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Optical anisotropy of polyvinyl alcohol films with metal nanorods under uniaxial tension

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The possibility of obtaining macroscale anisotropic thin films from polyvinyl alcohol with included metal nanorods under uniaxial tension conditions that do not lead to a change in the morphology of metal nanoparticles is shown. Silver and gold nanorods were obtained by directed growth from nuclei and then embedded in a polymer matrix based on polyvinyl alcohol. Initially isotropic films with absorption independent of the polarization of the probing light became anisotropic after stretching, which manifested itself in the dependence of the extinction spectra on the polarization of the probing radiation. The weakening of the longitudinal dipole plasmon resonance mode with the simultaneous enhancement of the transverse dipole plasmon resonance when the light polarization is rotated from 0° to 90° degree indicates the orientation of the nanorods in the film along the direction of its stretching. In addition to the change in absorption in the bands of dipole modes, a strong orientational dependence of absorption in the band of the quadrupole mode of the plasmon resonance of metal nanorods was found.

Keywords: plasmon resonance, metal nanorods, anisotropy, polyvinyl alcohol.

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Introduction

Many years research devoted to research into metal nanoparticles have led to the development of various application for their use in photonics and electronics. Applications in photonics are predominantly based on the existence of a localized surface plasmon, the excitation of which in a metal nanoparticle leads to a multiple enhancement of the incident radiation near its surface. The ability to control the spectral position of plasmon resonance from the near-UV to near-IR ranges by changing the size and shape of the particles themselves, as well as the dielectric constant of their environment, opens up prospects for their use in such various fields as biomedicine, the design of chemical and biological sensors, photovoltaics, photocatalysis, and others [1–4]. In recent years, much attention has been paid to controlling the polarization and amplitude of electromagnetic radiation using two-dimensional ordered nanostructures-metasurfaces [5].

It is well known that elongated metal nanoparticles, in particular nanorods (NR), have two resonances in their absorption spectrum, which correspond to collective electron oscillation along and across the particle [6–8]. These resonances have been observed experimentally and are well described by the quasi-static theory for spheroidal particles [9,10]. Of course, the degree of manifestation of each of the resonances in the absorption spectrum of the NR depends on their orientation relative to the polarization of the impinging radiation. This allows the use of NR, provided they are oriented, to develop dichroic metasurfaces.

Methods for fabrication of metallic NR have been developed quite well. These can be both chemical synthesis methods [11,12] and lithographic methods [13,14]. The latter allow to obtain two-dimensional structures of almost any desired configuration, but are quite expensive and currently cannot be scaled. Chemical synthesis allows to obtain large volumes of particles with a narrow distribution of size and shape, but a necessary condition for the use of particles formed in a colloidal solution is their spatial ordering.

One of the proven methods for ordering NR is their introduction into a polymer film with its subsequent stretching [15–18]. Polyvinyl alcohol (PVA) is often chosen as a polymer matrix, since films from it are quite easy to obtain during conventional drying, they are transparent in the visible range, have a low glass transition temperature, and the amount of possible stretching depends on the length of the molecules [19]. The orientation of the rods in the general direction is carried out by heating the polymer film with NR included in it to the softening temperature and subsequent stretching [20]. In this process, the NR in contact with the polymer chains adhere to the molecules and unfold along the stretching direction, and the degree of their orientation in this method can be close to 100%.

Despite the low glass transition temperature for stretching PVA films, they are heated to a temperature of approximately 80−150°C. At 150°C, the shape of gold NR [21] can change, and for silver nanoparticles, 70°C is enough to change the shape with significant changes in optical properties [22], which is a rather serious problem. To overcome this, we studied the effect of stretching PVA films with silver and gold NR on their optical properties at temperatures close to room temperature, and the softening of the polymer film was carried out by moistening it using a steam bath.

Methods and materials

Silver NR were obtained by two-stage synthesis using the method of directed growth from spherical seeds [23]. The seed solution was prepared by mixing 50 ml of a solution of 0.25 m MAgNO$_3$ and 0.25 mM trisodium citrate (coating agent) with 1.2 ml ice-cold 0.01 M NaBH$_4$ (strong reducing agent), while the solution was stirred vigorously for 30 s. When Ag$^+$ ions are mixed with trisodium citrate, the Ag$^+$ ions are coated with the COO$^-$group, which leads to the formation of a silver complex and subsequent reduction of the complex to silver nano-nuclei in the presence of sodium borohydride. When a reducing agent is introduced into the medium, the color of the solution instantly changes to light yellow, which indicates the formation of silver nanoparticles less than 10 nm in size. The nuclei were used through 1 − 2 h after preparation.

