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Mass Transfer Over the Surface of Metal Nanostructures Initiated and Stopped by Illumination

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1. Introduction

Metal nanostructures play an increasing role in modern technologies. Being far from the thermodynamic equilibrium they are vulnerable to the influence of external agents. In particular, thermal stability of metal nanostructure is an issue in many applications. In this contribution we are going to discuss one counterintuitive way of stabilization of metal nanostructure, namely, illumination. It is generally agreed that illumination will destroy nanostructure if do not leave it intact. Nevertheless, we found that in some circumstances illumination may lead to tiny restructuring of the nanostructure surface that improves its thermal stability. This restructuring is not readily observable after illumination but lead to a pronounce effect after annealing. Illuminated nanostructures acquire immunity to the heating and change their structure much more slowly than the nanostructures that were not illuminated in advance. Moreover, the final state of the illuminated nanostructures after annealing differs considerable from that of unilluminated one being much more similar to its initial state. Taking into account close connection between the structure and the optical properties of the plasmonic metal nanostructures it is not surprising that after annealing illuminated and non-illuminated regions may be differentiated by eye.

More traditionally, illumination may initiate structural changes of the metal nanostructures. In particular, reshaping of metal nanoparticles that support plasmon excitation was studied by optical means. Resonance enhancement of the transformation rate was observed in our experiments on the arrays of alkali metal nanoparticles.

On the other hand, illumination can initiate structural transformations of the organic molecules adsorbed on the surface of metal nanostructures. In our experiments silver nanoparti-

cles were prepared by vacuum evaporation on a sapphire substrate. Cyanine dye molecules were spread over the silver nanoparticle arrays by spin-coating technique. The samples were characterized by scanning electron microscopy and optical spectroscopy. A significant increase of the dye photoinduced transformation rate was observed. Simultaneously, an enhanced absorption and fluorescence were observed.

The extinction spectrum of the hybrid material was rationalized as a result of mutual interactions between the plasmon oscillations localized in the metal nanoparticles and resonance absorption and refraction of dye molecules. Plasmon resonances are shifted due to the anomalous refraction of dye molecules. Depending on the spectral position of the dye absorption band relative to the inhomogeneously broadened plasmon band this shift may lead to considerable clarification of the sample at particular wavelengths that was observed experimentally. On the other hand, the absorption of dye molecules is enhanced due to the incident field amplification in the near field of metal nanoparticles. Even when the dye absorption band overlaps with the tail of the plasmon band of silver nanoparticles, 3 to 5 times enhancement of the dye absorption was obtained. Besides that a nearly 4-fold increase of cyanine dyes fluorescence intensity in the presence of metal nanoparticles was observed.

The photoinduced transformations of the dye molecules situated in the near field of the metal nanoparticles were studied. The rate of the transformations on the surface of metal nanoparticles was found to increase as compared to that on the surface of a dielectric substrate.

2. Illumination as a control over the surface mass transfer

Mass transfer over the solid surfaces is of crucial importance in many technological processes like vacuum vapor deposition, heterogeneous catalysis and many others. For example, when the granular metal films are grown via Volmer-Weber growth mode the atoms evaporated from the source first impinge on the surface and then diffuse over it. A nucleus of a metallic phase is formed by several atoms met together after a long way through the surface made separately by each of them. Then, the nucleus grows incorporating new atoms that first diffuse over the substrate and then climb up the existing flat metal cluster to form a 3D nanoparticle. All these processes being random, the resultant nanostructure is highly irregular. Figure 1 plots the optical extinction spectrum of silver granular film grown on a sapphire substrate. The broad band with a maximum at 420 nm shown as curve 1 is due to the absorption by surface plasmons localized in the silver nanoparticles. The width of this band is so large because there are nanoparticles of different shapes in the film. In particular, the red tail of the plasmon band is due to the flat pancake-like nanoparticles. These shapes are metastable and transform into more round shapes when heated. The band shifts in this case to the blue as a whole.

Illumination provides a means of much more delicate action upon the particle. Being irradiated by ruby laser the granular film changes in such a way that its extinction spectrum acquire the form shown in Figure 1 by curve 2. The shape of the extinction spectrum evidenced the light initiated mass transfer process over the surface of metal nanoparticles.

