

## Laser-induced linear dichroism in planar self-organized silver nanostructures

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A method for obtaining metallic plasmonic nanostructures with linear dichroism, based on the method of burning out constant spectral dips, is proposed. Isotropic granular silver films obtained by physical vapor deposition in vacuum were irradiated with linearly polarized laser radiation in the spectral region of the plasmon resonance of their constituent nanoparticles. As a result of irradiation, the silver nanostructures change their sizes and shapes, and the films acquire a pronounced linear dichroism. Both the magnitude and the spectrum of linear dichroism depend on the state of the isotropic film before irradiation, which can be changed by heat treatment. For the unannealed films the dichroism does not change the sign over the entire spectral range studied and corresponds to the expected increase in the depth of the spectral dip for the light polarized parallel to the laser radiation polarization plane. For the annealed films, which consist of more distinctly formed and better separated nanoparticles, the dichroism value is greater, and the spectrum turns out to be sign-changing. The appearance of linear dichroism after laser irradiation is due to the differences in the change in the shape and size of the initially anisotropic nanoparticles that make up an isotropic film as a whole, depending on their orientation relative to the polarization plane of the laser beam.

**Keywords:** plasmon resonance, silver nanostructures, linear dichroism, laser radiation.

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### Introduction

The optical properties of metal nanoparticles are mainly determined by localized surface plasmon resonance — collective vibrations of conduction electrons about the ion core [1]. The position of the plasmon resonance depends on the size, shape, spatial arrangement of nanoparticles and the dielectric environment [2,3]. For spherical nanoparticles of the most widely used plasmonic metals (gold, silver, and copper), the plasmon resonance is in the visible range, with the fundamental dipole vibration being triply degenerate. When the shape of nanoparticles deviates from spherical, the plasmon absorption band splits. Metal nanorods are a striking example, which have two absorption bands corresponding to the excitation of plasmon resonance along and across the rod [4,5]. The degeneracy is also removed when a spherical nanoparticle approaches the boundary of two media [6]. The shift of the plasmon resonance can also be due to the interaction between particles, which leads to the dependence of resonant frequencies on the period in ordered arrays of nanoparticles located on the surface of dielectrics [7].

The deviation of the shape of a metal nanoparticle from a spherical one leads not only to a change in the resonant frequencies of plasmon oscillations, but also to a dependence of the absorption spectra on the orientation of the particle with respect to the polarization of the incident light. Recently, the linear and circular dichroism of plasmonic nanoparticles and nanostructures has been

actively studied [8–10]. The relevance of such research is associated with the creation of metasurfaces for controlling the polarization of light, modulators, data storage devices, encryption, polarized light spectroscopy and optical information processing.

The greatest value of linear and circular dichroism is currently achieved for metal metasurfaces obtained by lithographic methods [11–13]. The high cost and small processing area make these structures still of little use for large-scale production. Therefore, the search for new methods for obtaining metal plasmonic structures with the necessary characteristics is an urgent task.

In this study we propose a method for modifying metal nanostructures using high-power linearly polarized radiation. The method consists in burning dips in inhomogeneously broadened spectra of plasmonic nanostructures [14]. When applied to ensembles of metal nanoparticles, the hole burning method has a number of features, since under the action of laser radiation, resonant particles are heated and, depending on the heating intensity, change their shape and/or size, and also lose mass due to evaporation. This leads to corresponding changes in the absorption spectra. The action of polarized radiation on anisotropic particles depends not only on their size and shape, but also on their orientation. Therefore, the spectral dips for differently polarized radiation turn out to be unequal, which is manifested in the dichroism spectra. The present study is devoted to the study of the difference in light transmission during probing by radiation polarized collinearly and orthogonally

Energy density during irradiation of samples

Sample	Energy density, mJ/cm <sup>2</sup>
<i>w/o</i>	0
1	4
2	8
3	14
4	21
5	29
6	41
7	50

to laser radiation, i.e. induced linear dichroism of silver nanostructures.

