Giant Optical Activity in Quasi-Two-Dimensional Planar Nanostructures

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We examine the spectral dependence in the visible frequency range of the polarization rotation of two-dimensional gratings consisting of chiral gold nanostructures with subwavelength features. The gratings, which do not diffract, are shown to exhibit giant specific rotation ($\sim 10^4°/\mathrm{mm}$) of polarization in direct transmission at normal incidence. The rotation is the same for light incident on the front and back sides of the sample. Such reciprocity indicates three dimensionality of the structure arising from the asymmetry of light-plasmon coupling at the air-metal and substrate-metal interfaces. The structures thus enable polarization control with quasi-two-dimensional planar objects. However, in contradiction with recently suggested interpretation of experiments on larger scale but otherwise similar structures, the observed polarization phenomena violate neither reciprocity nor time-reversal symmetry.

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Advances in nano- and microscale fabrication have made possible the realization of artificial materials with extraordinary optical properties such as photonic crystal slabs and waveguides with ultraslow speed of light [1] or ''left-handed'' metamaterials with a negative dielectric permittivity and magnetic permeability [2,3]. Planar metal structures have attracted attention due to the fact that they are easily fabricated by electron-beam lithography and can be operated at room temperature. In such structures, strong coupling between light and the collective motion of electrons (plasmons) [4] leads to novel phenomena such as superefficient light transmission through subwavelength holes [5], reshaping of ultrashort optical pulses [6], suppression of light extinction [7], and enhanced second-harmonic generation [8–10]. The next important challenge in tailoring optical properties of metal nanostructures is polarization control, which would be crucial in various applications.

When a strong coupling between photons and surface plasmons exists, the optical properties of gratings can be controlled by the shape and ordering of metal particles on dielectric substrates. Subwavelength gratings of ordered rectangular elements show a pronounced difference in transmittivity for light with orthogonal linear polarizations [11], which are polarization eigenstates for such a structure. Attempts to create planar structures with circularly rather than linearly polarized eigenwaves have also been reported [12,13]. Such metamaterials possess optical activity, i.e., lead to polarization rotation as light passes through the structure [13,14].

In noncentrosymmetric bulk materials, optical activity arises from the spatial dispersion of the optical response and can be observed when two mirror-symmetric forms of the material exist [14]. Such materials are often referred to as chiral. When a linearly polarized light wave propagates in a chiral medium, the polarization plane azimuth rotates clockwise or counterclockwise depending on the handedness of the material.

Different patterns for left- and right-hand circularly polarized light were recently observed in diffraction from planar gratings with superwavelength period and square lattice, consisting of structures with fourfold rotation axis and no reflection symmetry [12]. The suggested interpretation of this result has opened a discussion on chirality in two dimensions [15,16], and the possibility of a violation of reciprocity and time-reversal symmetry has been mentioned [12,17].

In order to describe the optical properties of such planar structures, one may introduce the concept of a two-dimensional (2D) chiral object [15], which cannot be brought into congruence with its mirror image by in-plane rotations or translations and thereby possesses a sense of twist. One may expect that the polarization eigenstates of 2D structures composed of such objects would be circularly polarized. However, a peculiarity is that when observed from the back side instead of the front, the sense of twist of a 2D object is reversed. This suggests a nonreciprocal polarization rotation similar to that observed in the Faraday effect [14]. Nonreciprocity is related to the question of time-reversal symmetry of light-matter interaction [17]. However, these fundamental symmetries have only been discussed in the context of diffraction and colored imaging experiments [12,17]. Since these experiments involved beams propagating in different directions and including several spectral components, they do not address the reciprocity issue directly. The rotation of the polarization azimuth of a wave transmitted through a subwavelength grating has been reported in Ref. [13]. However, this

work was limited to a single wavelength, only one sense of twist of the sample, and one incidence. That is, in this experiment the influence of the surface plasmons on the circularly polarized eigenstates and reciprocity of the observed polarization effects could not be addressed. In order to clarify the mechanism responsible for the observed polarization effects in chiral nanogratings, one needs to perform transmission measurements in a wide spectral range at normal incidence in the direct and reciprocal scenarios.