Indeed, one can notice that the number of flat particles that contribute to the red absorption is reduced while the number of the more round particles that contribute to the yellow absorption is increased. Thus, laser illumination may be used to the fine tuning of the shape distribution of metal nanoparticle. This possibility may be employed to obtain the values of the plasmon dephasing times [1,2].

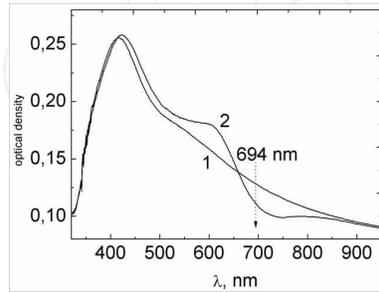


Figure 1. Light-induced mass transfer over the surface of silver nanoparticles. After illumination by three pulses of ruby laser with the fluence of 44 mJ/cm² the original extinction spectrum of the silver granular film on sapphire (1) transforms into (2). The observed changes in the extinction spectrum are due to the thermal diffusion of silver atoms over the surface of metal nanoparticles comprising the granular film.

The observed changes of the extinction spectrum are due to the contraction and reshaping of the nanoparticles in the course of the laser illumination. The sign variation of the optical density difference bears witness of an important role played by surface diffusion. Should evaporation be the sole consequence of the laser heating of the nanoparticles, one expects to observe only a dip centered at the laser frequency. Contrary to that, diffusion leads to the dip accompanied by a bump at a shorter wavelength, the laser frequency being in the mid-point between them. In reality both processes take place. A good fit to the experimental observations may be obtained with the formula that takes into account evaporation as well as diffusion. According to [3] the optical density difference ΔD is a function of the normalized laser detuning

$$x = \frac{\omega - \Omega}{\Gamma}, \quad (1)$$

where Ω is the laser frequency, ω is the frequency at which one observes the extinction difference and Γ is the dephasing rate of the plasmon resonance localized in the nanoparticles. This function reads as

$$\Delta D(x) = -A \frac{1}{1+x^2} + B \frac{x}{(1+x^2)^2}, \quad (2)$$

where A and B are the constants that define the relative contributions of the evaporation and diffusion processes, correspondently. Figure 2 plots the optical density difference ΔD ob-

tained experimentally as well as the theoretical curve computed according to Eqs. (1) and (2) with the following parameters $A=0.013$ and $B=0.36$. As B is much larger than A , one may conclude that it is the diffusion of silver atoms over the surface of silver nanoparticle that contributes most in the mechanism of the spectral hole burning while the contribution of evaporation is rather small.

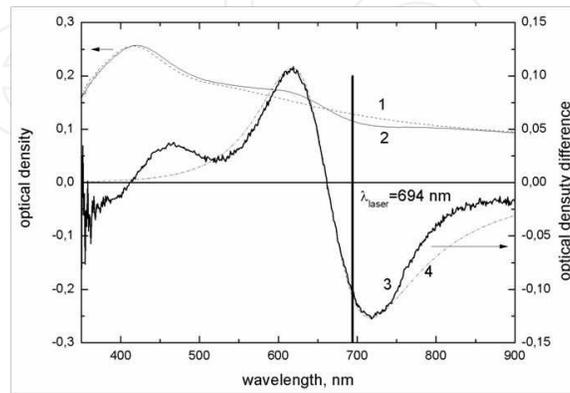


Figure 2. Optical density difference ΔD obtained experimentally (3) and the theoretical fit (4). Both curves are related to the right vertical axis. Two other curves related to the left vertical axis represent the optical density of the film before and after illumination.

To make a meaningful fit a slight shift of the laser frequency is required. As it was shown in [4], when the optical density of the film is considerable, as it is in our case, reflection is to be accounted for even though an individual particle absorb the light much stronger than scatter it. This additional contribution to the optical density of the film shifts the spectrum but does not affect the relative values of the diffusion and evaporation contributions.

