Chiral optical scattering from helical and twisted silica nanoribbons

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Helical and twisted silica nanoribbons, deposited in an in-plane direction and with a random orientation, on a quartz substrate showed chiral optical scattering, and the helical nanoribbons had a g-factor of the order of 10^{-2} below 250 nm. Their signs depend on the handedness of the nanohelices. The effect of the morphology and the orientation of the helices on the chiral optical scattering were investigated with simulations via the boundary element method.

The investigation of the chirality of solid materials has been the focus of intensive studies. While these studies have been performed mainly on crystalline and/or periodic structures,1 non-crystalline (non-ordered and non-periodic structures) materials also have the potential to show promising chiral properties.2 An interesting example is that of amorphous (non-crystalline) chiral silica synthesized via the sol–gel condensation of silica alkoxide with chiral organic molecular assemblies as templates. Numerous helical (morphologically chiral) nano-materials have been synthesized.3

In general, the optical activity (OA) observed from solid materials can be classified into three contributions: (i) absorption- and emission-based OA,4,5 (ii) refraction-based OA6 and (iii) elastic scattering or non-elastic Raman scattering-based OA.7 Absorption- and emission-based OA are the difference in the absorption or emission of left-handed (LH) and right-handed (RH) circularly polarized (CP) light. Absorption-based OA (circular dichroism (CD)) has been widely studied for the electronic spectrum of LH- or RH-nanohelices are obtained, respectively. These silica nanohelices showed chiral optical scattering and the helical nanoribbons had a g-factor of the order of 10^{-2} below 250 nm. Their signs depend on the handedness of the nanohelices. The effect of the morphology and the orientation of the helices on the chiral optical scattering were investigated with simulations via the boundary element method.

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We have previously shown that silica nanohelices can be obtained via the sol–gel reaction of tetraethoxysilane (TEOS) using molecular assemblies of the chiral surfactant [(C2H4-O1,2-((CH3)2N+C16H33)], with a tartrate counterion) as the organic template8 (Fig. S1, ESI†). With L- or D-tartrate as the counterion, RH- or LH-nanohelices are obtained, respectively. These silica nanohelices show strong vibrational circular dichroism (VCD) signals at the Si–O–Si asymmetric stretching vibrational band,9 but due to the transparency of silica in the UV-vis range, no electronic CD is expected. However, when dried on a substrate, these chiral silica nanoribbons show strong scattering in the UV range, which dominates the extinction and the absorption-based CD signals due to the high refractive index of silica. Therefore, when measuring the electronic CD signals it is very important to understand how the scattering affects the chiroptical signals with respect to the absorption-based signals. In this manuscript, we investigate and compare the optically...
which we will call extinction and $\text{CD}_{\text{ext}}$, respectively, hereafter.

which includes both scattering and absorbance contributions,

of the ribbons are shown.

no $\text{CD}_{\text{ext}}$ is observed (Fig. S2, ESI†).

When the silica nanohelices are dispersed in ethanol, the

pitch ($P$) are shown in Table S1 (ESI†).

Fig. 1a and b, the schematic images show the

volumes) and nonstoichiometric vacancies ($e.g.,$ oxygen).¹⁰ The amplitudes of the absorbance and $\text{CD}_{\text{abs}}$ intensities in the UV range are much smaller (~1/10 and ~1/33, respectively, at ~200 nm) than that of the extinction and $\text{CD}_{\text{ext}}$, indicating that the scattering and the chiral optical scattering (COS) signals are the dominant origin of the extinction and $\text{CD}_{\text{ext}}$. Again, upon calcination at 900 °C, both the absorbance and $\text{CD}_{\text{abs}}$ decreased.

Hereafter, we focus on the scattering intensity and the COS. As seen from Table S1 (ESI†), both the helical and twisted nanoribbons shrink after calcination in all dimensions (the pitch, the diameter and the length). This is directly reflected in the decrease of the scattering intensity. In order to investigate how this shrinking affects the COS, we compared the $g$-factors, which correspond to the normalization of the $\text{CD}_{\text{ext}}$ by the extinction. For both helical and twist ribbons, the $g$-factors before and after calcination are shown in Fig. 1e and f. No significant modification was observed both for the helical and twisted ribbons after calcination. For both morphologies, they showed a continuous decrease with increasing wavelength, showing a $g$-factor of ~0.015 (at 200 nm) for the helical ribbons and ~0.0035 (at 200 nm) for the twisted ribbons.

We then simulated the extinction and $\text{CD}_{\text{ext}}$ values as well as the scattering cross-section and $\text{CD}_{\text{scat}}$ values (Fig. 2 and Fig. S7, ESI†) of the individual helical and twisted silica ribbons before and after calcination using the measured values shown in Table S1 (ESI†), using the boundary element method (BEM), as described in the ESI†.¹¹ Using the dielectric function of silica given by Palik,¹² while ambient air is used as the medium. The simulations are performed by considering that the light beam is perpendicular to the helical/twisted ribbon (in-plane with the
substrate. CD$_{\text{ext}}$ and extinction cross-section values are very close to the CD$_{\text{scat}}$ and scattering cross-section values, respectively (Fig S7, ESI†), while the contribution of absorbance and CD$_{\text{abs}}$ is negligible, in good agreement with the experimental results. Thus, in the following discussion, CD$_{\text{ext}}$ is assimilated to CD$_{\text{scat}}$. Interestingly, the CD$_{\text{scat}}$ and the $g$-factors for helical ribbons are higher than those for twisted ribbons, also in good agreement with the experimental observations. In Fig S8 (ESI†), we show the simulation of the two structures in which we compare how the vectors perpendicular to the surface are arranged along the ribbons. These results show that the vectors at the surface of a twisted ribbon rotate with the highest angle only at the center of the ribbon, whereas those of a helical ribbon rotate all together with the same highest angle.

