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Optical chirality in AgCl-Ag thin films through formation of laser-induced planar crossed-chain nanostructures

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Irradiation of AgCl-Ag thin films by a linearly polarized He-Ne laser beam results in the formation of self-organized periodic nanostructures. As a result of secondary irradiation of the initially exposed sample by the same linearly polarized He-Ne laser beam, but with different orientations of polarization, a complex crossed-chain nanostructure forms. We found that such a complex nanostructure has noticeable chirality and increased optical anisotropy, resulting in optical activity of the sample. Double exposure produces two gratings, crossing each other with angle $\alpha$, which leads to the formation of crossed building blocks with chiroptical effects. It is established that the amount and the sign of the angle between the two laser-induced gratings ($\pm \alpha$) determine the amount and the direction of rotation of the linearly polarized probe beam, respectively. We have also observed an induced anisotropy-dependent ellipticity for the probe light, which is passed through the sample. It is shown that the amount of ellipticity depends on the angle $\alpha$. Published by AIP Publishing.

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I. INTRODUCTION

The formation of self-organized periodic nanostructures (SPN) in photosensitive AgCl thin films (d$_f$ $\sim$ 50 nm) doped by Ag nanoparticles (Ag-NPs; oblate spheroids $\sim$ 10 $\times$ 50 $\times$ 50 nm; Ref. 1) as a result of interaction of a He-Ne laser beam ($\lambda$$_{R}$=632.8 nm) with the film is a well-studied topic.\textsuperscript{2–8} Furthermore, the reorganization mechanism of SPNs under successive irradiation (i.e., double exposure) of the AgCl-Ag system by the laser beam, with different polarization states in each irradiation, has been studied in detail under different conditions.\textsuperscript{2–4} It is also reported that\textsuperscript{5,6} SPNs formed by circularly and elliptically polarized laser beams exhibit optical activity, which is induced because of SPN formation in the AgCl-Ag photosensitive thin film. Likewise, the induction of chirality in polymer-based optical materials by circularly polarized light is reported by another group in Ref. 9.

The formation of self-organized periodic nanostructures (sometimes called: spontaneous gratings) is described\textsuperscript{7} as a result of interference between the incident polarized He-Ne laser beam and the excited TE-modes in the slab photosensitive waveguide AgCl film and migration of Ag-NPs to minima of the interference field. The Ag-NPs are doped as a very thin island-film (d$_{Ag}$ $\sim$ 10 nm) on the AgCl layer [Fig. 1(a) and the top-right inset in Fig. 2]. The incident laser beam scatters from the Ag-NPs and some part of scattered light propagates in the AgCl film as a TE-mode of the AgCl slab waveguide thin film. The excited mode interferes with the incident light and then Ag-NPs start moving to the minima of the interference pattern to minimize their energy [Fig. 1(b)]. Formation of SPNs enhances the coupling of TE-modes to the AgCl layer, which in turn results in the increase of contrast of the interference pattern and consequently increases the rate of migration of the Ag-NPs to the minima of the interference pattern. This cycle repeats again and again [called: positive feedback of light (PFL)], thus, the SPN makes itself better and better. Detailed studies are carried out and reported to explain the mechanism of formation of SPNs.\textsuperscript{8} On the other hand, it is shown\textsuperscript{8} that the coupling of excited nano-plasmons in neighboring Ag-NPs leads to the enhancement of excited TE-modes in the initial stages of formation, which helps to produce better SPNs, but longer exposure results in the agglomeration of silver clusters within the minima of the interference pattern. At this stage, the electrical connection between tightly agglomerated clusters quenches the excited TE-modes, resulting in the domination of Gaussian profile of intensity of the incident laser beam. Such domination leads to the destruction of the formed SPN, because Ag-NPs under aforesaid conditions prefer to move to the periphery of the interaction area on the sample, where intensity is less than that of the center of the laser beam, to reduce their total energy. We learned from this result that long exposure to secondary irradiation destroys the initial SPN formed by the first exposure, and consequently the crossed-chain structure could not be achieved.

