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Plasmonic Ratchet Wheels: Switching Circular Dichroism by Arranging Chiral Nanostructures

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ABSTRACT

We demonstrate circular dichroism (CD) in the second harmonic generation (SHG) signal from chiral assemblies of G-shaped nanostructures made of gold. The arrangement of the G shapes is crucial since upon reordering them the SHG-CD effect disappears. Microscopy reveals SHG "hotspots" assemblies, which originate in enantiomerically sensitive plasmon modes, having the novel property of exhibiting a chiral geometry themselves in relation with the handedness of the material. These results open new frontiers in studying chirality.

Recently, the research on metamaterials has revealed several new electromagnetic phenomena, such as artificial magnetism and negative refraction,[1] extraordinary transmission,[2] cloaking,[3] and asymmetric transmission.[4] The intriguing optical properties of metallic nanostructures are of great current interest both for fundamental reasons and for practical applications.[5−8]

One of the most significant phenomena responsible for the spectacular advances in the field of nanophotonics is the field intensity enhancement which is observed in the immediate nanoscale surroundings of the nanoparticles. This enhancement results from, on the one hand side, the collective oscillations of electrons within the structures, which are known as surface plasmon resonances, and on the other hand, from the crowding of electric field lines in sharp curvatures, known as the electrostatic lightning rod effect.

While most of the research interest so far has focused on linear properties, there is a growing body of experimental studies of nonlinear behaviors.[9−14] Among them, second harmonic generation (SHG) is well-known for being surface and interface sensitive on the atomic level and is therefore very appealing for studies of the nonlinear optical properties of metal nanostructures.[15] Especially since, in the latter, large optical resonances and high surface-to-volume ratio favor greatly the technique. SHG is particularly suitable for granting insight into the interdependence of optical properties and the nanoscale morphology such as, for instance, chirality.

Indeed, chiral symmetry breaking has recently been reported from small defects in nanostructures.[16−19] Furthermore, using modern lithography techniques, planar chiral nanostructures were constructed.[20,21] This type of structure has recently attracted a lot of interest, as negative refractive index in chiral metamaterials was predicted[22] and reported.[23,24]

Here we demonstrate the presence of circular dichroism (CD) at the supraelement level, in the SHG signal from chiral nanostructures consisting of G-shaped elements made of gold. The arrangement of the nanostructures plays a crucial role since upon reordering them the SHG-CD effect vanishes. This new property can be ascribed to the particular positioning of the plasmon resonant modes in the structures, as explicitly evidenced by SHG microscopy. It is shown that the SHG signal originates in SHG "hotspots". Furthermore, depending on the handedness of the nanostructures, the SHG sources exhibit a ratchet wheel pattern with a different sense of rotation. This allows for the unprecedented possibility to optically determine the handedness of a material by observing it with a single circularly polarized light; i.e., no comparison with another handedness or another direction of the circularly polarized light is necessary.

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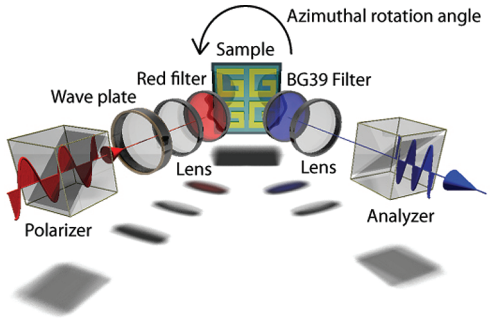

Figure 1. Diagram of the experimental setup for measuring the SHG-CD.

The samples consist of an array of nanostructures defined by electron-beam lithography, Au (25 nm) deposition, and standard lift-off procedure. The resulting periodic array of G-shape and mirror-G-shape structures lies on top of a Si(100)/SiO_2 substrate. The SiO_2 layer thickness was 200 nm. Figures 2a, 2b, and 3a show the three chiral structures investigated. The lateral size of each individual motif is 1 μm, the line width is 200 nm, and the separation between neighboring structures is 200 nm. The whole array covers an area of 2.5 $\times$ 2.5 mm^2. SHG-CD measurements were performed with a Mai-Tai femtosecond laser system at a wavelength of 800 nm. The initial beam polarization was set by means of a Glan-Thompson polarizer (see Figure 1). The rotation of a quarter wave plate modulated the polarization from left- to right-circularly polarized states. The fundamental light, having a power of 150 mW, was focused on the sample to a spot approximately 40 μm in diameter. The sample was mounted on a motorized rotation stage. The angle of optical incidence on the sample was 45°. After reflection, the second harmonic was filtered through a BG39 filter, while the 800 nm radiation was blocked. The beam then passed through an analyzer and reached a XP2020 photomultiplier tube. Please note that only the zeroth order of diffraction was studied. SHG microscopy images were collected with a confocal laser scanning microscope, Zeiss LSM 510 using a femtosecond pulsed Ti:sapphire laser directed to the sample by a dichroic mirror and a Zeiss 100×/1.46 oil immersion objective.[25] Circularly polarized light was obtained by inserting a quarter-wave plate between the scan head and the objective.