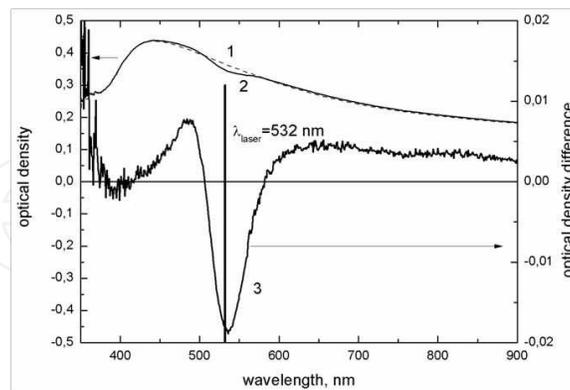


Figure 3. The original extinction spectrum of the silver granular film on sapphire (1) transforms into (2) after illumination by second harmonic of Nd:YAG laser. The optical density difference ΔD before and after illumination is given by curve (3). In this case contribution of the evaporation process is more pronounced than in the case of ruby laser illumination.

Figure 3 plots the hole burnt in the extinction spectrum of the silver granular film after illumination by the second harmonic of the Nd:YAG laser at 532 nm. Obviously, the dip follows

the laser frequency. On the other hand, relative contributions of the diffusion and evaporation processes in this case are different. Evaporation is much more evident in this case as compared with the case of ruby laser.

3. Initiation of the surface diffusion via a non-thermal laser action

Mass transfer described in the previous section was initiated by a crude force of a pulsed laser induced heating. More intriguing processes may be induced on the nanoparticle surface illuminated by cw lasers with low intensity. Heating is not operative in this case. Nevertheless, non thermal photo induced diffusion still causes the reshaping of metal nanoparticles. As the spectral position of the plasmon resonance is very sensitive to the particle shape, absorption spectroscopy may be employed to reveal this phenomenon. In the Figure 4 we present the results of the selective action of the low intensity cw diode laser on the ensemble of sodium nanoparticles on sapphire substrate. Due to the high reactivity of sodium this experiment was performed in a sealed glass cell with sapphire windows. Excitation of the surface plasmons localized in the sodium nanoparticles is responsible for the broad bell-shaped curve in the extinction spectrum. Illumination of the sodium granular film by a diode laser operating at the wavelength of 875 nm for 600 s with the power of 40mW produces tiny changes in the extinction spectrum. Although being small these changes are clearly visible in the differential spectrum also plotted in the Figure 4. Figure 5 and 6 plot the results of the similar experiments with lasers operating at the shorter wavelengths 852 nm and 810 nm. A striking feature of this experiments is that the laser action on the sodium nanoparticle shape is selective. Indeed, the zero crossing point of the differential spectrum is close to the laser wavelength and follows it as the laser wavelength changes. This may be clearly seen the Figure 7 where the position of the zero crossing point is plotted against the laser wavelength. At present we do not have a theoretical description of the spectral profile of the differential spectrum in this case. Nevertheless, one sees that general features are similar to the case of the heating induced reshaping. Non-thermally induced diffusion leads to the blue shift of the resonance frequencies of the plasmon resonances. Thus, the particles acquire more round shapes.

4. Inhibition of the surface diffusion by UV irradiation

Thin metal films on dielectric substrate are widely used in different applications ranging from microelectronics to heterogeneous catalysis. In most cases it is desirable that the structure preserves its properties for a long time. In particular, it is of practical importance to improve the thermal stability of the films. On the other hand, to reach such stability is not easy because the thin films are metastable. Thermal stability of the thin silver films is actively studied [5-7] because the agglomeration speeds up at the elevated temperature and leads to the undesirable changes in the film morphology as well as its chemical, electrical and optical properties.