## 1. Methods and materials

Granular silver films were obtained by the physical deposition of silver vapor (99.99%) on the surface of glass substrates (SP-7101) in a PVD-75 vacuum chamber (Kurt J. Lesker). Equivalent film thickness — 12 nm, deposition rate — 0.5 Å/s, substrate temperature — room temperature, residual vapor pressure in the chamber  $5 \cdot 10^{-7}$  Torr. After deposition, some samples were subjected to thermal annealing at a temperature of 200°C for one hour.

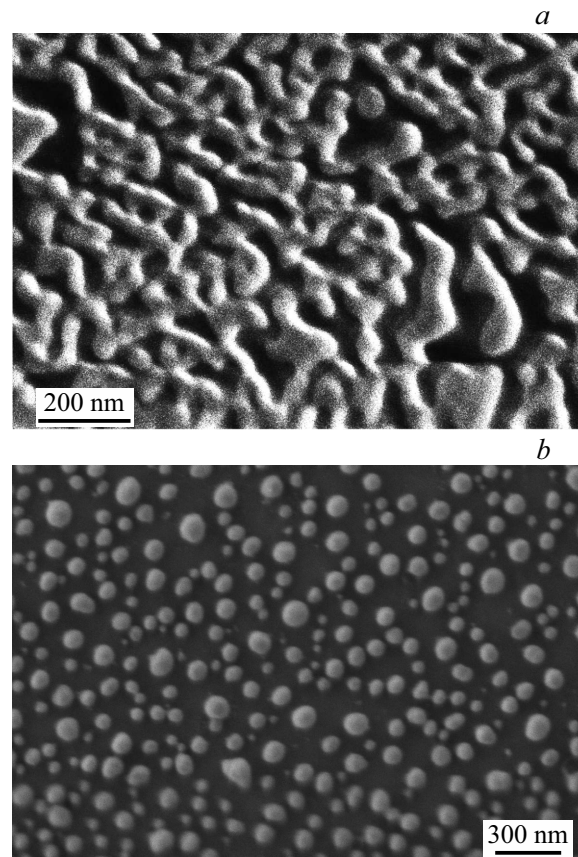
After deposition, the samples were irradiated with the second harmonic of a picosecond Nd:YAG laser (EXPLA PL2143) with linear polarization: wavelength  $\lambda = 532$  nm pulse duration  $\tau = 30$  ps, pulse repetition rate  $\nu = 10$  Hz, energy density from 4 to 50 mJ/cm<sup>2</sup> (table). The laser beam diameter was 500  $\mu$ m.

In the course of irradiation, laser radiation was scanned over the surface using a two-coordinate precision stage (ThorLabs) at a speed of 1 mm/s. The irradiated surface area was 0.49 cm<sup>2</sup>.

Before and after irradiation, the optical density spectra of the samples and the linear dichroism spectra were measured using a circular and linear dichroism spectrometer (Jasco-1500) with probing radiation polarized collinearly and orthogonally to the laser radiation. The intensity of the probing radiation was incommensurably lower than the intensity of the laser radiation and did not lead to any changes in the films. The linear dichroism spectra are shown as  $LD = OD_{\parallel} - OD_{\perp}$ , where  $OD_{\parallel}$  — is the optical density for light polarization parallel to the laser radiation polarization, and  $OD_{\perp}$  — perpendicular to it. The morphology of the samples was studied using scanning electron microscopy (SEM) Merlin (Zeiss).