To obtain NR silver with different aspect ratios, different amounts of ascorbic acid were added to a solution containing 0.25 ml 10 mM AgNO$_3$, 10 ml 0.05 M CTAB as a directing agent and 7 mM ascorbic acid as a weak reducing agent freshly prepared solution of silver nuclei (0.05 − 1 ml). Then 0.1 ml 1 M NaOH solution was added to this mixture. Finally, the solution was gently stirred to distribute NaOH throughout the solution volume. During 1 − 10 min, the color of the solutions gradually changed from orange to green depending on the number of added nuclei [12].

To obtain gold NR, a seed solution was first prepared by reducing Au^{3+} ions from HAuCl$_4$. Freshly prepared 0.5 ml 0.01 M NaBH$_4$ was added to a solution containing 0.20 ml 0.025 M HAuCl$_4 \cdot 3H_2O$ and 8.0 ml 0.10 M CTAB. The color of the solution immediately changed from yellow to brownish. Before use, the solution was kept at room temperature for 1.5 h. Then the same amount of gold and CTAB solutions was used to prepare the growth solution together with 40 μl 0.10 M AgNO$_3$. Next, 40 μl 1 M hydrochloric acid and 0.50 ml 0.10 M hydroquinone [12] were added. The solution was kept without stirring for two days.

To obtain a polymer film, fully hydrolyzed PVA with a molecular weight of 89000−98000 was gradually mixed with deionized water and slowly heated to 70°C with stirring until a pure transparent 10% aqueous PVA solution was obtained. The solution was then cooled to 35°C. Finally, the PVA solution was mixed with the colloidal solution of NR (1 : 4) and mixed well for 30 min. Next, the NR-PVA solution was distributed on a glass slide and dried until solidified for 48 h at room temperature. The film thus obtained was then kept in an oven at a temperature of 40°C for 24 h to dry completely [24].

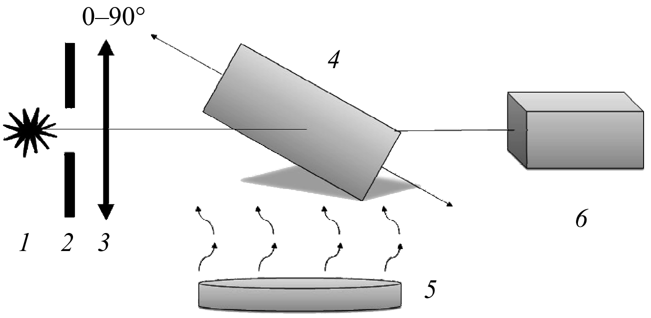

Figure 1. Scheme of an installation for stretching films based on an automatic XYZ coordinate stage and a multichannel photon analyzer PMA-12. *1* — light source, *2* — aperture, *3* — polarizer, *4* — sample attached to automatic XYZ stage, *5* — steam bath, *6* — detector.

The orientation of randomly located metal NR in the resulting composite film was carried out by uniaxial stretching of the sample with low heating and light humidification. To measure extinction spectra directly during film stretching, a setup was assembled based on an automated three-coordinate stage and a multichannel photonic analyzer (Fig. 1). A collimated linearly polarized beam of light passed through the sample and was detected by the receiver. The light polarization angle was varied from 0° (along the stretch) to 90° (across the stretch) using a linear polarizer. The films were stretched at intervals of 0.5 mm. The films were slightly heated and moistened using a steam bath.

Extinction spectra of colloidal solutions of metal NS and polymer films were recorded using 3600 UV/Vis-NIR (Shimadzu, Japan) and SF56 (LOMO, Russia) spectrophotometers and a PMA-12 multichannel photonic analyzer (Hamamatsu, Japan). The following reagents were used to obtain samples: silver nitrate (AgNO$_3$, 99.9%), sodium citrate dihydrate (99%), sodium borohydride (NaBH$_4$, 99%), cetyltrimethylammonium bromide (CTAB, 98%), l-ascorbic acid (99%), sodium hydroxide (NaOH, 98%), polyvinyl alcohol (PVA, MW 89000−98000, 99% hydrolyzed). All reagents were used without further purification.