In this Letter, we perform a spectroscopic study of the polarization properties of arrays of chiral gold nanostructures placed on a dielectric substrate and organized in a two-dimensional grating with a period smaller than the incoming light wavelength so that no diffraction takes place. The gratings with approximately 100 nm metal thickness are shown to exhibit giant specific rotation, which has opposite sign for structures with left- and right-hand twist. Measurements for light incident on the front (air-metal interface) and back (substrate-metal interface) sides of the samples reveal that the polarization phenomenon is reciprocal. This implies that polarization phenomena in planar chiral structures are due to the three dimensionality of the sample. Surface-plasmon-enhanced light-matter interaction results in significant 3D nonlocal optical effects seeded by the small but finite asymmetry at the air-metal and substrate-metal interfaces. The results are supported by numerical calculations as well as by fundamental symmetry arguments.

By using electron-beam lithography and argon sputter etching steps, we manufactured gratings with 500 nm period formed by a square lattice of metal nanostructures on a fused silica substrate. The chiral and achiral nanostructures having an 80 nm linewidth were composed of a 95 nm gold layer topped by 23 nm of chromium (see insets to Fig. 1). Since all gratings were designed to possess fourfold rotational symmetry about the substrate normal, the transmission coefficients for orthogonal linear polarizations should be the same. However, due to a slight astigmatism of the electron beam, the real samples exhibit some anisotropy.

Measurements were performed using Xe and W lamp as light sources and applying the polarization modulation technique with a photoelastic modulator [18,19]. Transmission spectra (Fig. 2) were measured using unpolarized light. They reveal the resonance features in the spectral range 600–800 nm, in which the optical response is governed by plasmon modes. The spectral positions of resonances are seen to be nearly the same for both chiral and achiral gratings. This is an expected result because all gratings were manufactured on the same substrate, had the same period and the same composition and thickness as the metal layer. The higher transmittivity of the achiral grating is mainly because its metal particles are smaller than those in the chiral ones.

To discriminate polarization effects that originate from the specific sense of twist of the structures and their residual anisotropy, we measured the polarization azimuth rotation and ellipticity of the transmitted light beam as a function of the sample orientation. In the real samples (see Fig. 1), the anisotropy caused by the nonequivalence of the X and Y axes manifests itself as oscillation in the azimuth

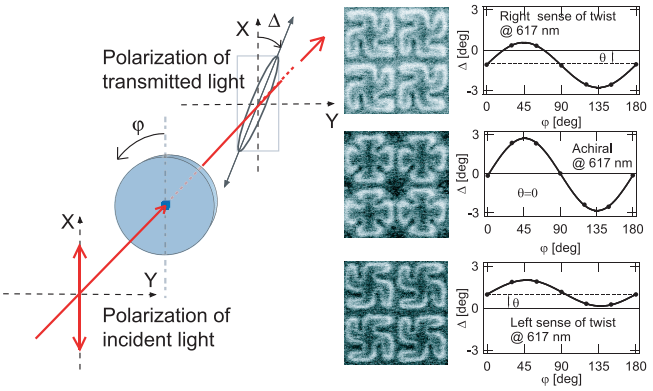

FIG. 1 (color). Experimental scheme and achiral, left- and right-hand twisted grating. Light from xenon (350–700 nm) and tungsten (600–1100 nm) lamps was unpolarized for transmission measurements and vertically linearly polarized for polarization measurements. Examples of the measured dependence of the polarization azimuth rotation angle Δ on the substrate angle φ is shown in insets. For the chiral gratings, the offset θ, which is a measure of chirality, is expected to be nonvanishing and to have opposite sign for structures with left- and right-hand twist.

