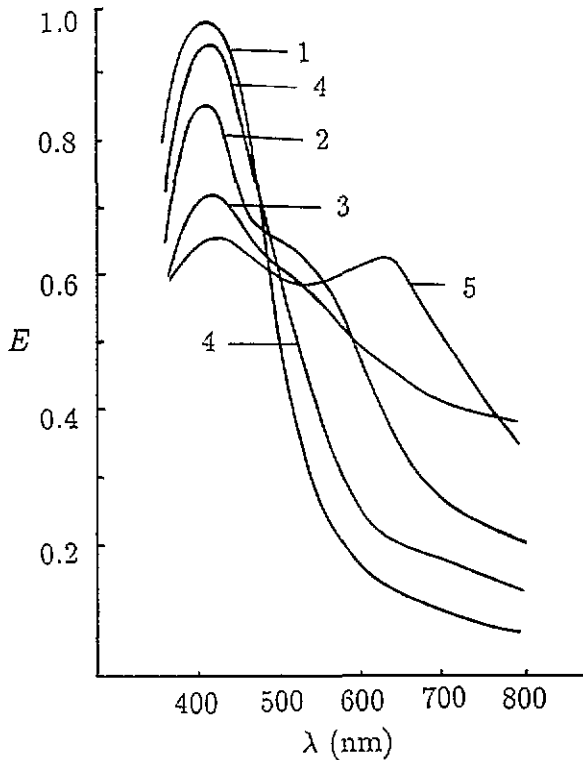
Figure 2. Changes in the absorption spectra of silver hydrosols (based on Collargol) irradiated with a series of 200 excimer XeCl laser pulses ($\lambda = 308$ nm): curve 1, before irradiation; curve 2, after irradiation, $J = 50$ mJ cm^{-2}; curve 3, after irradiation, $J = 90$ mJ cm^{-2}; curve 4, after irradiation with Ar-ion laser ($\lambda = 514.5$ nm), $I = 50$ mW cm^{-2} and a time of exposure of 2 h; curve 5, after direct exposure to solar radiation for about 20 h.

Figure 2 illustrates the changes in extinction spectra of the hydrosols, exhibiting an increase in absorption in the long-wavelength range. The spectral changes are shown for different modes of irradiation. The experiments show that the long-wavelength wing keeps increasing with both increasing pulse energy density (see curves 2 and 3 in figure 2, corresponding to $J = 50$ mJ cm^{-2} (curve 2) and 90 mJ cm^{-2} (curve 3)) and increasing number of pulses. Curve 1 corresponds to the spectrum of the unirradiated medium. It should be noted that, in all the experiments, the absorption increase in the long-wavelength spectral range is accompanied by a decrease in absorption in the region of the main resonance, which is associated with the reduced fraction of free monomers. A further increase in exposure may result in sedimentation of the dispersive material due to formation of giant clusters (larger than 1 μm) or in its deposition on the vessel's walls. This is accompanied by an increase in the total transparency of the solution.

2.2. Experiments with an argon ion laser

The parameters of the laser are as follows: wavelength, 5145 Å; power density, 200 mW cm^{-2}. Two freshly prepared samples were used.

(a) *Sample 1.* After a 7 min exposure to argon ion laser light, the sample showed no changes, nor during the next 2 h, as if it had not been irradiated at all.

(b) *Sample 2*. A 14 min exposure to 200 mW cm^{-2} laser light induced no changes into the sample; no changes were observed for the next 2 h either. Curve 4 in figure 2 shows the spectral changes under irradiation with an exposure time of 2 h ($\lambda = 5145$ Å; $I = 50$ mW cm^{-2}).

We should note that increases in power density and time of exposure (up to about a few hours) again resulted in stimulated aggregation.

2.3. *Experiments with non-monochromatic light*

As mentioned above, the exposure of non-aggregated solution to daylight reduced the time of aggregation to 2 or 3 h.

To obtain quantitative results, the following experiments were carried out. Two cells with non-aggregated hydrosol prepared from Collargol were irradiated with light of intensity 7.5 mW cm^{-2} and band width about 2000 cm^{-1} at $\lambda_1 = 370$ nm and $\lambda_2 = 410$ nm, both filtered from a mercury lamp light. For radiation at λ_1 and λ_2 the aggregation times were 5 h and 7 h, respectively. During the first 4 h the spectra of both solutions did not change. After that time, in the solution irradiated with $\lambda_1 = 370$ nm light, aggregation was completed within 1 h. In the second solution irradiated with $\lambda_2 = 410$ nm light, this process took about 3 h.