Results and discussion

The extinction spectra of aqueous solutions of nuclei and NR are presented in Fig. 2.

In the absorption spectrum of the silver seed solution (Fig. 2, *a*), there is a characteristic band with an absorption maximum at 390 nm, typical for spherical particles with a size of 7−9 nm. In the absorption spectra of NR, several absorption bands of different intensities are usually observed, two of which are associated with dipole plasmonic oscillation along the axis of the nanorod (longitudinal resonance) and in the perpendicular direction (transverse resonance) [25], and the rest with higher modes orders [26,27]. In our case, the long-wavelength maximum is due to the excitation of the longitudinal plasmonic resonance, and the short-wavelength maxima are due to the excitation of the transverse (the shortest wavelength) and quadrupole resonances.

The optical properties of plasmonic NR are strongly influenced by changing the aspect ratio [28]. In particular, increasing the aspect ratio of the NR reduces the frequency of longitudinal resonance. It is important to note that the change in the aspect ratio of NR in solution depends on the concentration of nuclei added to the solution. As the amount of added seeds decreased, the ratio of the length of the resulting NR to the diameter increased, which was manifested in the absorption spectra by a shift of the long-wavelength peak to the longer-wavelength side. Changes in the absorption spectra led to visible changes in the color of the colloids.

The absorption spectrum of gold NR (Fig. 2, *b*) was measured in heavy water (D_2O) as a solvent in order to avoid the influence of the high absorption of ordinary water in the IR area of the spectrum. Just as in the case of Ag NR, the absorption spectra of Au NR contain three absorption bands corresponding to the excitation of longitudinal and transverse dipole plasmon modes and a quadrupole mode.

Figure 3 shows the extinction spectra of the stock colloidal solution of metal nanoparticles, the solution after mixing the polymer with the particles, and the film itself after drying, normalized to the long-wavelength maximum. The inserts show images of NR obtained on a scanning electron microscope.

The absorption spectra at each stage of sample preparation retain three plasmonic bands, which allows to judge the stability of the NR when transferred from the stock solution to the matrix. The shift of the peaks to longer wavelengths is associated with an increase in the refraction index of PVA (1.53) relative to water (1.33) [28,29].

The process of stretching a polymer film with particles was carried out under constant spectral control. Absorption spectra of polymer films were recorded at different polarization orientations of the incident light relative to the stretching direction with an interval of 10° of both the primary film and during stretching, where 0° corresponds to the polarization of the probe radiation along the stretching direction, and 90° — in the perpendicular direction. The films were stretched smoothly without sudden jerks in increments of 0.5 mm in a steam bath to avoid damage to the fragile thin film. Figure 4 shows the extinction spectra of films initially and those stretched by a factor of 2 and 3.

The original NR films were insensitive to the polarization of light, and the extinction spectra recorded at different linear polarizations of the incident radiation coincide with each other. Thus, a film with silver NR (Fig. 4, *a*) intensively absorbs light in the areas of short-wave (386 nm), central (470 nm) and long-wave (667 nm) absorption peaks, regardless of the direction of light polarization. The stretching of the film leads to the appearance of a significant anisotropy of absorption. When probing with light polarized perpendicular to the direction of stretching, the long-wave peak of a doubly stretched film decreases significantly, and in a triple-stretched film it almost completely disappears. The amplitude of the short-wave maximum (386 nm), on the contrary, will increase with a change in the polarization angle from 0° to 90°, and the magnitude of the changes is also maximum with threefold stretching.

Similar results were obtained for a film containing gold NR (Fig. 4, *b*). In contrast to films with silver NR, the long-wavelength extinction maximum of films with gold NR is located outside the measured wavelength range. The increase in absorbance may be due to a change in the optical path when the film is deformed or due to the deposition of water vapor. There are ground changes for the maximum at a wavelength of 660 nm, and the nature of the changes was comparable to the average maximum for silver NR — when the polarization angle changed from 0° to 90°, there was a significant decrease in the absorption of the film.

As was said, the absorption spectra of metal nanorods consist of several maxima, the spectral position of which is determined by a geometric factor [29,30]. Typically, NR have two maxima, corresponding to plasmonic modes excited along and across the particle, and the absorption efficiency of NR depends on the direction of light polarization and is maximum when coinciding with the excited plasmonic resonance. In addition, to dipole plasmonic oscillations, excitation of higher order modes is possible in long nanorods and particles larger than 100 nm. In our paper, the spectrum of the absorbance of the NR at all stages of sample preparation, consists of three maxima, the short-wavelength and long-wavelength ones are associated with dipole resonances along the short and long axes of the NR, and the middle peak can be associated with the excitation of a quadrupole resonance, also caused by collective oscillations of electrons along the axis nanorods.