## 2. Experimental results

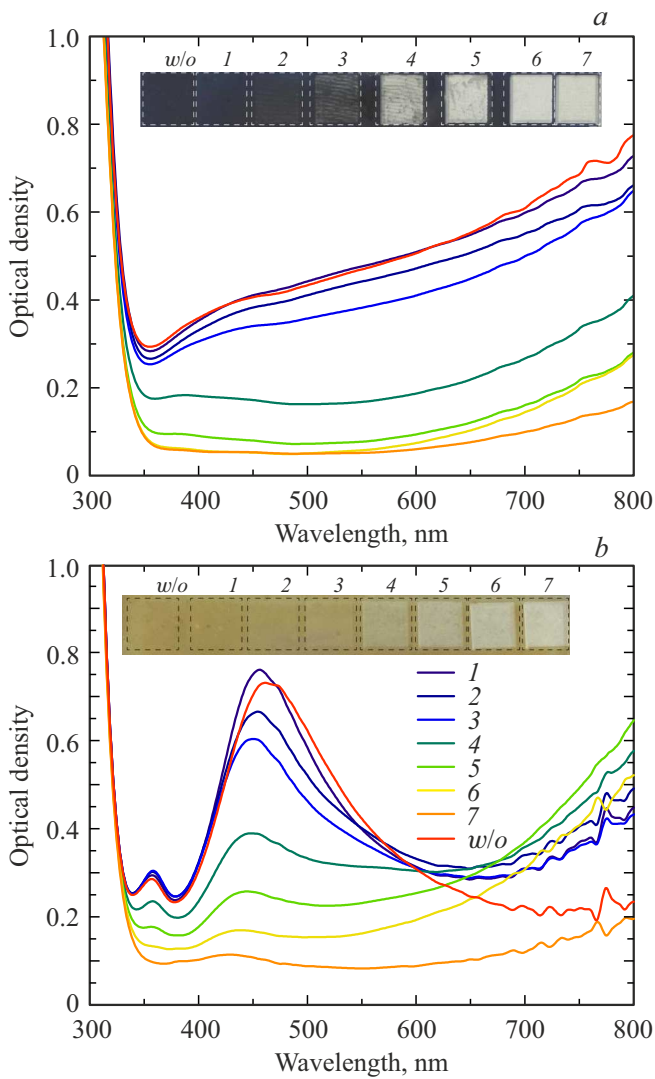
As a result of vacuum deposition of silver, complex labyrinth structures are formed on the substrate surface (Fig. 1, *a*). As can be seen from Fig. 1, *b*, subsequent annealing of the silver film at 200°C leads to the formation of individual nanoparticles that differ in shape and orientation.



**Figure 1.** Electron microscopic image of a granular silver film formed on a glass surface before (*a*) and after (*b*) annealing at 200°C. The equivalent film thickness is 12 nm.

Figure 2 shows the optical density spectra of silver nanostructures immediately after deposition (Fig. 2, *a* — red curve) and after annealing (Fig. 2, *b* — red curve). Unannealed films are characterized by a weakly pronounced broad plasmon resonance band, which is due to the complex shape of metal nanoparticles and their interaction due to their close proximity to each other [15]. Annealing leads to a narrowing of the absorption spectrum and the formation of a pronounced plasmon resonance band. The width of the plasmon absorption spectrum is due to the large spread of nanoparticles in shape and size.

Laser radiation enters the long-wavelength shoulder of the plasmon resonance of the annealed film and the short-wavelength shoulder of the unannealed film. Figure 2 shows the optical density spectra of samples after irradiation with laser pulses with different energy densities. Heating and evaporation of silver leads to a decrease in the optical density of unannealed films with an increase in the radiation intensity in the entire spectral range. For annealed films, in addition to a decrease in optical density, a short-wavelength shift of the plasmon resonance is observed. A significant change in the optical density can be associated with the processes of ablation of metal nanoparticles under the action of intense laser pulses.



**Figure 2.** Change in the optical density of silver films under the action of laser irradiation: unannealed film (a), film annealed at 200°C (b). *w/o* — before irradiation (red curves), 1–7 — after irradiation with increasing pulse energy density (1 — minimum energy, 7 — maximum). The inserts show photographs of the samples.