Recent studies\textsuperscript{5,6} show that formation of SPN under circularly (CPL) and elliptically polarized light (EPL) results in the induction of optical gyrotropy in thin AgCl films, doped by Ag-NPs. In other words, a linearly polarized probe light experiences a rotation (more than 1$^\circ$ @ $\lambda$$_{p}$ = 650 nm, in our case) and becomes an EPL after passing through the AgCl-Ag layer containing the SPN. In the above-mentioned references, it is shown that if the SPN is formed by right-handed EPL or CPL, then the probe beam

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rotates to the right and if the SPN is formed by left-handed EPL or CPL, then the probe beam rotates to the left. It means by changing the polarization state of the incident light (the He-Ne laser beam, in our case), one can have a limited control over the amount and sign of the laser-induced optical activity in the AgCl-Ag film. In Ref. 5, with the purpose of distinguishing and separating the contribution of chirality and the induced anisotropy in the observed optical activity of samples, a standard experiment was carried out,10,11 which is repeated in the same manner in the present work. In this order, one should measure the angle of optical rotation ($\alpha$) of the linearly polarized probe light ($E_p$) for different angles ($\phi$) of the sample relative to the $E_{o1}$ (Fig. 3). It is well defined that10–13 the offset of sinusoidal variation of $\theta(\phi)$ at $\phi=0^\circ$ represents the chirality, and its amplitude represents the magnitude of induced anisotropy of the irradiated samples.

There are many interesting researches14–27 showing that planar metasurfaces and metamaterials containing 2D and 3D arrays of metallic gammadions, asymmetrically split rings and crossed shaped building blocks in a dielectric matrix exhibit noticeable optical activity. But, in most of the above-mentioned works, expensive and rarely available instruments and techniques have been used to produce such structures. It should also be mentioned that, in contrast to our structures, which act in the visible region, the above-mentioned reported structures are mostly functional in the near IR region and longer wavelength of the spectrum.

Becoming acquainted with planar metasurfaces and metamaterials made by the formation of aforesaid structures, and at the same time knowing the properties of SPNs in thin AgCl-Ag photosensitive films, brought us to a conclusion that through formation of two SPNs at the same location on the sample (while they are crossing each other) by double exposing using a linearly polarized He-Ne laser beam, one can produce an environment similar to the metamaterials,
which is able to influence the polarization of the probe beam and present the optical activity, due to induced anisotropy and also formation of chiral building blocks. Intersecting SPNs produce crossed shapes or deformed prolate S-shape building blocks (down-right inset in Figs. 2–4). Such samples also may indicate a negative index of refraction, which needs very precise measurements, and is not investigated in the present work.

FIG. 3. Experimental setup for measuring the induced optical rotation ($\theta$), at different angles of the sample ($\phi$) relative to the polarization vector of the incident probe light ($E_p$). A schematic image of the induced criss-crossing gratings, which produce enantiomers (shown in gray) at intersecting locations of the two gratings, is shown as down-right inset.

FIG. 4. Definition of left-handed (a1, a2), and right-handed (b1, b2) chiral building blocks. A building block could be considered as a chiral one if one could not produce the same enantiomer by reflection (c), or its mirror image by rotation (d).
By this method, we can have limited control over the amount and sign of rotation of the polarization vector of the probe beam by determining the amount and sign of angle \( \alpha \) (the angle between polarization directions of laser beams at two successive exposures). The angle \( \alpha \) also determines the induced ellipticity of polarization of the probe beams after passing through the double exposed sample. Tuning the optical activity via morphology and lattice spacing in 3D metamaterials is also reported in Refs. 28 and 29.

II. EXPERIMENTS AND RESULTS

A. Sample preparation method

The thin film of AgCl (\( d_f \approx 50 \text{ nm}, n_f = 2.06 \)) is deposited on a glass substrate (\( n_s = 1.52 \)) by deposition under vacuum (\( p_v \geq 10^{-3} \text{ mm Hg} \)) from a molybdenum (Mo) evaporation boat. Afterwards, the AgCl/glass system was coated by a very thin layer of silver (\( d_{Ag} \approx 10 \text{ nm} \)) under the same vacuum conditions. Such very thin layer would be in the form of an island-nano-layer, i.e., silver is distributed on the AgCl film as granular nanoparticles (Fig. 2). This granular layer makes the Ag/AgCl/glass system a photosensitive thin film, which can simultaneously act as a slab waveguide. The thickness of the AgCl layer, \( d_f \), is chosen equal to the cut-off thickness of the AgCl slab waveguide to excite only the TE_{0,mode} of the waveguide (calculated from the slab waveguide dispersion equation according to Ref. 30).