In the PVA films obtained as a result of drying, the nanorods are located randomly, as in a solution, which is confirmed by the absence of dependence of absorption on the direction of linear polarization of the probing radiation. At stretching the long PVA molecules unwind, turning the metal nanorods along the stretching direction. In this case, a strong anisotropy of the absorption spectra appears when probed with linearly polarized light, which increases as the film stretches. Absorption in the short-wavelength transverse plasmonic resonance band of silver nanostructures was maximum when the electric vector of the impinging radiation **E** was perpendicular to the direction of stretching, and in the long-wavelength longitudinal plasmonic resonance band — when **E** coincided in direction with the direction of stretching. The behavior of the middle peak with a change in light polarization was similar to the long-wavelength maximum. For gold NR, changes in absorption in the short-wave transverse resonance band were insignificant. At the same time, the

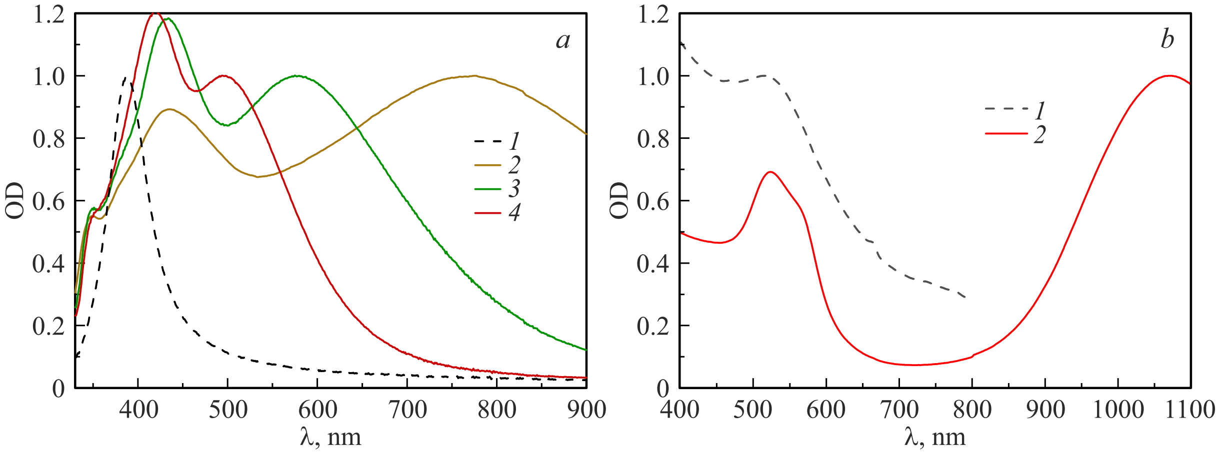

Figure 2. (*a*) Extinction spectra of a series of spherical nuclei samples (*1*) and NR silver with different additions of nuclei (0.5 (*2*), 0.1 (*2*), 0.05 ml (*3*)), normalized to the maximum of the longitudinal localized resonance (LLR). (*b*) Normalized extinction spectra of freshly prepared gold spherical nuclei (*1*) and NR (*2*).