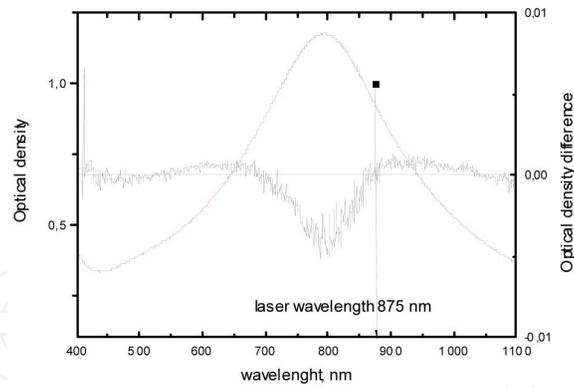


Figure 4. The broad bell-shaped curve represents the absorption band due to the surface plasmons localized in the sodium nanoparticles on the sapphire substrate. Tiny changes of the extinction spectrum after illumination for 600 s with 40mW cw diode laser at 875 nm are revealed by plotting the difference spectrum.

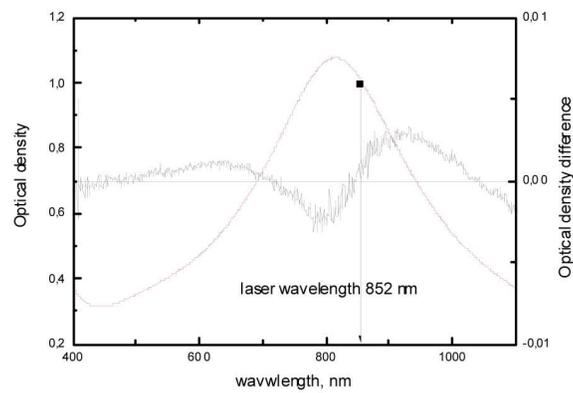


Figure 5. Same as Figure 4 with cw diode laser illumination at 852 nm.

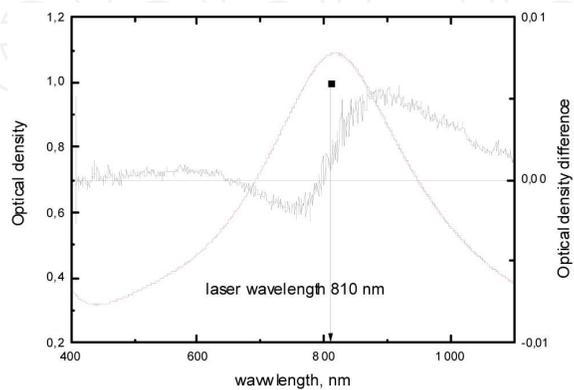


Figure 6. Same as Figure 4 with cw diode laser illumination at 810 nm.

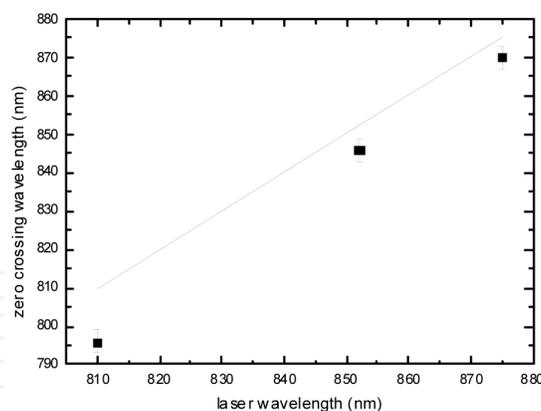


Figure 7. Selectivity of the laser action is made evident by the strong correlation between the position of the zero crossing point (squares) and laser wavelength. The straight light aids the eyes to see that this correspondence is not perfect.

Here we report on the new phenomenon of thin silver film stabilization under UV illumination. The illumination itself does not lead to any noticeable changes in the film appearance. At the same time, the illuminated films demonstrate enhanced stability against heating.

The films were obtained by thermal evaporation of silver on a sapphire substrate kept at the room temperature. The film prepared in vacuum was transferred into a glass cell with the sapphire windows. Then, the cell was evacuated and, finally, sealed off the vacuum system. UV radiation was produced by a mercury lamp. An optical filter was used to deliver radiation in the range from 300 to 400 nm. The intensity of UV illumination was set to 20 mW cm⁻². The duration of illumination was typically about 3 hours. To be on the safe side, only one half of the film was illuminated with the UV light. Another part of the film was used as a reference that undergoes just the same annealing procedures as the part, which was treated with the UV light.