The experiment has revealed the following characteristic behaviour of aggregation. First, aggregation starts only after continuous light irradiation for a few hours. Second, the rate of aggregation depends on both the intensity and the wavelength of the irradiating light. The highest rate of aggregation is observed when using radiation in the wavelength range from 370 to 450 nm. No photostimulated aggregation was observed in hydrosols irradiated by IR light. This leads us to suggest the existence of a red threshold.

3. Discussion

We believe that photostimulated aggregation of metal particles in water solution can be explained as follows. Because the Fermi energy is dependent on the radius of a particle (Schmidt-Ott *et al* 1980, Nagaev 1983, Grigorieva *et al* 1986), particles with different radii, when immersed into an electrically conducting medium, exchange electrons to balance their electrochemical potentials. The acquired opposite charges generate electrostatic forces, which cause aggregation of monomers. Owing to photoemission of electrons, light increases the rate of electron exchange and recharging, the magnitude of electrostatic forces and consequently the rate of aggregation.

This hypothesis is supported experimentally.

(a) Let us first consider the red threshold of photostimulated aggregation. A threshold wavelength can be estimated from the equation

$$\hbar\omega_{th} - \varphi = 0 \tag{1}$$

where ω_{th} is the threshold frequency and $\varphi = \varphi_F - \varphi_W - \varphi_d$ (φ_F is the Fermi energy of the monomers, φ_W is the affinity energy of electrons for water molecules and φ_d is the energy of the electrical double layer (Voyutsky 1976). In our case, this layer is formed in particular because the electric charges of electrolyte ions are adsorbed by the monomer surface. The

Fermi energy depends on the radius R of a monomer. The variable part of energy can be roughly described as (Nagaev 1983, Grigorieva *et al* 1986)

$$\delta\varphi_F = 5.4/R \tag{2}$$

where $\delta\varphi_F$ is given in electron volts and R in Ångströms. The experimental values of φ_F for $R = 30$, 27 and 20 Å can be found in the work of Schmidt-Ott *et al* (1980). In our case, $\varphi_F = 4.5$ eV for $R \geqslant 30$ Å. The value of φ_W is 0.9 eV (Kikoin 1970). The value of φ_d is not exactly known and can range from a few electronvolts to a few hundredths of an electronvolt (Voyutsky 1976).

(b) We measured the photocurrent directly with the use of an electrical bridge circuit in order to exclude the electrolytic component contribution. Sedimentation occurred on both electrodes, being more abundant on the negative electrode.

(c) For a volume fraction of silver of the order of 10^{-6}, the mean distance $\bar{r}$ between monomers was estimated to be 5×10^{-6} m and the energy $U(\bar{r})$ of the van der Waals interaction for $R \ll \bar{r}$ was (Barash 1988)

$$U(\bar{r}) = \tfrac{3}{4}(hc/\lambda_{ps})(R/\bar{r})^6 \tag{3}$$

which is much smaller than kT. Here λ_{ps} is the wavelength corresponding to the frequency of a surface plasmon.

(d) By applying the Fowler–Nordheim law for the quantum yield Y from small metallic particles

$$Y(\hbar\omega) = c(\hbar\omega - \varphi)^2 \tag{4}$$

and using data from Schmidt-Ott *et al* (1980) and Nagaev (1983), one can find that it takes fractions of a second for closely spaced monomers to recharge under the action of near-UV radiation with an intensity of about 7.5 mW cm^{-2}, whereas for mean distances $\bar{r}$, the time τ_d of diffusive electron exchange is

$$\tau_d = \bar{r}^2/6D \tag{5}$$

where D is the diffusion coefficient. We assume that the transport of charges is mainly caused by the diffusion of negative water ions, formed as a result of the capture of electrons by water molecules. Then $D = 10^{-9}$ m^2 s^{-1} (Kikoin 1970). For $\bar{r} = 5 \times 10^{-6}$ m we obtain

$$\tau_d = 0.43 \times 10^{-2} \text{ s.}$$

For the monomer radius $R = 15$ nm, the probability of charge transfer from one monomer to another at a distance $\bar{r}$ during the time τ_d is

$$W = R^2/\bar{r}^2 = 0.9 \times 10^{-5}. \tag{6}$$

So the characteristic time of diffusion transport of one electron from one monomer to another is

$$\tau' = \tau_d/W = 0.47 \times 10^3 \text{ s.} \tag{7}$$

The energy of electrostatic interaction between two oppositely charged monomers given by $E = q^2/4\pi\epsilon_0\epsilon\bar{r}$ exceeds kT when they exchange more than 27 electrons and the charge magnitude exceeds $q = 27e = 27 \times 1.6 \times 10^{-19}$ C. This requires as long as

$$\tau = 27\tau' = 1.27 \times 10^4 \text{ s} = 3.5 \text{ h}. \tag{8}$$

These rough estimates are in agreement with the experimental value of photoaggregation time $\tau = 7$–4 h in the field of weak non-monochromatic light.