The AFM image of the surface of a non-irradiated Ag/AgCl/glass system is shown in Fig. 2. Uniformly distributed Ag-NPs on the surface of the samples are apparent. AFM analysis of these images shows that these Ag-NPs are oblate and have about 10 nm height and 40–50 nm radius.

In our experiments, instead of rotating the polarization direction of the laser beam for the second exposure, we rotated the sample relative to the initial direction of polarization of the first exposure in Fig. 4. The results are shown in Fig. 5.

If we rotate the sample after the first exposure to the left, then we make an optically left-handed criss-crossing nanostructure [Fig. 4(a)], and if we rotate it to the right, then we make the right-handed one [Fig. 4(b)]. By means of left- or right-handed structure, we mean the case when the laser beam propagates toward us, then the clockwise direction is called: the right-handed structure and the counterclockwise direction of rotation for the second exposure is called: left-handed one.

B. Small-angle scattering

As the granular layer of Ag scatters the propagating excited TE_{0,mode} of AgCl slab waveguide within the layer, the mode during the propagation scatters and therefore there is no unique direction and a narrow angular distribution of propagation vector \( \beta \) around the main direction exists. This leads to a domain structure of the forming SPN (Fig. 6), which in turn results in scattering of propagating modes in each domain from the neighboring domain on its way. This scattering can be observed on the screen which is placed in front of the sample during the interaction [top-left inset in Figs. 7 and 8(a)]. This scattering pattern is called Small-Angle Scattering (SAS). The detailed and complete explanations for SAS pattern appearance are presented in Refs. 3, 4, 6, and 8. Thus, the appearance of SAS pattern helps us to judge about the formation of SPN and even its quality.

C. Real-time observation of diffraction pattern from the formation of SPN

As the period of formation of SPN (\( \rho = \frac{2\pi}{\lambda} \approx 418 \text{ nm} \)) is less than the wavelength of the interacting laser beam...
(λ_R = 632.8 nm), observing the diffraction pattern from the formed SPN in real-time during the process is almost impossible using traditional methods. In order to observe the diffraction pattern during the SPN formation to control the process, we used a real-time method of observation introduced in Ref. 31 and developed in Ref. 32. In this method, a transparent buffer layer of cryolite (Na3AlF6; n_b = 1.32) was coated on the glass substrate before the AgCl layer. Thus, the cut-off thickness of TE0-modes for AgCl on this new substrate should be recalculated, which equals d_{c1} = 32 nm. The thickness of cryolite was chosen to be about 500 nm. More details of calculations and explanations are presented in Ref. 32. By making the system Ag/AgCl/cryolite/glass, excitation of radiative TE-modes, which have leakage into the substrate, occurs and one can observe the diffraction patterns of forming SPN in real time [Figs. 8(a) and 8(b)]. Using this method, we can follow the formation process of SPN, especially during the second exposure, to prevent overdose irradiation of the samples, which destroys the already formed SPN as we explained in the Introduction.

After rotation, the existing first grating diffracts the incident He-Ne laser beam, i.e., the second exposure with a new polarization direction [Fig. 8(c)]. Then, longer exposure leads to the formation of the second grating with the new direction but at the same place (the interaction area). Formation of the second SPN leads to the appearance of its diffraction and SAS patterns [Fig. 8(a)]. While intensity of the second diffraction pattern increases, the intensity of the first one decreases [Fig. 8(d)], because the amount of available Ag-NPs for the construction of SPN in the interaction area on the sample is constant and limited. We stop the second exposure when the intensities of diffraction patterns become equal. In this way, we can be sure that the two crossing gratings are similar (Figs. 4, 8, and 9). Such criss-crossing gratings produce building blocks with “A”, “T”, “L”, “Z”, “Z”, “Z” ... shapes in the intersection points of the two periodic structures, depending on the size and the number of Ag-NPs available in each particular intersection point (Fig. 9). These building blocks could be considered as planar chiral ones, if it could not be obtained, their mirror image is obtained by shifting or rotating them around their center [Figs. 4(c) and 4(d)].