Parts c and d of Figure 2 show the SHG response as function of the quarter wave plate rotation angle, from the chiral structures in Figure 2a and Figure 2b, respectively. The measurement procedure consisted of recording a SHG pattern for different sample orientations. This method takes advantage of the fact that chirality is unaffected by rotation while anisotropy averages out. In all, 36 SHG patterns were recorded and averaged, each taken in steps of 10° azimuthal rotation of the sample. At 45° and 135°, the quarter wave plate produces right and left circularly polarized light, respectively. The obtained data show a clear difference in SHG efficiency for left and right circularly polarized light. As expected, this circular dichroism reverses upon changing the handedness of the sample.

Surprisingly, no SHG circular dichroism was observed

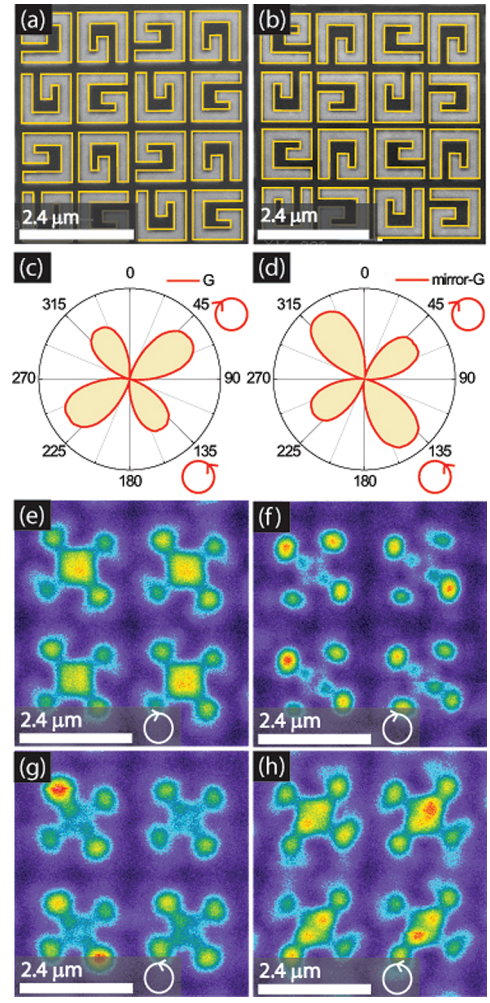

Figure 2. In (a) and (b), SEM pictures of the samples with G- and mirror-G-shape structures. The yellow lines have been added around the edges of the structures in order to improve the visibility. In (c) and (d), the SHG intensity as function of the angle of rotation of a quarter wave plate. The oriented circles indicate the directions for left- and right-hand circularly polarized light. The polarizer−analyzer combination was P−S. SHG microscopy images are shown dependent on the direction of circularly polarized light in (e) and (g) for the G samples and in (f) and (h) in the mirror-G samples. The color-coded intensities increase from purple, through yellow to red.

from the sample shown in Figure 3a; see Figure 3b. This was also verified upon reversing the handedness; these data are not shown here since they are essentially the same.