One can easily find that two monomers with charges differing by about $27e$ approach each other faster than the above-estimated time. Taking into account the electrostatic force and the viscosity η of water of 1 mPa s, from the equation

$$m\ddot{r} = q^2/4\pi\epsilon_0\epsilon r^2 - 6\pi\eta R\dot{r} \tag{9}$$

one has $\tau_c = 10$ s. Therefore the longest time in the above-discussed time hierarchy is the diffusion time τ and it determines the basic dynamics of photoaggregation.

(e) The rate of photostimulated aggregation depends on both the rate of emission and recombination of photoelectrons and the difference in monomer charges. The limiting value of the charge allowing for recharging depends on the difference in the radii of monomers. For the adopted model, recharging will occur until the energies of the occupied upper state in positively and negatively charged monomers become equal. Therefore in the energy interval

$$\Delta\varphi_F = \varphi_{F1} - \varphi_{F2} = 5.4\,\Delta R/R_1 R_2 \tag{10}$$

the number of states will be $N = \Delta\varphi_F\,\nu(\varphi_F) > 27$, where

$$\nu(\varphi_F) = (2/3\pi)\varphi_F^{1/2}/\varphi_0^{3/2} \tag{11}$$

is the density of electronic states near the Fermi energy (Hasche *et al* 1990). Here $\varphi_0 = \hbar^2/2mR$, where m is the electron mass. This allows one to estimate the minimum value of ΔR for which the charge difference between two interacting monomers is $27e$, which corresponds to $E(\bar{r}) = kT$. At $\Delta\varphi \simeq 4.5$ eV, $R = 30$ Å, $\nu(f) = 2 \times 10^3$ eV^{-1} and $\Delta R \simeq 2.5$ Å.

Thus we may suggest that the process of opposite charging induced by light may be the reason for the aggregation of monomers with the diameters differing by about 7% or more. Another important conclusion is that with increasing intensity and frequency of radiation the aggregation time is limited by the value of τ_d, which can be about a few milliseconds.

Acknowledgments

References

Barash Yu S 1988 *Van der Waals Forces* (Moscow: Nauka) (in Russian)

Butenko A V, Shalaev V M and Stockman M I 1988a *Z. Phys.* D **10** 91–2

—— 1988b *Zh. Eksp. Teor. Fiz.* **94** 109 (Engl. Transl. 1988 *Sov. Phys.–JETP* **67** 60)

Butenko A V, Chubakov P A, Danilova Yu Ye, Karpov S V, Popov A K, Rautian S G, Safonov V P, Slabko V V, Shalaev V M and Stockman M I 1990 *Z. Phys.* D **17** 283–9

Cohen M I and Knight W D 1990 *Phys. Today* December 42–50

Creighton J A, Blatchford C G and Albrecht M G 1979 *J. Chem. Soc., Faraday Trans.* II **75** 790

Grigorieva L K, Lidorenko N S and Nagaev E L 1986 *Zh. Eksp. Teor. Fiz.* **91** 1050–61

Hasche F, Ricard D and Flytzanis C 1990 *J. Opt. Soc. Am.* B **3** 1647–55

Heard S M, Griezer F, Barrachough C G and Sanders J V 1983 *J. Colloid Interface Sci.* **93** 545

Karpov S V, Popov A K, Rautian S G, Safonov V P, Slabko V V, Shalaev V M and Stockman M I 1988 *Pis. Zh. Eksp. Teor. Fiz.* **48** 5 (Engl. Transl. 1988 *JETP Lett.* **47** 243)

Nagaev E L 1983 *Sov. Phys.–Solid State* **25** 1439–47

Schmidt-Ott A, Schurtenberger P and Siegman H C 1980 *Phys. Rev. Lett.* **45** 528–31, 1284

Shalaev V M and Stockman M I 1987 *Zh. Eksp. Teor. Fiz.* **92** 509 (Engl. Transl. 1987 (*Sov. Phys.–JETP* **65** 287)

—— 1988 *Z. Phys.* D **10** 71–8

Kikoin I K (ed) 1970 *Tables of Physical Values* (Moscow: Atomizdat) (in Russian)

Voyutsky S S 1976 *The Course of Colloid Chemistry* (Moscow: Khimiya) (in Russian)