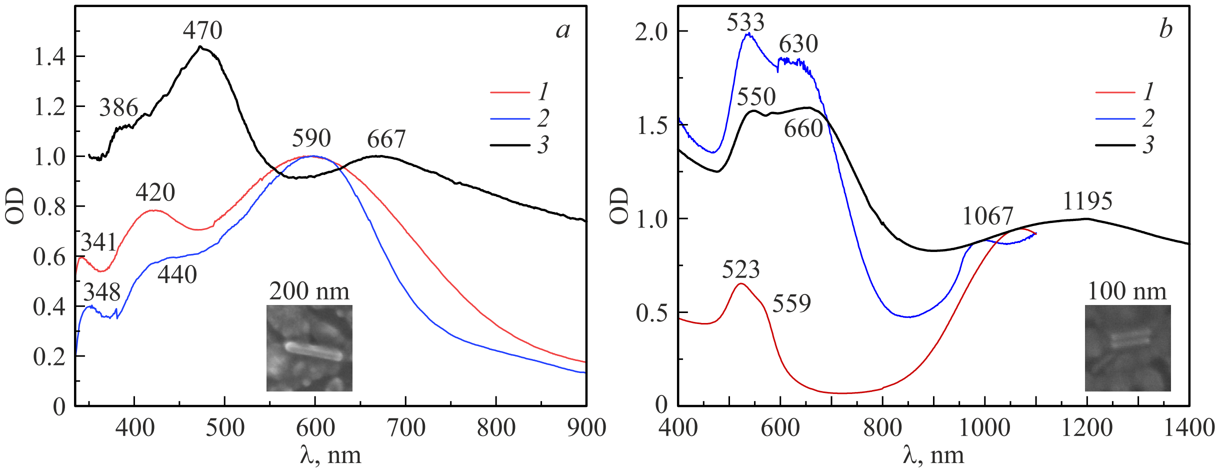

Figure 3. Absorption spectra of the stock colloid NR (*1*), a mixture of PVA + NR (*2*) solutions and a dried film (*3*), normalized to the maximum LLP for silver (*a*) and gold (*b*) NS.

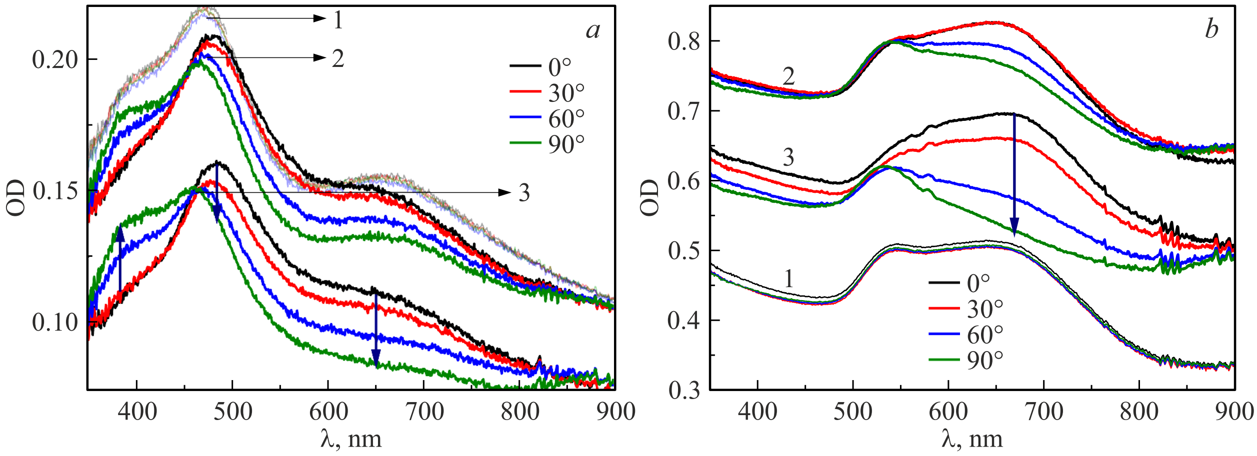

Figure 4. Absorption spectra of Ag (*a*) and Au (*b*) NS-PVA films without stretching (*1*) and with stretching of a factor of 2 and 3 , measured when the probe radiation is polarized along the stretching direction (0°) and perpendicular to it (90°).

long-wave maximum was outside the measured wavelength range. But, as in the case of silver NR, a significant decrease in the intensity of the central peak was observed when the polarization changed from 0° to 90°. It was shown in the paper [31] that higher order modes cannot be excited in a NR when the vector is directed across the NR. Therefore, it is not surprising that this peak is also very sensitive to changes in light polarization, provided that all NR are oriented along the direction of film stretching.

Conclusion

The possibility of obtaining highly anisotropic PVA films with metal NR when they are oriented during stretching at a temperature close to room temperature has been demonstrated. Such conditions for obtaining samples prevent changes in the morphology of NR, which can occur when they are heated. The measured extinction spectra confirm that unstretched composite films are optically isotropic due to the random orientation of metal nanorods interstitial in the polymer matrix. Stretched films, in contrast, are optically anisotropic at the macroscale due to the stretch-induced uniform orientation of the metal nanorods. The installation created during the work allows to monitor the appearance and development of anisotropy of polymer films with interstitial metal nanorods directly during their mechanical deformation.

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Conflict of interest

The authors declare that they have no conflict of interest.

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