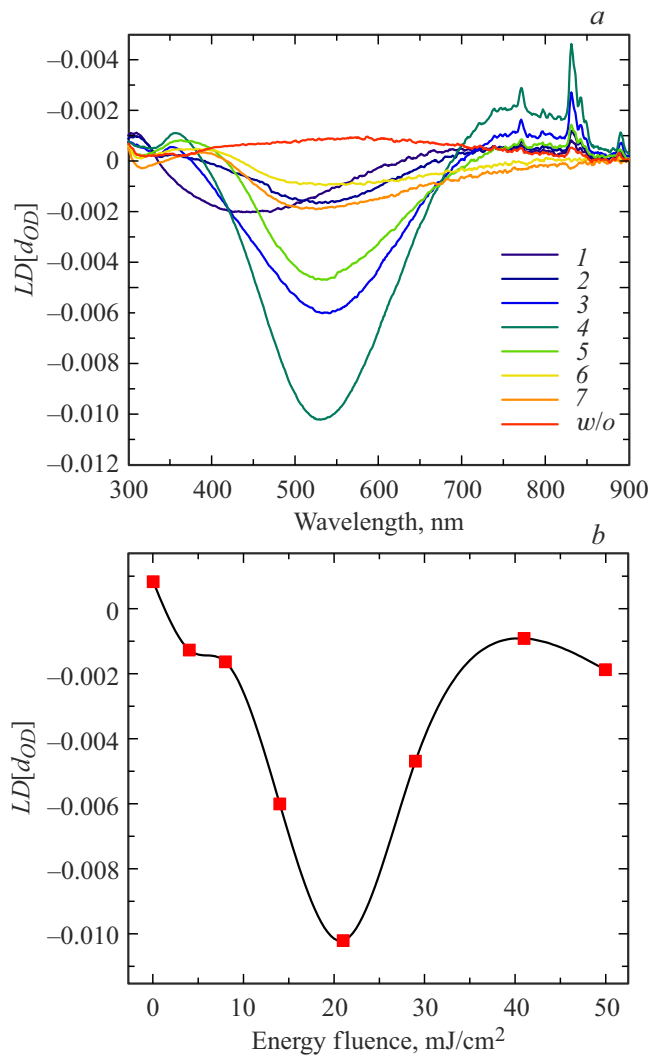
In addition to spectral changes, the action of linearly polarized laser radiation leads to unequal absorption of light polarized parallel and perpendicular to the polarization of the laser beam. Figures 3 and 4 show the linear dichroism spectra of the samples at various laser radiation energies. Before irradiation, the linear dichroism signal is close to zero for all samples.

Laser irradiation leads to an increase in the linear dichroism signal with increasing laser radiation energy. In all cases, the main features are observed at wavelengths close to laser radiation. However, there are fundamental differences between the linear dichroism spectra for unannealed and annealed films.

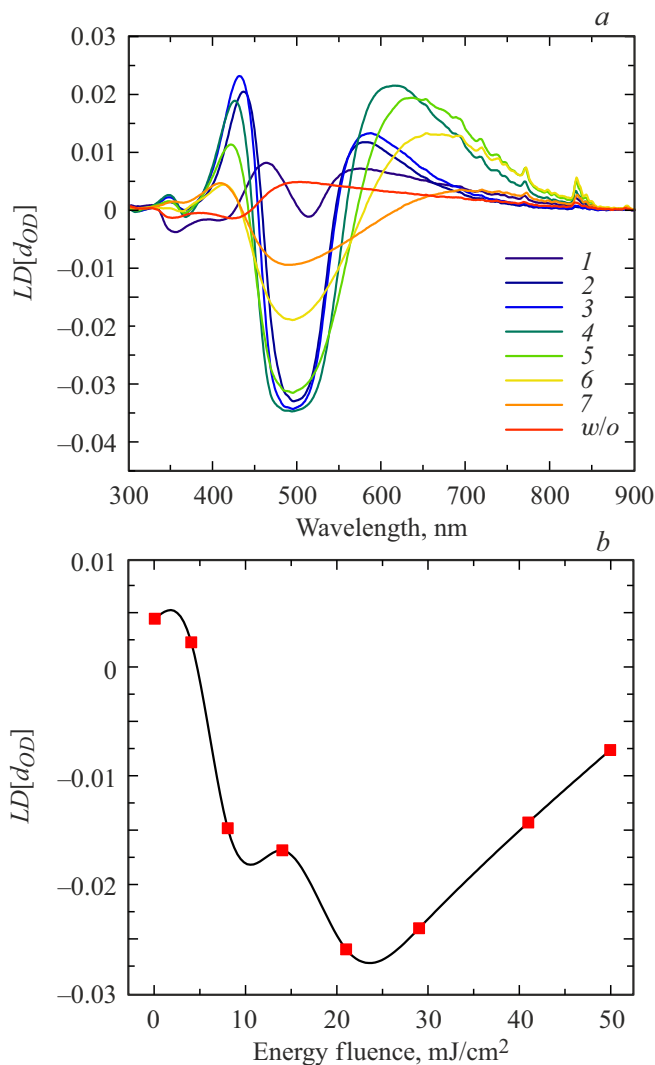
In the linear dichroism spectra of unannealed films (Fig. 3, a) one broad peak is observed at the laser radiation

