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# Strong Rotational Anisotropies Affect Nonlinear Chiral Metamaterials

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Because of their lack of mirror symmetry, chiral meta/ nanomaterials<sup>[1,2]</sup> have recently enabled several remarkable phenomena, such as negative refractive index,<sup>[3]</sup> superchiral light,<sup>[4]</sup> enhanced enantiomeric chemical sensing,<sup>[5]</sup> and use as broadband circular polarizers<sup>[6,7]</sup> or detectors.<sup>[8]</sup> In all of these cases, key for the performance of the materials are their characteristic chirality parameters. These parameters can be probed with both linear and nonlinear chiroptical (chiral-optical) techniques. The latter have an advantage because nonlinear chiroptical effects are known for being much more pronounced than their linear optical counterparts.<sup>[9-11]</sup> Moreover, nonlinear chiroptical effects address a different aspect of chirality and can therefore provide complementary information to that from linear chiroptical effects. For instance, linear circular dichroism (CD) originates from the interaction of electric and magnetic dipoles. Its nonlinear counterpart-second harmonic generation circular dichroism (SHG-CD)-can be sensitive to chirality purely in the electric dipolar response and does not require nonlocal effects. This sensitivity to chirality originates from the fact that the three electromagnetic fields involved in secondorder optics can probe the three directions of space.<sup>[12]</sup> It is therefore possible to use nonlinear chiroptical techniques to discriminate between local and nonlocal (magnetic) contributions.<sup>[13,14]</sup> Additionally, there are nonlinear chiroptical effects that do not have a linear optical counterpart. The need for complementary chiroptical techniques is particularly poignant in the cases of complex interactions. This is, for instance, the case in superchiral light enhancement of molecular properties near plasmonic nanostructures. Indeed, in such a case, the chirality of the electromagnetic fields of light, that of the nanostructures, and that of the molecules all play a role and need to be disentangled. However, whereas the link between linear chiroptical response and the chirality parameter has been clearly established, in the nonlinear case this is far from being achieved. The sensitivity advantage of the nonlinear response leads to

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complications as the technique can become too sensitive, making it difficult to separate the desirable and undesirable contributions to the SHG signal. An example of an undesirable complication is extrinsic chirality,<sup>[15,16]</sup> which affects the non-linear susceptibility tensor components in SHG.<sup>[17,18]</sup> Any anisotropy present in the sample can have a similar effect and our work here focuses on highlighting the effects of rotational anisotropy. We begin by selecting the sample geometry.

Chirality is intrinsically a 3D property; however, a great number of works have focused on so-called "planar" nanostructures. A few recent examples include S-shaped nanostructures,<sup>[19,20]</sup> three- and fourfold symmetric propellers,<sup>[21]</sup> and heptamers.<sup>[22]</sup> These planar chiral nanostructures are very attractive because of their ease of fabrication with electron beam lithography. The necessary 3D symmetry-breaking arises from a dissymmetry along the axis perpendicular to the sample plane,<sup>[23]</sup> for instance, due to the presence of a substrate on one side of the sample and air on the other. Although planar meta/nanomaterials are thus 3D, it is clear that their threedimensionality is not very pronounced. At optical frequencies, various 3D structured meta/nanomaterials have been proposed, such as rosettes,<sup>[24,25]</sup> twisted arcs,<sup>[26]</sup> 3D shuriken,<sup>[27]</sup> stacked split rings,<sup>[28,29]</sup> oligomers,<sup>[30,31]</sup> gyroids,<sup>[32]</sup> and helices.<sup>[33-36]</sup> Of all these examples, the latter (i.e., the helix) is the archetypical chiral structure. The strong interaction of nanohelices with circularly polarized light (CPL) gives rise to large chiroptical effects, such as circular dichroism. This makes them attractive for applications involving CPL.<sup>[6,8,37–39]</sup> Thus, the nonlinear optical response of helical metamaterials is of particular interest as they already demonstrate strong linear chiroptical effects. However, until recently it has been very difficult to fabricate high quality helical metamaterials for use at optical frequencies.