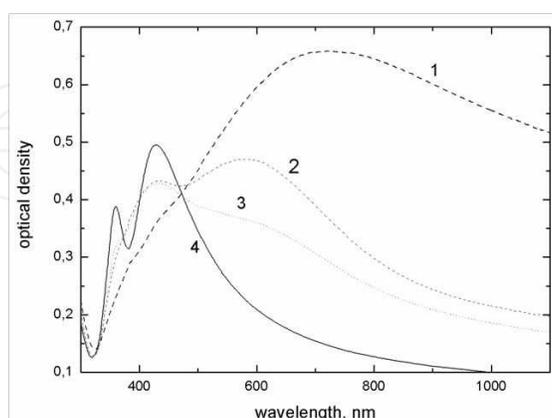


Figure 8. Extinction spectra of the thin silver films on sapphire: Extinction spectra of silver films on sapphire. Curve 1 was obtained after deposition and holding at room temperature for 3 hours. Curves 2 and 4 show the results obtained after annealing of the unirradiated film at 200°C for 5 and 30 minutes, respectively. Curve 3 shows the result obtained after annealing of the irradiated film at the same temperature for 30 minutes.

Figure 8 shows the results obtained in the course of annealing of the films. Just after the deposition the films undergo although very slight but noticeable changes. For this reason, the curve designated as 1 represents the extinction spectrum of the film that was held at room temperature for 3 hour. This time required for the film to come into its metastable state that may be preserved for many days. Illumination with the UV radiation does not lead to any changes of the extinction spectrum. Hence, curve 1 represents the extinction spectra of the irradiated as well unirradiated film. In the course of annealing at 200°C the unirradiated film passes through the states with the extinctions represented by curves 2 and 4. Curve 2 corresponds to annealing for 5 minutes and curve 4 corresponds to annealing for 30 minutes. Curve 3 corresponds to the annealing of the irradiated film for 30 minutes. Obviously, the annealing of the irradiated film proceeds much slowly than that of the unirradiated film. The final result of the annealing of the irradiated film is not so dramatic as that of unirradiated film.

These observations obtained via optical means were confirmed by scanning electron microscopy. Microphotographs are shown in Figure 9. After annealing of an unirradiated film its structure transforms into an array of well separated nearly spherical nanoparticles that may be seen in the image 4 of Figure 9. These changes are in accord with the blue shift and narrowing of the plasmon resonance represented by curve 4 in Figure 8. On the other hand, in image 3 of Figure 9 one finds much more in common with the image 1 of the initial film. This corresponds to the optical extinction spectrum 3 with a prolonged red tail resembling the red tail of the initial film 1.

It is to be mentioned that these results are representative in that sense that annealing at higher temperatures (up to 280°C) and for longer times (up to 3 hours) changes nor the morphology neither extinction spectra of the films.

Using of the UV light is essential for obtaining the described stabilization effect. We tried the irradiation at the wavelength of 440, 530 and 810 nm with the same intensity and duration of the irradiation and seen no effect of irradiation at this wavelengths on the films thermal stability.

5. Light induced transformations in the layers of organic molecules spread over the granular metal films

Cyanine dye molecules include a chain made of an odd number of methine groups bound together by alternating single and double bonds and two heteroaromatic rings at both ends of the chain. The structure of the cyanine dye molecules used in our experiments is shown in the Figure 10. Being adsorbed on the surface of a solid material, dye molecules form a layer with several preferable orientations of the long molecular axis relative to the surface normal. Heating and illumination are known to cause the reversible as well as irreversible mass transfer in the molecular layer that may be used for sensing and information recording applications [8,9]. It is tempting to study the possibility of enhancing these properties of the dye molecular layers by spreading them over the metal nanostructures. If the absorption

bands of the plasmon excitations in the metal nanostructure coincides or lies close to the absorption bands of the dye molecules one expects the mutual interaction between two resonances that may lead both to their enhancement as well as inhibition.