wavelength, which corresponds to a higher transmission of light polarized collinearly to the laser radiation polarization. Figure 3, b shows the values of linear dichroism as a function of the radiation energy density at a wavelength of 532 nm. The highest value of linear dichroism  $LD = -0.01$  was achieved at the laser radiation energy density  $21 \text{ mJ/cm}^2$ , above which the linear dichroism signal began to decline. When irradiated with laser pulses with a higher energy density, the film becomes thinner, and the dichroism decreases along with the optical density.

The linear dichroism spectrum of the annealed films is sign-changing with a sign change on both sides of the laser radiation wavelength (Fig. 4, a). The dependence of linear dichroism on the radiation energy density was also investigated, as shown in Fig. 4, b. The maximum value of the linear dichroism of the annealed films at a wavelength of 532 nm is 2.5 times greater than that of the films not annealed at the same laser pulse energies. The



**Figure 3.** a — linear dichroism spectra of unannealed silver films before (*w/o*) and after irradiation with increasing laser pulse energy (1–7). b — dependence of linear dichroism at a wavelength of 532 nm on the energy density of laser pulses.



**Figure 4.** *a* — linear dichroism spectra of silver nanostructures before (*w/o*) and after irradiation (*1–7*). *b* — dependence of linear dichroism at a wavelength of 532 nm on the energy density of laser pulses.

signal maximum ( $LD = -0.035$ ) is somewhat shifted to the shortwave region relative to the laser radiation wavelength, with a slight shortwave shift with increasing pulse energy, while the shortwave and longwave peaks of the opposite sign shift to shortwave and longwave with increasing laser pulse energy. region of the spectrum, respectively.

### 3. Discussion

As mentioned above, laser radiation selectively heats particles for which the plasmon resonance coincides with the radiation wavelength. In this case, a dip appears in the optical density spectra at the wavelength of laser radiation. If the particles are anisotropic, and the laser radiation that causes heating and modification of the particles is linearly polarized, then the depth of the dip depends on the orientation of the particles relative to the plane of

polarization of the radiation. This means that for weak probing radiation, the ensemble of particles after irradiation will exhibit linear dichroism. In the case of anisotropic particles of a fairly simple shape, for example, nanorods, the interaction with light turns out to be maximum when the light is polarized along the nanorod axis [16]. Linear dichroism was also observed in more complex particles with rotational axes of the third order [17]. Several spectral modes of plasmon resonance are excited in such particles, corresponding to various „inhomogeneities“ of a large particle.

In this study, two cases were considered. The first one — unannealed films — corresponds to complex structures, for which plasmonic properties are determined by small roughness, interaction between closely spaced particles and, by analogy with metasurfaces, holes in the film. In this case, due to such complexity, each structural element can correspond to several plasmon modes at different frequencies, and a very wide extinction spectrum is characteristic. Laser radiation will interact immediately with many different particles, the maximum interaction will be for particles and structures in which both the wavelength of the plasmon resonance coincides with the wavelength of the radiation, and the orientation relative to the polarization of light.