Herein, we have investigated a chiral metamaterial made of nanohelices, with substantially subwavelength dimensions  $(\langle \lambda/10 \rangle)$ . As the archetypical chiral geometry, the helical design is particularly suitable because it is pronouncedly 3D, it gives rise directly to superchiral field configurations along the center of the helix, and its structural chirality parameter is straightforward to estimate as a function of varying dimensions.[33,40] Within this metamaterial, we clearly identify three different rotational anisotropies and demonstrate how they can mask the true chiral effect, rendering the SHG-CD signals unreliable. Our experimental results highlight the need for a general method to extract the true chiral contributions to the SHG signal. Here, we use a method for approximating these contributions. Although not fully rigorous, this method yields three measures of the chirality: averaged SHG-CD, direct inspection of the chiral component of the effective susceptibility tensor, and evaluation of the chiral coefficients that, as we show, can be deduced from a fit to the data. All three measures are shown to be in agreement.



The nanohelices are grown using a combination of block copolymer micelle nanolithography and dynamic oblique angle deposition.<sup>[41]</sup> Micelles with Au nanoparticle cores are spincoated onto the substrate. Plasma etching then embeds the seeds into the substrate creating a quasihexagonal array. The seeded substrate is mounted at an oblique angle and rotated during the evaporation process in order to fabricate the helices by shadow growth. **Figure 1**a shows the dimensions of the nanohelices under investigation, which have a pitch of 37 nm, height of 81 nm, wire thickness of 18 nm, inner diameter of 28 nm, and outer diameter of 55 nm. A representative scanning electron microscopy (SEM) cross section of a wafer containing right-handed (RH) nanohelices is also shown. Both left- and right-handed nanohelices are investigated experimentally.

Our experimental setup is designed in order to reveal contributions from all the nonlinear susceptibility tensor elements and it is shown in Figure 1b. Pulsed laser light with a central wavelength of 800 nm and a pulse width of 100 fs is linearly polarized to give either S (vertical) or P (horizontal) polarizations. Light then passes through a quarter-wave plate (QWP) that is mounted on an automatic rotation stage and rotates in steps of 5°. After the QWP, an optical filter (BG39) removes extraneous SHG from the beam that is then focused to a spot size of  $\approx$ 50 µm on the sample. The sample itself is mounted on an automatic rotation stage and is rotated in steps of 3° during the experiments. The angle of optical incidence is 45°. Reflected light is filtered to block the fundamental beam and collimated with a lens. An analyzing polarizer (analyzer) selects either the S- or P-polarized components of the 400 nm SHG signal. The SHG is detected with a photomultiplier tube, whose



**Figure 1.** Nanohelices and experimental configuration. a) Profile and top-down schematics of left-handed nanohelices showing sample dimensions with side on SEM of right-handed nanohelices. b) Experimental setup for continuous polarization measurements of the SHG. Averaging the measurements over all azimuthal orientations mimics the response of an isotropic sample.

electron pulses are first preamplified and then detected with a gated photon counting system. Upon rotation of the QWP, we perform what is known as a "continuous polarization measurement"<sup>[42]</sup> that can very clearly reveal the presence of anisotropies when combined with sample rotation.

Because continuous polarization measurements are much more sensitive in the case of SHG than in the linear optical case, we reveal clear one-, two-, and threefold anisotropies in the samples. Furthermore, we identify the origins of these anisotropies. For each set of continuous polarization measurements, the polarization-anisotropy can be mapped as in Figure 2a.<sup>[43]</sup> The map shows how the reflected linear optical intensity  $(\lambda = 400 \text{ nm})$  depends on the sample's azimuthal angle (on the y axis) and on the QWP angle (on the x axis). Along the QWP axis, since an analyzer is present after the samples, Figure 2a shows that the brightest intensity is detected when incident light is linearly polarized along the direction of the analyzer, as we would expect. Along the sample rotation axis we can see a unidirectional anisotropy, which is due to end termination of the nanohelices. The CD effect appears very small: at 400 nm, the difference in reflected light for right and left CPL, normalized by their sum, is of the order of 0.01 (see CD spectrum in Figure S1 of the Supporting Information). By contrast, the SHG continuous polarization maps are much more revealing.