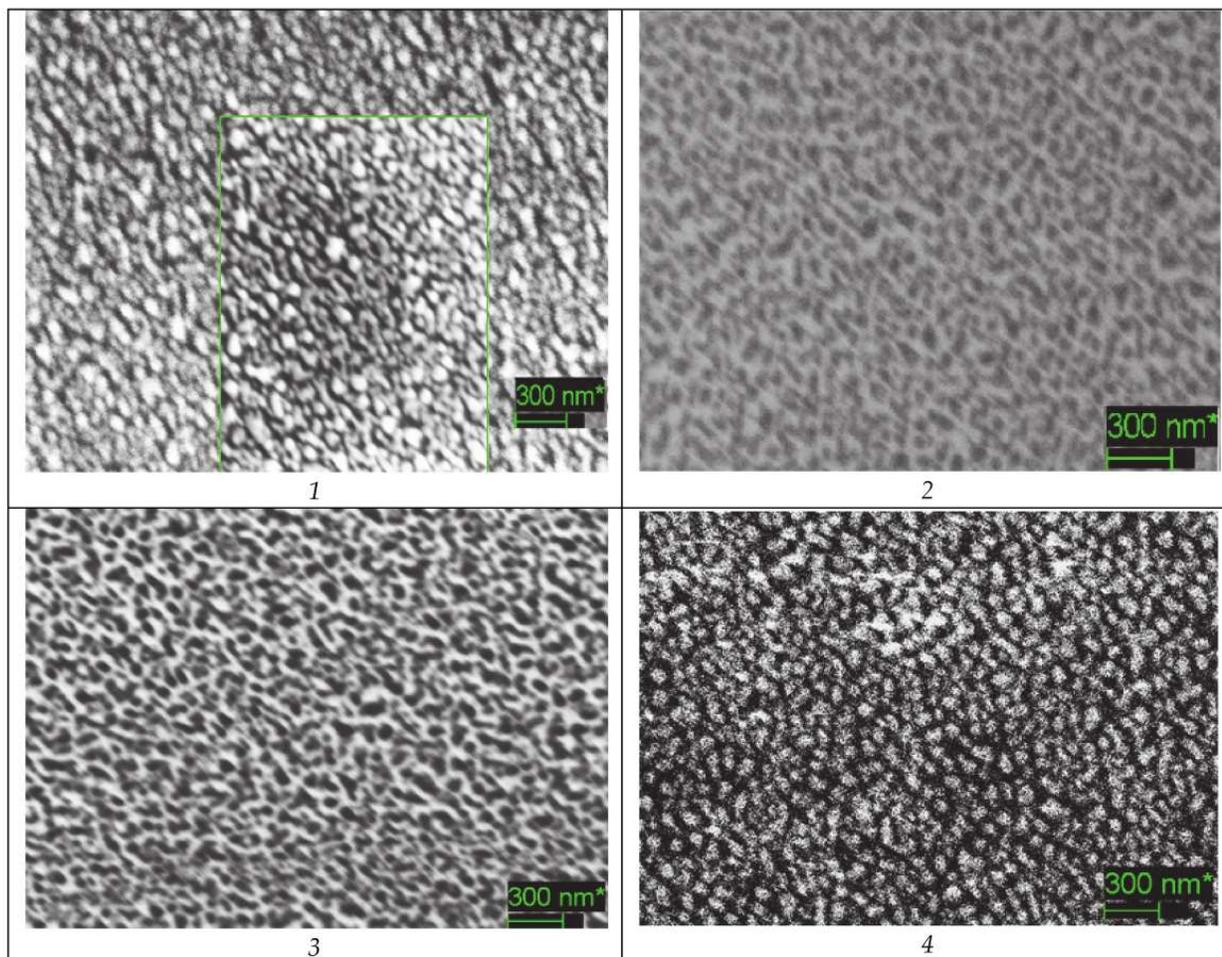


Figure 9. SEM images of silver films: Micrograph 1 represents the original unirradiated film. Micrographs 2 and 4 represent the results obtained after annealing of the unirradiated film at 200°C for 5 and 30 minutes, respectively. Micrograph 3 represents the result obtained after annealing of the irradiated film at the same temperature for 30 minutes.