At sufficiently low energies, the interaction of laser radiation with nanoparticles is similar to thermal interaction, as a result of which the shape of the particles changes and they become more rounded, i.e. their anisotropic properties decrease. A further increase in energy leads to such effects as fragmentation of metal particles and their ablation [18–20]. In our case, ablation plays an important role, since the optical density decreases significantly with increasing pulse energy. Both processes lead to a selective change in the film morphology and the appearance of linear dichroism, which reaches a maximum at laser pulse energy densities of the order of 20–25 mJ/cm<sup>2</sup>. With a further increase in energy, laser radiation interacts more and more with the long-wavelength shoulder of the absorption band of nonresonant particles, changing the overall morphology of the film due to ablation processes. This leads to a cardinal decrease in the extinction of the samples (Fig. 2) and a decrease in linear dichroism (Fig. 3).

In the case of annealed samples, the maximum dichroism of the irradiated films is greater, and the differential absorption spectrum is more complex. First, the maximum value of linear dichroism 0.035 is reached not exactly at the wavelength of laser radiation. The maximum is shifted towards the center of the plasmonic absorption band, since the plasmon band in the annealed film is more pronounced than in the case of the unannealed film. Second, far from the laser radiation wavelength, the sign of linear dichroism turns out to be opposite to that expected from the point of view of the predominant burning of resonant particles. To interpret the discovered phenomenon, it is necessary to take into account more complex processes that accompany the burning of resonant particles, in particular, the fragmentation of large particles considered in [21,22].

If the discontinuity occurs in the direction of polarization of the acting radiation, then the closely spaced fragments formed will provide increased absorption of radiation. On the other hand, the melting of an elongated particle leads not only to a decrease in the absorption of light of the corresponding polarization at the resonant frequency, but also to the appearance of a particle that resonantly absorbs radiation of the same polarization, but already in the short-wavelength region. Without entering here into a detailed consideration of various mechanisms that can result in the formation of an excess of particles that absorb radiation of the same polarization as the acting laser radiation, we note that it is necessary to describe in detail the shape of nanoparticles, since even in the simplest model of a nanoscale triaxial frequency ellipsoid plasmon excitations depend on the ratio of all three semiaxes, which was used above.

## Conclusion

The possibility of creating linear dichroism in an isotropic granular metal film under the action of intense linearly polarized radiation, the frequency of which falls into the plasmon absorption band of nanoparticles constituting the film, has been experimentally demonstrated. The appearance of anisotropy is caused by the selectivity of light exposure, depending not only on the frequencies of collective electronic excitations of individual particles, but also on their orientation relative to the radiation polarization plane.

With an increase in the irradiation intensity, the dichroism of the irradiated film increases to a certain limit, after which a decrease begins due to the complete ablation of the material at high pulse energies. The method of burning spectral dips used made it possible to obtain silver nanostructures with a difference in optical densities with respect to light with mutually perpendicular polarization directions equal to 0.035. Despite the relatively small magnitude of the detected effect, the possibility of inducing anisotropy by light in initially isotropic self-organized metal nanostructures is of fundamental interest and opens up the possibility of obtaining plasmonic nanostructures with various types of anisotropy of optical properties over large areas without using low-performance and expensive methods of electron lithography.

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## Conflict of interest

The authors declare that they have no conflict of interest.