We then investigated how modification of the pitch and length of the ribbons affects the scattering intensities, the CD$_{\text{ext}}$ values and the $g$-factors. Fig. S9 (ESI†) shows the simulations of how the $g$-factor at a wavelength of 200 nm evolves with the length (at a fixed pitch and diameter) and pitch (at a fixed length and diameter), respectively, of a single helical or twisted ribbon. The corresponding extinction and CD$_{\text{ext}}$ values are shown in Fig. S10 (ESI†). The incident light is perpendicular to the axis of the helix. We observe clearly that for pitches and lengths in the range of the helical and twisted ribbons observed for the present system ($P$, 25–150 nm; $L$, 200–500 nm), the $g$-factors of the COS signals do not vary much as both the cross-section and CD$_{\text{scat}}$ decrease for the calcined helices with decreased dimension. As shown in Fig. S10 (ESI†), when the size of the ribbon decreases during the calcination, both CD$_{\text{ext}}$ and extinction vary in the same direction (CD$_{\text{ext}}$↑ and extinction↑ for increasing $L$, whereas both CD$_{\text{ext}}$↓ and extinction↓ for increasing $P$) compensating the variation in each other.

Globally, these simulated data are in very good agreement with the experimental data. A slight difference is likely due to the fact that the simulation is done on one helix whereas the measurements are done on the ensemble of helices with large size polydispersities (Fig. 3), leading to inter-helix scattering. Also, the variation in the refractive index of silica before and after calcination is not taken into account in the simulation. Indeed, the refractive index should depend on the density of the helices.

Finally, we compared the effect of the quantity of silica nanoribbons on the substrates. As shown in Fig. 3, various thicknesses of silica nanoribbon films were prepared on the 2 × 2 cm$^2$ quartz substrates and the extinction and CD$_{\text{ext}}$ values were measured. While the intensity of the extinction increased linearly with the quantity of silica nanoribbons (Fig. 3a), CD$_{\text{ext}}$ intensity increased much more slowly beyond 50 µg cm$^{-2}$ of silica nanohelices (Fig. 3b), and the $g$-factor over this range decreased (Fig. 3c) with the concentration of helices. Scanning electron microscope (SEM) images confirmed that 25 µg cm$^{-2}$ of silica nanoribbons was enough to homogeneously cover the quartz surface of the substrate (Fig. 3d). In order to understand the decrease in the COS signal ($g$-factor) for the larger quantities of silica helices, we investigated the effect of the orientation (in-plane or out-of-plane of a helix on the COS signal by simulation. As shown in Fig. 3f and Fig. S17 (ESI†), the out-of-plane helix showed an opposite simulated CD$_{\text{ext}}$ signal from that of the in-plane helix. Although a similar coverage of the surfaces was observed for the top views of all the films, the cross-section SEM images of these films clearly showed the difference in their thicknesses. For the 25 and 50 µg cm$^{-2}$ films, the silica layer thicknesses (0.18 µm and 0.35 µm, respectively), are thinner than the average length of the silica nanohelices. On the other hand, in the case of the 200 µg cm$^{-2}$ film, the silica layer (3.2 µm) is thicker than the average length of the silica nanohelices. These results indicate that in the thinner layer (<50 µg cm$^{-2}$), only in-plane orientation is allowed, whilst in the thicker layers (>100 µg cm$^{-2}$), in-plane and out-of-plane orientations of silica nanohelices (Fig. 3e) can co-exist. Also, electromagnetic interaction between helices in the thicker layers of helices and the multiple scattering can perturb the polarization of the scattered light. These results can be compared with the drop-casted films of cut and non-cut nanoribbons (Fig. S12, ESI†). Non-cut silica nanoribbons show a smaller COS. In both cases, either for the highly concentrated
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drop-cast film or the non-cut film, silica nanohelices are strongly aggregated in 3D directions with a high proportion of out-of-plane helices.

We investigated the chiral optical scattering from helical and twisted silica nanoribbons deposited on substrates parallel to the surface with random in-plane orientation. Using a CD spectrometer in both transmission and diffuse reflection mode, we demonstrated that the contribution of the absorbance and absorbance-based CD is present but negligible compared with the scattering and COS. Helical ribbons show larger COS and g-factors compared with twisted ribbons. For both morphologies, the variation of g-factor was negligible after calcination. All results are in good agreement with the simulation performed on a single helix oriented perpendicular to the incoming light. The simulation of the COS on a helix oriented parallel to the incoming light shows the opposite signal from that of the helix oriented perpendicular, which is probably the origin of the decrease in COS for the aggregated helices which contain the helices oriented out of plane. The g-factors observed for helical ribbons are of the order of $10^{-2}$, which is surprisingly high for materials made from silica alone. Thus, the strategy shown here represents an original and promising method to create fadeless circular polarizers while keeping good transparency in the visible range, with one of the most abundant inorganic atoms, Si, and O by simple coating of silica nanohelices on transparent films.

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Conflicts of interest

There are no conflicts to declare.

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