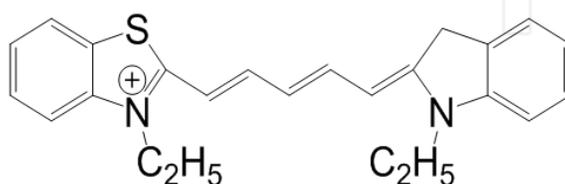


Figure 10. Structure of the cyanine dye molecule used in the experiments.

In our experiments silver nanoparticles were prepared by vacuum evaporation on a sapphire substrate. Cyanine dye molecules were spread over the silver nanoparticle arrays by

spin-coating technique. To achieve the homogeneity of the molecular layers the substrate spins with the rate of 4000 revolutions per minute. The dye layer thickness was set by the concentration of the solution used for spin coating. It was further checked by dissolution of the dye layer in the known quantity of solvent and determination of the dye concentration in it via optical means. The dye layer thickness in our experiments varied from 0.1 to 10 monolayers.

A special attention was paid to the stability of the granular metal film in the course of the dye deposition by spin coating technique. It was found that the as prepared granular metal film is not stable enough to ensure the reproducibility of the results. For this reason the granular metal films obtained via vacuum vapor deposition were suspended in ethanol overnight. After this treatment the optical density of the granular metal films reduces substantially due to the loss of the metal particles with low adhesion to the substrate. Those particles that remain on the surface after such treatment withstand many cycles of spin coating by dyes and subsequent rinsing in ethanol without noticeable changes in their morphology and optical properties.

Figure 11 plots the extinction spectrum of the dye molecular layer coated on the granular silver film on the sapphire substrate (curve 3). For comparison, extinction spectra of the dye molecular coated on the bare sapphire substrate (curve 1) and the granular silver film without dye (curve 2) are shown as well. The dye molecules contribution to the extinction of a hybrid material is revealed by the curve (4) that is the difference between (3) and (2). Clearly, the dye molecules absorbed much stronger when they are put in the vicinity of the silver nanoparticles as compared to the dye molecules on the bare sapphire substrate, the surface densities of the dye molecules being the same in both cases.

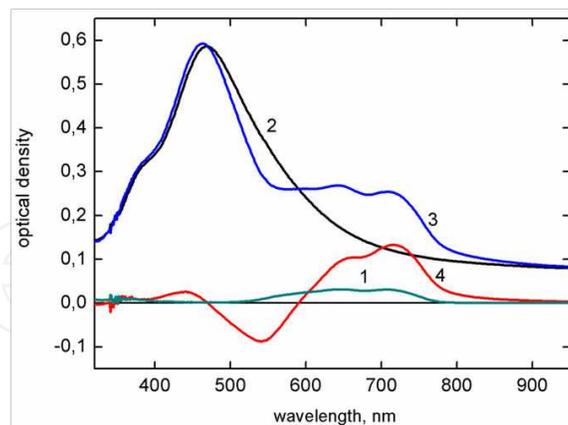


Figure 11. Extinction spectra of the dye layer on the sapphire substrate (1), the granular silver film on the sapphire substrate (2), and the dye layer coated over the granular silver film on the sapphire substrate. The curve (4) plots the difference between (3) and (2), i.e. the dye molecules contribution to the extinction of a hybrid material. Clearly, the dye molecules absorbed much stronger when they are put in the vicinity of the silver nanoparticles as compared to the dye molecules on the bare sapphire substrate, the surface densities of the dye molecules being the same in both cases.

The curve (4) in the Figure (11) demonstrates not only the fact that the absorption by dye molecules is enhanced in the vicinity of silver nanoparticles but also a more subtle effect of

the reduced absorption of silver nanoparticles being coated by dye molecules. This may be rationalized by considering the inhomogeneous broadening of the plasmon band and the anomalous dispersion associated with the absorption bands of the dye molecules. It is well known that the spectral position of the plasmon resonance depends on the refractive index of the surrounding material. Near the blue edge of the dye absorption band the anomalous dispersion leads to the low values of refractive index. Hence, the frequency of the plasmon resonance is expected to rise and its spectral position to shift in the blue direction. As in the spectral range under consideration the relative concentration of the nanoparticles rises with the rise of the resonance frequency, the above mentioned shift of the resonance frequencies of plasmon oscillations leads to the observed reduction of the hybrid material extinction. One can expect that the extinction maximum shifts as well. Such a shift indeed observed but it is rather small due to the damping of the plasmon resonance by interband transitions in silver.