Using the setup shown in Fig. 7, we could observe and measure both the SAS and the real-time diffraction patterns simultaneously [Figs. 8(a)–8(d)]. As it can be seen from Fig. 7 (right inset), the diffraction efficiency of the forming SPN increases with the exposure time. It happens because of the positive feedback of light that we explained earlier. At the same time, after rotation of the sample, the diffraction pattern of the initial SPN starts decreasing, and simultaneously the diffraction pattern of the second SPN along the new orientation appears [Fig. 8(d)]. We stop the second exposure, when intensities of the two patterns become equal. It should be mentioned that detailed investigations in Ref. 8 show that the growth process of the SPN has an oscillating character, i.e., perfection of the formed SPN has no
linear relation with the exposure duration time. It is due to
the change in the size and the distance of Ag-NPs from each
other during the interaction with the laser beam. The effects
of size and matrix of Ag-NPs on their optical properties
have been studied recently by other researchers. From
the data presented in Ref. 8, we estimated that the total
exposure time should be longer than 45 minutes to achieve
an optimum irradiation time.

FIG. 8. (a) SAS pattern, real-time diffraction, and exiting TE-modes; (b) SAS and diffraction pattern for the first grating; (c) SAS and diffraction pattern from the first grating after rotation of the sample equal to angle a; (d) SAS and diffraction patterns from both initial and the second gratings simultaneously.

FIG. 9. The criss-crossed (double exposed) sample, (a) Schematic image; (b) AFM image at $\alpha=45^\circ$. The enantiomers (chiral building blocks) are indicated by yellow broken lines.
D. Spectroscopic studies

We measured the absorption spectra of the samples, in the visible range of spectrum, for different angles $\pm \alpha$ (Fig. 10) for non-polarized probe light, and horizontal and vertical linearly polarized probe lights, as well. As it can be seen from Fig. 10, there is a peak around the wavelength 520 nm, which is related to the surface plasmon resonance of such complex silver clusters. Figure 10(a) shows that the non-irradiated sample does not exhibit noticeable dichroism as it has a uniform distribution of silver nano-granules on its surface and there is no preferred orientation or any chain-like structure. Also, one can see that there is a dichroism $\Delta D = D_{\parallel} - D_{\perp}$, where $D_0$ is the optical density of the sample ($D = -\log T$, where $T$ is the transmittance of the sample) when the polarization of the probe beam is parallel to the direction of initial polarization orientation of the linearly polarized incident laser beam in the first exposure, $E_p \parallel E_{0\parallel}$, and $D_\perp$ is for the case when $E_p \perp E_{0\parallel}$. As our Ag-NPs are the oblate ones, the small dichroism in the peak of surface plasmon resonance in Fig.10(a) can be interpreted. The amount of $\Delta D$ and even its sign differ for different angles $\alpha$. Our measurements show that for $\alpha = 90^\circ$, the $\Delta D$ is maximum. The absorption spectra of non-polarized probe beams in cases $\alpha = 0^\circ$ and $\alpha = 90^\circ$ are almost the same [Figs. 10(a) and 10(d)]. The blue or red shift of the peaks in different angles $\alpha$, compared to the case $\alpha = 0^\circ$, could be related to the geometry of the building blocks of the SPN, which in turn have effects on their interaction with the matrix or each other, and consequently, their plasmonic characteristics.33

E. Optical rotation and induced ellipticity measurements

In order to measure the laser induced optical activity, we applied the standard method introduced in Refs. 14 and 36, using the setup shown in Fig. 3. In this method, the amount of optical rotation ($\theta$) of a linearly polarized probe light ($E_p$) is measured after passing through the sample. This measurement is conducted for different orientations of the sample relative to the polarization vector of the incident laser beam at the first exposure (called angle $\varphi$). The results of these measurements are shown in Fig. 11. As it can be seen from Fig. 11, the variation of $\theta$ vs. $\varphi$ has a sinusoidal behavior. We can fit an appropriate curve to the experimental data. By definition, the amount of off-set of the fitted curve gives...
a measure of the induced chirality of the sample, and the maximum amplitude of the curve represents the optical anisotropy of the sample.