For the SHG measurements, the detected light was also at the wavelength of 400 nm and illumination was at 800 nm. The reflectance spectrum of a typical sample is shown in Figure 2b. Figure 2c shows a map of the continuous polarization measured, performed with SHG. The red dashed lines on the anisotropy map in Figure 2c show where the incident fundamental beam is linearly P- polarized. SHG response (averaged along all four red dashed lines in Figure 2c) gives the polar plot in Figure 2d, where the angular axis is the sample azimuthal angle. A clear onefold anisotropy is observed that can be attributed to the end of the helices, which all have identical orientation in our sample. For the S-in P-out polarizer-analyzer configuration, the polar plot in Figure 2e shows a twofold anisotropy. This anisotropy can be ascribed to the electric dipole originating from the end of the helix. The influence of such dipoles has recently been addressed in the literature.<sup>[34,44]</sup> In addition to the twofold anisotropy of these dipoles, a threefold anisotropy can also be observed. In Figure 2c, incident left CPL light is indicated with green dashed lines and the corresponding SHG response is shown as a polar plot in Figure 2f. A clear threefold anisotropy is evident and it is associated with the quasihexagonal array of the helices on the sample surface. The polarization-anisotropy maps for both left- and right-handed nanohelices can be found in Figures S2-S5 (Supporting Information) along with polar plots for specific incident-detection polarization configurations.

The anisotropies have a dramatic effect on the SHG chiroptical response of the chiral metamaterials. This is evidenced by the SHG-CD when studied as a function of azimuthal sample rotation. Both P- and S-polarization components of the SHG intensities are recorded for left and right CPL incident on the sample. The normalized SHG-CD is calculated as<sup>[9,18,42]</sup>

$$SHG - CD_{P/S} = \frac{I_{P/S}^{RCP} \left(2\omega\right) - I_{P/S}^{LCP} \left(2\omega\right)}{I_{P/S}^{RCP} \left(2\omega\right) + I_{P/S}^{LCP} \left(2\omega\right)}$$
(1)







**Figure 2.** SHG continuous polarization measurements for the right-handed nanohelices are much more sensitive than linear optical ones. a) Polarization–anisotropy color map of linear intensity ( $\lambda$  = 400 nm) for sample angle and QWP angle. P-in P-out refers to the position of the polarizer and analyzer, respectively. b) Reflectance spectrum of the right-handed helices. c) Polarization–anisotropy color map of SHG intensity for sample angle and QWP angle. The red dashed lines indicate linearly polarized light incident on the nanohelices. The green dashed lines indicate left circularly polarized light incident on the nanohelices. d–f) SHG intensity of nanohelices as a function of the sample azimuthal orientation for different polarizer and analyzer combinations, as shown above.

where  $\omega$  is the frequency of light and  $I_{P/S}^{RCP/LCP}(2\omega)$  is the intensity of the SHG, with superscripts denoting the handedness of incident CPL and subscripts referring to the polarization component of the signal. In our samples, the SHG-CD as a function of sample azimuthal rotation is shown in **Figure 3**, for both left- and right-handed helices. The opposite chirality of the two samples is apparent as their SHG-CD profiles are mirror images of each other. However, it is also very clear that the SHG-CD changes its value across the full range (1–0), reaches zero, and even reverses sign depending on the angular position

of the sample. This reversal is not because the chirality of the sample reverses as the substrate is being rotated, but is due to the anisotropy contributions described above. Measuring the SHG-CD from a chiral sample, without taking into account sample orientation, is therefore an insufficient way to evaluate the nonlinear chiroptical response of a chiral metamaterial.

However, the chiral contribution to SHG can be better approximated from an effective isotropic chiral metasurface. By definition, an isotropic chiral surface (i.e., isotropic in the plane) does not depend on angular position. The effective response

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**Figure 3.** Normalized SHG-CD for left-handed (top) and right-handed (bottom) nanohelices as a function of the sample azimuthal angle. S-polarized (orange circles) and P-polarized (blue circles) components of sample response.

from an isotropic chiral surface can be created by averaging the continuous polarization measurements over all sample rotations. In **Figure 4**, the SHG intensity is plotted as a function of quarter-wave plate rotation angle for the right-handed helices (in red) and the left-handed helices (in green). The four panels correspond to the four principal polarizer–analyzer configurations, which are indicated by the corresponding experimental diagrams, for clarity. It should be noted that this method is not strictly rigorous; however, it does produce results that are consistent. Indeed, from these data it is possible to extract three different measures of the chirality that are all in good agreement.