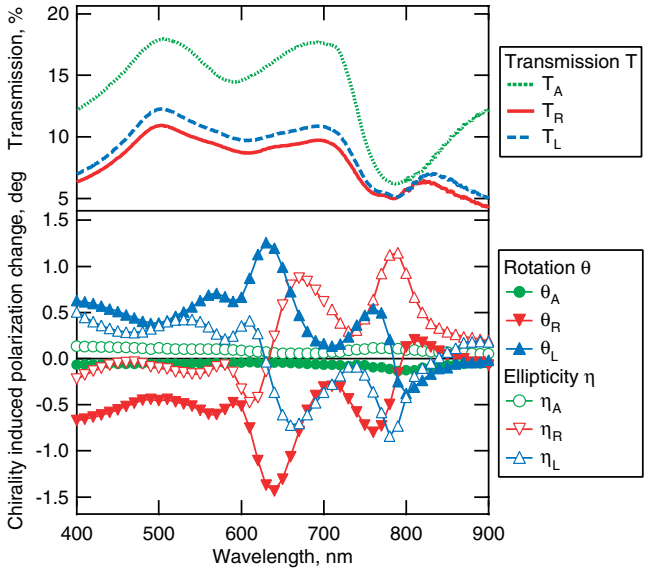

FIG. 2 (color). Transmission (top) and chirality-induced polarization azimuth rotation and ellipticity (bottom) spectra of the achiral (subscripts A), left- (L), and right-hand (R) twisted gratings of a 95 nm gold layer topped by 23 nm of chromium. Spectra exhibit plasmon resonances in vicinity of 600 nm and 800 nm. Polarization azimuth rotation θ (solid triangles) and ellipticity η (open triangles) have the same magnitude but opposite sign for the gratings with the opposite twist.

rotation and ellipticity with a period of 180°. The magnitude of the oscillations corresponds to the differences in the effective absorption coefficient and refractive index for orthogonal linear polarizations. The offsets θ and η of the average position of polarization azimuth rotation and ellipticity from zero correspond to the chirality-originated differences in the effective absorption coefficient and refractive index for the two circularly-polarized components. They are called therefore the chirality-induced polarization azimuth rotation and ellipticity, respectively.

One can observe from Fig. 2 that θ and η are close to zero for the achiral grating, and have the same magnitude but opposite sign for gratings with left and right senses of twist. The measured polarization azimuth rotation and ellipticity angle are of the order of 1° and have a strong frequency dependence characteristic of surface-plasmon enhancement. This clearly indicates the potential of such planar structures in nanoscale polarization control. By varying the nanostructure height we found that the polarization rotation increases with the metal layer thickness. If we introduce the specific rotation, which is conventionally used to characterize bulk chiral materials, its magnitude reaches an anomalously high value of $10^{4^\circ}/\mathrm{mm}$ and also varies with the metal thickness. This is at least partly due to the dependence of the photon-plasmon coupling on the height of the nanostructure. However, the quantitative description of this phenomenon is beyond the scope of the present Letter in which we discuss the fundamental symmetry properties of the polarization effect.

Another important experimental result is that both θ and η remain the same independent of whether the light is incident on the front or back side of the sample. This indicates that the observed effect is *reciprocal* and that the polarization state of light would be restored by double pass in opposite directions through the chiral nanogratings. Such a symmetry property suggests that, even in thin quasi-2D planar structures, the observed polarization effects manifest 3D optical activity analogous to that observed in quartz crystals. The important difference, however, is that the specific rotation of the nanogratings is about 3 orders of magnitude larger than that of quartz [14].

Qualitatively, our results can be understood in terms of the Kuhn model [14], which is widely used to describe optical activity of chiral molecular media. In this model, the molecule is represented by two nonparallel coupled oscillators displaced by a finite distance. In our samples, the incident light is converted into surface plasmons at the first metal-dielectric interface and then back at the second one. The role of the Kuhn oscillators can therefore be assigned to the plasmon oscillations at the two interfaces. The finite metal thickness already separates the plasmons along the sample normal. However, it is evident, based on symmetry considerations, that for a sample with high rotational symmetry about the surface normal but no twist, the two plasmons must oscillate in the same direction and cannot give rise to polarization rotation. In our case, the twist as well as the different properties of the two interfaces ensure that the two plasmons oscillate in different directions and polarization rotation can occur. The polarization rotation in planar gratings can also be seen as a manifestation of a mesoscopic mechanism for optical activity, which is due to the asymmetry of the nanostructured metal-dielectric interfaces. It is very different from the microscopic mechanism of chirality that occurs in a bulk medium and originates from the symmetry of the electronic wave functions.

Quantitatively the observed polarization phenomenon can be described in terms of a rigorous diffraction theory by numerically solving the electromagnetic boundary value problem for the entire structure [11]. Figure 3 shows the calculated transmission and rotation spectra for chiral nanostructures manufactured from gold stripes of 100 nm height and 80 nm width of the substrate. Since we did not account for the 23 nm thick Cr layer, the obtained absolute values do not exactly match the experimental ones. Calculations also reveal a fine structure of the plasmon resonance that was suppressed in the experimental spectra. In an ideal gold grating, our calculations predict a shift of the spectral position of the maximum rotation (590 nm) with respect to the plasmon resonance (550 nm) as one may expect for conventional optical activity [14]. The calculations also reveal that a linearly polarized light field incident on one interface will acquire new polarization components at the second one, in agreement with the Kuhn model.