From Fig. 11, we can see that the anisotropies of the non-irradiated sample and the double exposure sample at \( \alpha = 90^\circ \) are minimum and almost have the same values, but for the samples irradiated by a linearly polarized laser beam (double exposure with \( \alpha = 0^\circ \)), induced anisotropy has its maximum value, while its chirality is minimum.

Our observations confirm that the linearly polarized probe beam after passing through the sample in addition to the rotation experiences an induced ellipticity depending on angle \( \alpha \).

To measure the induced ellipticity, one could measure the intensity of the probe beam using a setup shown in Fig. 3, at \( \phi = 0 \), for different angles of the analyzer (called angle \( \psi \)). The results of this experiment (the polarization diagram) are shown in Fig. 12 (the blue “x” data points). The orientation and the ratio of the major axis to the minor one determine the ellipse of the polarization of the transmitted probe light. Its azimuth represents the azimuth of polarization ellipse. But, as this measurement has too many tasks to be accepted as a precise one, and repeating it for several samples takes a long time, we used the following procedure:

It is well known that an elliptically polarized light can be represented by Stocks parameters as a vector

\[
S = S_0 \begin{pmatrix}
1 \\
\cos(2\chi) \cos(2\theta) \\
\cos(2\chi) \sin(2\theta) \\
\sin(2\chi)
\end{pmatrix},
\]

(1)

where \( \tan(\chi) \) is the ellipticity and \( \theta \) is the optical rotation angle. As is shown in Ref. 37, we can use the following relation between the angles \( \chi \) and \( \theta \) with intensity of the probe beam after the analyzer, which is calculated from Eq. (1)

\[
I(\psi) = S_0 \left[ \frac{1}{2} + \frac{\cos(2\chi) \cos(2\theta)}{2} \cos(2\psi) + \frac{\cos(2\chi) \sin(2\theta)}{2} \sin(2\psi) \right]
\]

(2)

or in a simplified form as

\[
I(\psi) = E + F \cos(2\psi) + H \sin(2\psi).
\]

(3)

Therefore, by changing the \( \psi \) and recording the intensity \( I(\psi) \), one can determine the coefficients in Eq. (3) by fitting an appropriate curve. Determining the coefficients \( E, F, \) and \( H \), we can calculate the values of \( \chi \) and \( \theta \). Plotting the aforementioned curve in the polar diagram (solid red curves in Fig. 12), we concluded that we can use this method measuring only a few points around the minimum signal to avoid the huge amount of measurement in the classical polarization diagram (the blue “x” data points).38
In order to better interpret the mentioned results, we plotted the dependence of optical rotation of samples due to chirality ($\theta_{ch}$) on angle $\alpha$ on the base of data from Fig. 11 and also the variation of the induced ellipticity versus angle $\alpha$, both at $\varphi = 0^\circ$ (Fig. 13), on the basis of the explained ellipsometry. Thus, the rotations which are shown in Fig. 13(a) is only due to the chirality of the building blocks of the sample, which is called chiroptical rotation, and anisotropy has no role in it. On the other hand, as it can be seen from Fig. 13(a) for $\alpha = 0^\circ$ at $\varphi = 0^\circ$ (no chiral building blocks), still there is very small chiroptical rotation ($\theta_{ch} \neq 0^\circ$) which may be related to the geometry of the Ag-NPs (oblate clusters) giving them a small intrinsic chirality.