From Figure 4, SHG-CD can be accurately measured. The positions of the quarter-wave plates corresponding to CPL are indicated with oriented circles on the Figure. The obtained SHG-CD values are shown in **Table 1** and, as they are large, they indicate a strong SHG contribution from chirality.

Another way to evaluate the chirality is by measuring the SHG intensity in the P-in S-out polarizer–analyzer configuration. Within the electric dipole approximation, the SHG intensity is directly proportional to the chiral tensor component of the nonlinear susceptibility. In Figure 4, the S-polarized SHG intensity (S-out) is plotted in the bottom left panel and P-in corresponds to the quarter-wave plate position along 0°, 90°, 180°, 270°, and 360°. The SHG intensity at these points is 100 counts s<sup>-1</sup>, which is nearly 50% of the maximum SHG intensity in any polarizer–analyzer configuration. Therefore, this second way to measure SHG also indicates a strong SHG contribution from chirality. The exact contribution to the SHG signal from the chiral tensor element compared to the achiral elements can be determined from fitting all the data in Figure 4. Our fits are plotted with solid lines on the figure. Using a well-established formalism,<sup>[42,45,46]</sup> the SHG intensity can be expressed as

$$I(2\omega) = \left| f E_{\rm P}^2(\omega) + g E_{\rm S}^2(\omega) + h E_{\rm P}(\omega) E_{\rm S}(\omega) \right|^2$$
(2)

where  $E_{\rm P}$  and  $E_{\rm S}$  are the P- and S-polarized components of the incident fundamental fields, respectively. The coefficients *f*, *g*, and *h* are each linear combinations of complex second order susceptibility tensor elements. For an isotropic chiral surface these elements are  $\chi_{zxx} = \chi_{zyy}$ ,  $\chi_{zzz}$ ,  $\chi_{xyz} = -\chi_{yzx}$ ,  $\chi_{xzx} = \chi_{yyz}$ , leading to

$$f_{s} = -2\sin(\theta)\cos(\theta) \chi_{xyz}$$

$$g_{s} = 0$$

$$h_{s} = 2\sin(\theta) \chi_{yyz}$$

$$f_{P} = \sin(\theta) \left[\cos^{2}(\theta) \chi_{zxx} + \sin^{2}(\theta) \chi_{zzz} - 2\cos^{2}(\theta) \chi_{xxz}\right]$$

$$g_{P} = \sin(\theta) \chi_{zxx}$$

$$h_{P} = -2\sin(\theta)\cos(\theta) \chi_{xyz}$$
(3)

where  $\theta$  is the angle of incidence, z is the direction along the surface normal, and the subscripts P and S indicate the measured polarization state of the SHG intensity. From these expressions it can be seen that the coefficients  $f_{\rm S}$  and  $h_{\rm P}$  depend only on the chiral tensor component. Finding values for these coefficients, by fitting to the data, allows the chiral contribution to the SHG to be quantified without the effect of rotational anisotropy.

Values for the best fits are shown in **Table 2**. The fitting procedure only gives information about the relative magnitude and phase of the tensor components. It is for this reason that the chiral coefficients are chosen to be real. Therefore, the phases of all other tensor components are relative to the chiral coefficient and the absolute magnitude of the chiral contribution is easier to extract. The fitting coefficients are subjected to strong restrictions. The results from both samples were fitted simultaneously, forcing all of the achiral coefficients in the left-handed helices to have the same value and sign as in the right-handed helices. The chiral coefficients were left free to account for the fact that left- and right-handed helices are physically different samples, where minor variations in the fabrication are to be expected. As Table 2 illustrates, both the left- and right-handed helices yield strong and opposite chiral coefficients.

Although the fits follow the main features of the data very well, as confirmed by the *R*-squared data in Table S1 (Supporting Information), they are not perfect. There are several reasons for this: Very restrictive fitting constraints were used all achiral tensor components are identical for both samples, even though the samples are physically different, as they were prepared separately. Minor variations can also be expected due to the measurement procedure, where the laser spot does not remain exactly in the center of the rotation axis and consequently travels through slightly different regions where occasional fabrication defects can be present. The measurements themselves take up to 24 h and, during this time, laser intensity can fluctuate slightly. Such laser power fluctuations can also occur due to daily temperature variation in the lab.