Our calculations also show that the polarization effect vanishes when the sample becomes mirror symmetric along the sample normal, i.e., when the grating is sandwiched between two identical dielectric substrates. In other

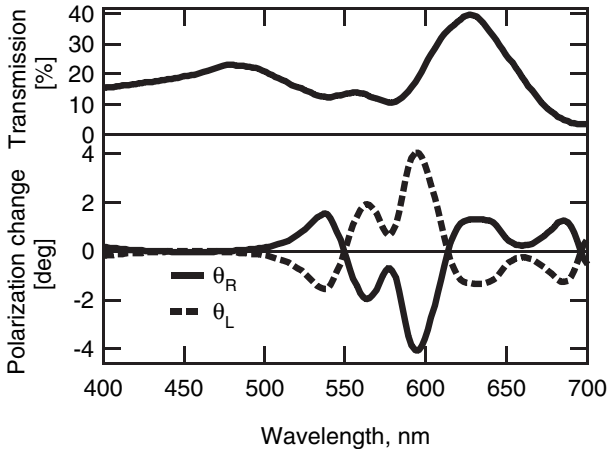

FIG. 3. Calculated transmission (top) and polarization azimuth rotation (bottom) spectra for right- and left-twisted gratings composed of 80 nm linewidth gold nanostructures of 100 nm height on the fused silica substrate. Both gratings show the same transmission but opposite polarization azimuth rotation.

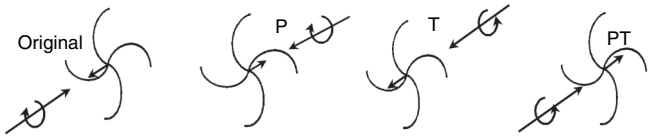

FIG. 4. Interaction of a 2D chiral object on a substrate (normal indicated by the arrow) with circularly polarized light and its transformation under P, T, and combined PT.

words, the grating changes the polarization of light in transmission only when all reflection planes are removed. However, the polarization effect is always reciprocal resembling conventional optical activity in bulk media.

Fundamental symmetry arguments also support our results regarding the role of dimensionality in the polarization effects. To see this, we consider the interaction of a left-hand circularly polarized wave with a 2D object with right sense of twist placed on a transparent substrate (Fig. 4). The substrate breaks the mirror symmetry and thus defines a unique third direction, the normal vector $\vec{n}$. The invariance of the light-matter interaction with respect to combined space and time inversion (PT invariance) ensures that a right-hand circularly polarized wave applied from the other side of the substrate will interact the same way with a 2D object with left sense of twist. However, when we remove the substrate (i.e., the vector $\vec{n}$) and consider a 2D structure, the PT invariance implies that both left- and right-hand circularly polarized waves will interact identically with the object leaving no room for any polarization effect. That is, any polarization sensitivity must arise from the 3D character of the structure, i.e., from the presence of the air-metal and substrate-metal interfaces. Moreover, since neither P nor T should be violated in optics, space- and time-reversed scenarios should also be equivalent to the original ones. One can observe from Fig. 4 that the time-reversed scenario corresponds to light incident on the back side of the sample, i.e., time-reversal symmetry alone implies reciprocity of light propagation. Therefore, experimentally observed reciprocity implies invariance of the light-matter interaction with respect to both P and T inversion.

In conclusion, we have demonstrated giant specific rotation of polarization when light is transmitted through chiral nanogratings at normal incidence and without diffraction. The giant polarization effect arises from the enhancement of light-matter interaction through surface plasmons whose velocity is much lower than that of photons. Since the light is converted into plasmon wave at the first interface and recovered at the second interface [4,5], the light wave acquires a large phase shift during transmission through the metal grating of nanoscale thickness. Our results therefore show that optical activity in planar structures originates from the 3D nature of the grating, and does not violate time-reversal symmetry. The polarization effect is reciprocal and vanishes as soon as we introduce a symmetry plane that coincides with the plane of the grating. The interpretation of recent diffraction and imaging experiments in planar chiral structures therefore does not require violation of time reversality assumed in Refs. [12,17]. The demonstrated giant specific rotation with subwavelength chiral structures indicates their strong potential for controlling polarization, which is crucial for various photonics applications.

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