In Fig. 14, chiroptical rotations ($\theta_{ch}$) at different wavelengths ($\lambda_{Blue} = 460$ nm, $\lambda_{Green} = 520$ nm, $\lambda_{Red} = 620$ nm) of the linearly polarized probe beam are shown. It can be seen that the amount of rotation differs for different wavelengths, and its sign depends on whether it is longer or shorter than the wavelength of the surface plasmon resonance absorption peak of our samples ($\lambda_{SPR} \approx 520$ nm in our case, Fig. 10). These results are in good accordance with theory presented in Ref. 39. From Fig. 14, it is clear that for SPNs formed at angle $+\alpha$, the sense of rotation is in opposite direction of the case when the SPN is formed at angles $-\alpha$, for the whole range of spectrum, which means information about the conditions of SPN formation (amount and sign of angle $\alpha$ and wavelength of the incident light) are recorded within the structure and can be read by the probe beam. If we plot the best line passing through the experimental data points, it can be seen that the line of right-handed structure intersects the line for the left-handed one at $\theta_{ch} \neq 0^\circ$ and $\lambda = 512$ nm, which differs from $\lambda_{SPR} \approx 520$ nm in our case, by about 1.5%. It may be because of experimental error and also the shape of Ag-NPs individually, which is oblate and has an intrinsic chirality, and also collectively as agglomerated clusters.

We also calculated and plotted the scattering indicatrices (using COMSOL Multiphysics - RF Module) for wavelengths for which we measured the chiroptical rotations at $\varphi = 0^\circ$ for both right- and left- handed building blocks (for example: $\_d$ and $\_e$ ones) (insets of Fig. 14). As is seen, the scattering indicatrix for $\lambda_{Red} = 620$ nm has its maximum value and its orientations are in opposite direction for SPNs generated at $\pm \alpha$. This can be extended for other wavelengths. But, for wavelengths around $\lambda_{SPR} \approx 520$ nm, the chiroptical rotation has its minimum value for both right- and left-handed induced structures. At $\lambda_{SPR} \approx 520$ nm, where the absorption is maximum (Fig. 10), the indicatrix shows very weak scattering from the chiral building blocks. It could be related to the fact that for wavelengths at which absorption and dichroism are high (Fig. 10), the chiroptical effect is weak.

We also tried to quantify the induced optical chirality by measuring and experiment-based calculations for the circular dichroism ($CD = T_R - T_L$, where $T_R = \frac{I_R}{I_0}$ and $T_L = \frac{I_L}{I_0}$ are transmission coefficients for right-handed and left-handed
circularly polarized probe beams, respectively. \( I_B \) and \( I_L \) are their intensities, and \( I_0 \) is the intensity of the baseline probe beam), and the dissymmetry factor \( g = \frac{CD}{4I_B + I_L} \), Ref. 40). Due to our technical limitations, we only measured the CD and consequently the dissymmetry factor, \( g \), for three wavelengths \( \lambda_B = 460 \text{ nm}, \lambda_G = 520 \text{ nm}, \) and \( \lambda_R = 620 \text{ nm} \) for \( \alpha = +45^\circ \).

Due to our technical limitations, we only measured the CD and consequently the dissymmetry factor, \( g \), for three wavelengths \( \lambda_B = 460 \text{ nm}, \lambda_G = 520 \text{ nm}, \) and \( \lambda_R = 620 \text{ nm} \) (Fig. 15). For the blue probe light, the precision of our measurement is not only, at \( \alpha = \pm 45^\circ \) using the finite element method (FEM) using COMSOL software (Table I). From Fig. 15 and Table I, we can see that the experimental values are about 10 times smaller than the theoretical ones. It is due to the fact that other shapes like: \("\alpha" \ "\eta" \ "\xi" \ "\zeta" \ "\eta''" \ "\zeta''" \ "\zeta'''" \ ... exist as building blocks in the intersection points of the two periodic structures, concurrently [AFM images (Fig. 5)], which leads to the difference between the measured CD and the \( g \) factor and the calculated ones (Table I).

Our calculations are done only for similar \( \alpha \) and \( \beta \) shaped chiral units, and the influence of other shapes is not taken into account in the used calculation model, which leads to the difference between experimental and calculated results. The outcomes of our investigations show that (i) with an increase of the wavelength of the probe beam, the dissymmetry of the samples increases for both experimental and calculating studies and (ii) the existence of diversity in the shapes of the chiral building blocks reduces the contribution of the chiroptical effects of each group of shapes in the total optical rotation of the samples.