**Figure 4.** Continuous polarization SHG measurements averaged over all azimuthal sample orientations. Polarizer–analyzer configurations are shown above and below graphs. Experimental (open circles) and theoretical fits (solid lines) results for reflected SHG of right-handed (red) and left-handed (green) nanohelices. Solid black grid lines indicate linearly polarized incident light. Dotted gray grid lines indicate circularly polarized incident light and handedness is denoted by arrows at the tops of the graphs.

Finally, while the fits are based on the dipole approximation, it is not to be excluded that a small contribution to the SHG signal is observed from higher order multipoles. This would show mainly where the signal is weakest, i.e., the S-in case, and indeed these lowest signals are least well reproduced by our fits.

Another potential source of imperfection for the fits is that our measurement procedure could, in principle, induce an extra anisotropy. Indeed, while the samples are rotated, the direction of light polarization remains the same. This direction could therefore become privileged, inducing a unidirectional anisotropy, especially if near-fields are resonantly enhanced and coupled between the nanostructures. In order to verify this possibility, we performed sample rotation measurements at normal incidence, where the polarization is parallel to the surface and the resulting anisotropy would be the strongest. The experimental setup diagram and the data are shown in Figure S6 of the Supporting Information. For both the left- and right-handed helices the data do seem to indicate a unidirectional anisotropy; however, in these experiments the data are oriented very differently. Because the illumination conditions were identical, this difference clearly demonstrates that the source of the SHG anisotropy is attributable to the structure of the samples.

As we have seen, extracting information on the chirality in SHG experiments is not trivial for an anisotropic surface. Here, we assume that the averaged SHG response can correspond to the response of an isotropic chiral surface. This is not necessarily always true and, even for an isotropic surface, there are

**Table 2.** Values for fitting coefficients for left- and right-handed nanohelix samples. Uncertainty of the fitting coefficients corresponds to standard deviation. Values without uncertainty are subject to constraints. The *R*-squared values for the fits are provided in Table S1 of the Supporting Information.

I H helices

 $f_{\rm P} = 3.6 (\pm 0.30) - i9.23 (\pm 0.15)$ 

 $g_{\rm P} = 2.3 (\pm 0.18) - i1.1 (\pm 0.19)$ 

| Table 1. | Averaged | SHG-CD | values | for | left- | and | right-handed | nanohelix |
|----------|----------|--------|--------|-----|-------|-----|--------------|-----------|
| samples  | i.       |        |        |     |       |     |              |           |

| samples.            |      |       |   | $h_{\rm P} = -7(\pm 0.12)$                     | $h_{\rm P} = 11.7(\pm 0.17)$ |
|---------------------|------|-------|---|--|------------------------------|
|                     | LH   | RH    | S | $f_{\rm S} = -7$                               | $f_{\rm S} = 11.7$           |
| SHG-CD <sub>p</sub> | 0.76 | -0.55 |   | $g_{\rm S}=0$                                  | $g_S = 0$                    |
| SHG-CD <sub>s</sub> | 0.82 | -0.77 |   | $h_{\rm S} = -2.97(\pm 0.32) + i9.7(\pm 0.17)$ | $h_{\rm S} = -2.97 + i9.7$   |
|                     |      |       |   |  |                              |

P

Signal polarization

**RH** helices

 $f_{\rm P} = 3.6 - i9.23$ 

 $g_{\rm P} = 2.3 - i1.1$ 



difficulties that should be pointed out. For instance, SHG-CD measures the squared sum/difference of chiral and achiral components, and it can therefore be increased by increasing the achiral contribution, just as well as by increasing the chiral contribution. The direct measurement of the chiral tensor component (P-in S-out) is only valid in the electric dipole approximation; higher order contributions can affect it. Finally, the fitting method used here can result in solutions that are not unique. All of these limitations clearly highlight the need for a general method to extract the true chiral contributions to the SHG signal.

In conclusion, the SHG response from metamaterial nanohelices is presented. The strong effects of anisotropy on the SHG are demonstrated by the polarization–anisotropy maps. Furthermore, rotational anisotropy is shown to dramatically affect the chiroptical effect of SHG-CD. Our results highlight the need for a general method to extract the true chiral contributions to the SHG signal. Such method would be highly useful, as SHG can probe the chirality in ways that are different and complementary to linear chiroptical measurements. As such, it will undoubtedly be indispensable, as nanofabrication techniques advance, to give us more sophisticated chiral metamaterials.

### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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