In order to understand the source of the SHG from our samples, SHG microscopy was performed. Parts e and g of Figure 2 show the microscopy images obtained from the sample in Figure 2a. We can see arrays of SHG "hotspots" assembled in different patterns, depending on the direction of incoming circularly polarized light. Noticing the scale in these figures, we observe that the dimensions of a single pattern correspond to the size of a unit cell constituted of four G (or mirror-G) elements. In particular, in Figure 2e, the SHG sources form a rather homogeneous central square that connects all four Gs in the structure's unit cell; see Figure 2a. Surrounding the square are four "hotspots", which exhibit a comet-like shape that leads to an overall ratchet wheel

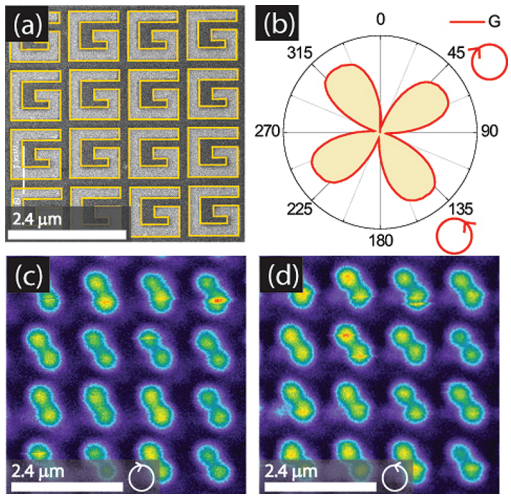

Figure 3. In (a), SEM picture of the samples with G-shape structures. The yellow lines have been added around the edges of the structures in order to improve the visibility. In (b), the SHG intensity as function of the angle of rotation of a quarter wave plate. The oriented circles indicate the directions for left and right circularly polarized light. The polarizer−analyzer combination was P−S. In (c) and (d), the SHG microscopy images for the sample illuminated with right and left circularly polarized light, respectively.

pattern. Upon reversal of the direction of circularly polarized light, in Figure 2g, the central square part appears to be depleted while the SHG sources in the four surrounding hotspots brighten. All of these features reverse with respect to the direction of incoming circularly polarized light upon imaging the opposite handedness; see parts f and h of Figure 2. Especially, it should be noted that the direction of the ratchet wheel changes from Figure 2a to Figure 2h.

The SHG "hotspots" themselves originate from the plasmon modes in the nanostructures, most likely in the regions of high charge density. It is therefore apparent that the SHG-CD observed in the far field experiments originate in enantiomerically sensitive plasmon modes, which are excited in the structures for left- and right-hand circularly polarized light. In particular, we find that, for the Gs, a ratchet wheel shaped plasmon is excited with right-hand circularly polarized light, while for the mirror-Gs a ratchet wheel with opposite sense of rotation is excited with left-hand circularly polarized light.

Regarding the absence of SHG-CD in Figure 3b, we must consider that this might result from a destructive interference between the radiating elements in our samples, occurring, for instance, at the particular angle of optical incidence that was used. In order to eliminate this possibility, SHG microscopy at normal incidence was performed and the results are displayed in parts c and d of Figure 3. In each figure, two clearly distinguishable SHG sources appear to be situated on each G; however, there is no noticeable difference in intensity or pattern between the two figures for right- and left-hand circularly polarized light. There was also no difference upon imaging the opposite handedness; these results are again not shown since they are essentially redundant. Parts c and d of Figure 3 unambiguously establish that the absence of SHG-CD occurs at the radiating level itself and is not far field specific. Furthermore, the data demonstrate that the arrangement of the nanostructures is decisive for the SHG-CD effect. Indeed, for the particular geometry in Figure 2, plasmon modes can be excited across the unit cell of four Gs (or mirror-Gs), while for the geometry in Figure 3 this is clearly not the case.

Please note that the effect of enantiomerically sensitive plasmon modes has already been observed in linear optics[26] and that recent theoretical advances suggest that it could soon be possible to relate classical optical calculations to SHG-CD properties.[27] Nevertheless, it should be emphasized that in our case the plasmon is not only enantiomerically sensitive but appears to be, itself, of chiral geometry.

In conclusion, we presented a counterintuitive relationship between chirality and circular dichroism. We demonstrated the presence of CD at the supraelement level in the SHG signal from chiral nanostructures consisting of G-shaped elements made of gold. It was shown that the source of SHG constitutes an assembly of "hotspots", which originate in the plasmon modes propagating in the nanostructures. It was established that the arrangement of the nanostructures is crucial for the expression of SHG-CD. SHG microscopy revealed that SHG-CD is attributed to suprastructural plasmon modes, which exhibit a ratchet wheel shape with direction of rotation that depends on the handedness of the material. These results open new avenues of exploration for the relationship between chirality and circular dichroism, a subject which is of great current importance in metamaterials.

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