In Ref. 40, up to 40% dissymmetry factor in the near infrared region is reported, which is because of very well-ordered arrays of similar 3D helical structures. Our results (Table I) indicate an approximate 4% dissymmetry factor in the visible range of the spectrum, which is due to the diversity in shapes of chiral building blocks of the SPN. The disadvantage of our method is relatively low dissymmetry factor, but it also has advantages such as: (i) functioning in the visible region; (ii) controllability of the amount and sign of the optical rotation; and (iii) simplicity of the method.

### III. DISCUSSION

As it was explained in previous sections, self-organized periodic nanostructures (SPNs) in AgCl-Ag waveguide thin films are formed as a result of interaction with a polarized He-Ne laser beam. This interaction leads to interference between the incident light and the TE-modes of the waveguide film and migration of silver nanoparticles to the minimum of the interference pattern. These SPNs can perfect themselves through the positive feedback mechanism, which is explained in the Introduction.

The formation of SPNs could be controlled by studying SAS and diffraction patterns in real time (Figs. 7 and 8). Double exposure of the samples to two identical linearly polarized light sources, but with deferent directions of polarization (with the angle between them being \( 0^\circ < \alpha < 90^\circ \)) leads to the induction of optical activity, which is due to two factors: (1) induced anisotropy and (2) optical chirality. Our experimental results show that after such treatment, the size of the complex clusters increases relative to the non-irradiated samples [Fig. 2(a)], and at the same time gets a wider size distribution. Such criss-crossing nanostructures (Figs. 5 and 9) exhibit noticeable optical activity (Fig. 11). Using a standard method \(^{10,11}\) we measured the optical rotation and distinguished the portion of induced optical anisotropy and chirality (Fig. 11). Our observations show that the sign and the amount of angle \( \alpha \) determine the sense and amount of optical rotation. It should be related to the symmetry and the shape of building blocks of the optically active sample (Figs. 4 and 9). Anisotropy induces optical rotation,\(^6\) on the other hand, our method produces many chiral elements which shape our structure. In such structures, the major factor for optical rotation is the chiroptical effects.

As we mentioned before, in Refs. 6 and 39, it is discussed that in the variation of optical rotation (\( \theta \)) versus the angle of sample rotation, \( \varphi \), the offset from the horizontal axis, the optical rotation at \( \varphi = 0^\circ \) (Fig. 3), indicates the optical rotation due to the chirality of the material (we call it: \("chiroptical rotation, \theta_{ch}\"\)), and the amplitude of this variation represents, quantitatively, the anisotropy of the sample. As it can be seen from Fig. 10, for different angles \( \alpha \), the rotations due to chirality and anisotropy differ.

Measuring the amount of chiroptical rotation, \( \theta_{ch} \), for different angles \( \alpha \), indicates that for the samples irradiated at \( \alpha = 0^\circ \) (with maximum anisotropy and absence of chiral building blocks), we obtain \( \theta_{ch} \approx 0^\circ \), and for \( \alpha \) about \( 45^\circ \) (high anisotropy accompanied by the existence of chirality), the angle \( \theta_{ch} \) has its maximum value [Fig. 13(a)]. As is explained in Ref. 36, anisotropy enhances the chiroptical effects. Therefore, if we plot the variation of ellipticity of the probe beam, passed through the irradiated samples, at different angles \( \alpha \) at \( \varphi = 0^\circ \) [Fig. 13(b)], we find that induced ellipticity of the probe beam has its maximum value for \( \alpha = 0^\circ \) (maximum anisotropy and absence of chirality, i.e., \( \theta_{ch} = 0^\circ \)) and for other angles \( \alpha \) where both chirality and anisotropy

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**TABLE I.** Experimental and calculated CD and dissymmetry factor \( g \) for wavelengths: \( \lambda_B = 460 \text{ nm}, \lambda_G = 520 \text{ nm}, \) and \( \lambda_R = 620 \text{ nm} \) at \( \alpha = +45^\circ \).