## References

- [1] A. Moores, F. Goettmann. *New J. Chem.*, **30** (8), 1121 (2006). DOI: 10.1039/b604038c
- [2] K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz. *J. Phys. Chem. B*, **107** (3), 668 (2003). DOI: 10.1021/jp026731y
- [3] K.S. Lee, M.A. El-Sayed. *J. Phys. Chem. B*, **110** (39), 19220 (2006). DOI: 10.1021/jp026731y
- [4] J. Zheng, X. Cheng, H. Zhang, X. Bai, R. Ai, L. Shao, J. Wang. *Chem. Rev.*, **121** (21), 13342 (2021). DOI: 10.1021/acs.chemrev.1c00422
- [5] G.A. Wurtz, R. Pollard, W. Hendren, G.P. Wiederrecht, D.J. Gosztola, V.A. Podolskiy, A.V. Zayats. *Nature Nanotechnology*, **6** (2), 107 (2011). DOI: 10.1038/nnano.2010.278
- [6] K.V. Baryshnikova, M.I. Petrov, T.A. Vartanyan. *Phys. Stat. Sol. (RRL) Rapid Research Lett.*, **9** (12), 711 (2015). DOI: 10.1002/pssr.201510330
- [7] D.R. Dadadzhyanov, T.A. Vartanyan, A. Karabchevsky. *Nano-materials*, **10** (7), 1265 (2020). DOI: 10.3390/nano10071265
- [8] M.R. Shcherbakov, B.B. Tsema, A.A.E. Ezhov, V.I. Panov, A.A.E. Fedyanin. *JETP Lett.*, **93** (12), 720 (2011). DOI: 10.1134/S0021364011120149
- [9] S. Requena, H. Doan, S. Raut, A. D'Achille, Z. Gryczynski, I. Gryczynski, Y.M. Strzhemechny. *Nanotechnology*, **27** (32), 325704 (2016). DOI: 10.1088/0957-4484/27/32/325704
- [10] X.T. Kong, L.V. Besteiro, Z. Wang, A.O. Govorov. *Advanced Materials*, **32** (41), 1801790 (2020). DOI: 10.1002/adma.201801790
- [11] Y. Chen, X. Yang, J. Gao. *Light: Sci. & Appl.*, **8** (1), 1 (2019). DOI: 10.1038/s41377-019-0156-8
- [12] M.R. Shcherbakov, P.P. Vabishchevich, M.I. Dobynde, T.V. Dolgova, A.S. Sigov, C.M. Wang, A.A.E. Fedyanin. *JETP Lett.*, **90** (6), 433 (2009). DOI: 10.1134/S0021364009180064
- [13] M. Ren, E. Plum, J. Xu, N.I. Zheludev. *Nature Commun.*, **3** (1), 1 (2012). DOI: 10.1038/ncomms1805
- [14] T. Vartanyan, J. Bosbach, F. Stietz, F. Träger. *Appl. Phys. B*, **73** (4), 391 (2001). DOI: 10.1007/s003400100714
- [15] K.L. Góeken, V. Subramaniam, R. Gill. *Phys. Chem. Chem. Phys.*, **17** (1), 422 (2015). DOI: 10.1039/c4cp03739a
- [16] B.N. Khlebtsov, N.G. Khlebtsov. *J. Phys. Chem. C*, **111** (31), 11516 (2007). DOI: 10.1021/jp072707e
- [17] G.Q. Wallace, S.T. Read, D.M. McRae, S.M. Rosendahl, F. Lagugn-Labarthe. *Advanced Optical Materials*, **6** (6), 1701336 (2018). DOI: 10.1002/adom.201701336
- [18] G. González-Rubio, A. Guerrero-Martínez, L.M. Liz-Marzán. *Accounts of Chem. Research*, **49** (4), 678 (2016). DOI: 10.1021/acs.accounts.6b00041
- [19] L. Delfour, T.E. Itina. *J. Phys. Chem. C*, **119** (24), 13893 (2015). DOI: 10.1021/acs.jpcc.5b02084
- [20] N.V. Tarasenko, A.V. Butsen, E.A. Nevar. *Appl. Surface Science*, **247** (1–4), 418 (2005). DOI: 10.1016/j.apsusc.2005.01.093
- [21] N.A. Toropov, I.A. Gladskikh, P.S. Parfenov, T.A. Vartanyan. *Optical and Quantum Electronics*, **49** (4), 1 (2017). DOI: 10.1007/s11082-017-0996-5
- [22] P.V. Gladskikh, I.A. Gladskikh, M.A. Baranov, T.A. Vartanyan. *Opt. Spectrosc.*, **128** (6), 713 (2020). DOI: 10.1134/S0030400X20060065