The photoinduced transformations of the dye layers were observed under the action of the second harmonic of the Nd:YAG laser at the wavelength of 532 nm. Five pulses of 8 ns duration were delivered on the surface. The fluence was kept at the value of 8 mJ cm^{-2} to avoid burning of the spectral holes described above. First, the laser induced transformations were observed in the molecular layers on the bare sapphire substrate. Figure 12 plots the optical density of the dye layer before illumination (1) and after illumination (2). These changes may be interpreted as the departure of the molecules that form the aggregates from each other. In the extinction spectrum this process is seen as the reduction of absorption in the wings and the increase of absorption in the central part the band.

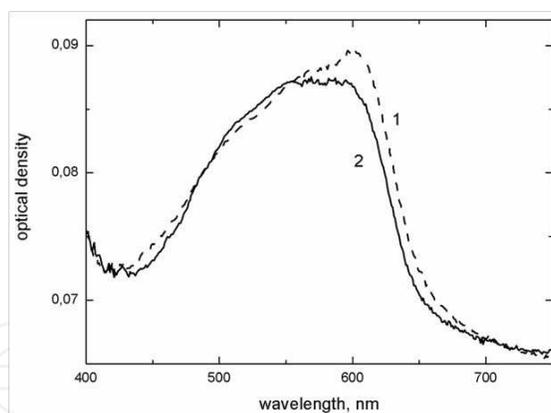


Figure 12. Optical density of the dye layer on the bare sapphire substrate before illumination (1) and after illumination (2).

The molecular movement under illumination in the case of the dye layer coated on the granular metal film is quite different. Figure 13 plots the optical density of the dye layer before illumination (1) and after illumination (2). To facilitate comparison with the case of the bare sapphire substrate absorption of the silver granular film was subtracted. One can easily see that even the sign of the laser induced is different from the case of dye layer on the bare sapphire substrate. As absorption in the wings rises one can conclude that the dye molecules moves to each other to produce the aggregated forms.

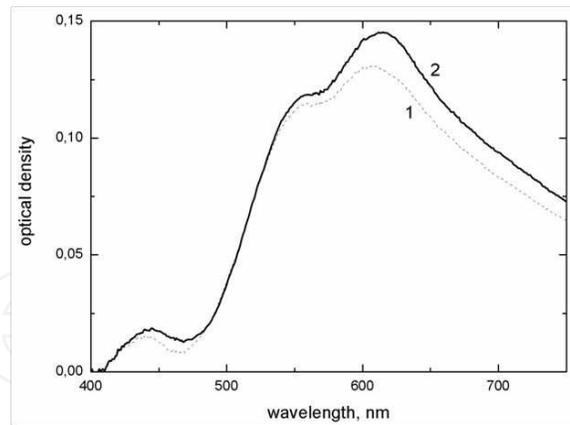


Figure 13. Optical density of the dye layer coated on the granular silver film on the sapphire substrate before illumination (1) and after illumination (2).

6. Conclusion

In this contribution we have presented experimental evidences that illumination is a convenient control of surface mass transport. This starts with the ordinary thermal action of light. In the case of granular metal films that consist of a collection of nanoparticles, this thermal action may be highly selective because the narrow band laser irradiation interacts strongly only with those particles that possess the plasmon resonance at the laser wavelength. Thus, although the diffraction limit avoids possibility to restrict the area of interaction tighter than a fraction of the wavelength, selectivity of the laser action is obtained in the spectral domain. Even the low intensity illumination may be used to initiate the mass transfer over the surface of metal nanoparticles. The selectivity of the laser action has been demonstrated in this case too.

An important issue of the thermal stability of thin metal films may be addressed with the ultraviolet irradiation. In this case we have shown that the granular silver film irradiated with UV light reduces its susceptibility to the thermal stress to a great extent.

Finally it was shown that the dye molecular movement initiated by illumination is quite different in the case of the dye molecules spread over the bare sapphire substrate and the granular metal film on the sapphire substrate.

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