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<th>Dissymmetry experimental</th>
<th>Dissymmetry calculation</th>
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</tbody>
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coexist and the induced ellipticities have very small value. Hence, it seems that in the absence of chirality, the induced ellipticity for the probe beam is mostly due to the anisotropy of the sample, and when the chirality exists, the induced ellipticity would be suppressed by the chiral building blocks resulting in very small induced ellipticity (close to the linearly polarized one). On the other hand, as is shown in Ref. 6, the induced birefringence is maximum for the case when the SPN is formed by linearly polarized light, i.e., when we have a maximum of anisotropy. This birefringence is responsible for the induced ellipticity. Because of the range of size of the Ag-NPs in our experiments, the measures of anisotropy for the cases when $15^\circ < \alpha < 75^\circ$, are not distinguishable, which leads to almost equal induced ellipticities [Fig. 13(b)]. But, optical rotation is maximum around $\alpha = 45^\circ$ [Fig. 13(a)], for which anisotropy is the highest among those cases, where $\alpha \neq 0^\circ$. As has been mentioned before, high anisotropy enhances the chiroptical effects, which increase the angle of optical rotation of the probe beam ($\theta$).

From Fig. 14, we can conclude that in addition to the sensitivity of induced optical rotation to the left-handedness or the right-handedness of structure and its geometrical parameters, it is also a function of wavelength of the probe beam. For those wavelengths, where surface plasmon resonance peak happens, scattering of the probe beam is minimal and the chiroptical rotation is correspondingly minimum.

Therefore, for double exposed AgCl-Ag thin films, the formed planar chiral building blocks (Fig. 9) are the primary cause for optical rotation of the probe beam, although depending on angle $\alpha$, in addition to the chiroptical effects the induced anisotropy enhances the induced optical activity of the samples. If the shape and the size of our chiral building blocks were the same and identical, the induced optical activity could be stronger, but as these building blocks are the result of intersecting of two linear gratings, which are made of Ag-NPs and clusters, they have diverse shapes. This fact influences the total amount of angle of induced optical rotation and gives it a distribution, similar to size distribution of Ag-NPs. Any imperfection of building blocks negatively influences the induced optical activity, such as: the poor quality of the Ag nano-layer because of impurities, large clusters, sticking to the surface of some of the Ag-NPs, or ..., which make the forming SPN imperfect, resulting in a wide diversity of shapes for the building blocks of SPN and consequently weaker induced chiroptical effects. As is shown in Refs. 8 and 41, coupling between neighboring Ag-NPs considerably influences the absorption and scattering of light by the clusters, which in turn, as we know, causes a change in the CD and strength of the induced optical activity. Thus, the sample preparation procedure should be very adequate and precise to obtain samples with good quality and repeatable response to the probe beam.

IV. CONCLUSION

The formation of self-organized periodic plasmonic nanostructures in slab waveguide AgCl thin films, doped by silver nanoparticles, under two successive irradiation by linearly polarized He-Ne laser beams with different orientations of polarization is studied. It is found that such treatment makes the samples optically active. The sense and amount of optical activity depend on the sign and the amount of angle between the two polarization vectors of first and second exposure (angle $\alpha$). AFM investigations show that such successive irradiation results in the formation of two criss-crossing SPNs, for which in the intersecting parts, planar chiral building blocks are generated. Experimental measurements indicate that such elements exhibit chiroptical effects and have a major role in the induced optical activity. In addition to the induced chirality, anisotropy is induced in the samples, which is also a function of angle $\alpha$. The angle $\alpha$ determines the geometry and symmetry of building blocks of the formed SPN, which in turn determines the portion of chirality and the anisotropy of the sample in the induced optical gyrotropy. Formation of the criss-crossing SPN was controlled, simultaneously, by observation of small-angle scattering patterns and real-time method for diffraction pattern studies during the procedure. Consistent calculation and experimental measurement results indicate that the angle of optical rotation $\theta$, in addition to the angle $\alpha$, is a function of wavelength of the probe beam. The shape, abundance, geometry, left- or right-handedness and degree of symmetry of the building blocks are functions of angle $\alpha$ and its sign. Our samples are optically active in the visible range of spectrum, and the method of their preparation is relatively simple and inexpensive.

The presented method may be applied to produce metamaterials and metasurfaces activated in the visible region of spectrum. Another important issue, which needs to be addressed by doing very precise experiments, is the existence of probable induced negative index of refraction. An experimental study in this direction is being carried out.

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