Quantification of chirality from electron tomography data

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Background and aims.

Some optical nanomaterials exhibit the intriguing property of absorbing differently left- and right-handed polarized light. This optical handedness often arises from morphological chirality, the fact that mirrored shapes do not superimpose, but the quantitative relationships between morphology and optical properties are poorly understood. Establishing this knowledge requires accurate characterization the nanomaterials' morphology, as well as the calculation of chirality descriptors relevant to the optical properties of interest [1]. A prime example of such combination is the quantification of helicity from electron tomography (ET) three-dimensional (3D) reconstructions, which we previously presented [2]. Applied to wrinkled or twisted geometries such as those of chiral Au nanorods (NRs), this method informs about the helical character of the NRs and their handedness and is an excellent predictor of the sign of their circular dichroism (CD) spectra. However, helicity is a radially averaged measure, which limits its local interpretation, and entails strong geometrical assumptions, which limits its value for non-helical shapes even as they may still be chiral and exhibit clear optical handedness.

Here, we explored how different descriptors of chirality obtained from ET reconstructions can complement each other to link nanoscale morphology and optical handedness. To understand how local chiral features were varying, we first implemented a measure of their orientation, providing insights into both global and local handedness [3]. To overcome geometrical assumption, we then studied methods quantifying asymmetry on the basis of the difference between a geometry and its mirror image, including the Hausdorff chirality measure [1,4]. We finally tested if, beyond individual metrics, chiroptical performance could be statistically linked with a learned combination of morphological and chirality descriptors.

Methods.

As a prerequisite to study and establish chiral descriptors, a large dataset of ET reconstructions of chiral Au NRs was assembled. The particles in this dataset were typically 50-150 nm-long and were synthesized by seed-mediated growth. Two synthesis pathways were included: micelle-templating, whereby chiral micelles coil around achiral Au NR seeds, resulting in the growth of wrinkled particles whose helical morphology is characterized by a narrow pitch and a small helical orientation; chemical-inducing whereby chiral molecules such as amino-acids induce the preferential growth of high order, chiral surface facets. This latter approach yields highly helical, twisted structures with long pitches and high helical orientations when starting from single-crystalline seeds, but also strongly deformed, asymmetrical structures without clear geometrical handedness nor helical character but a handed optical signal when starting from pentatwinned seeds. In addition, the dataset includes the optical properties of all batches from which the particles are sampled, including absorption and CD spectra.

ET tilt-series were obtained in high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and typically span 130-140° in 2 or 3° increments. 3D reconstructions were performed using the SIRT, expected maximization (EM) or constrained SIRT algorithms with in-house code or the ASTRA toolbox.

Surface orientation was computed using the ImageJ plugin OrientationJ while other computations and the statistical analyses were performed in python or Matlab with in-house code.

Results.

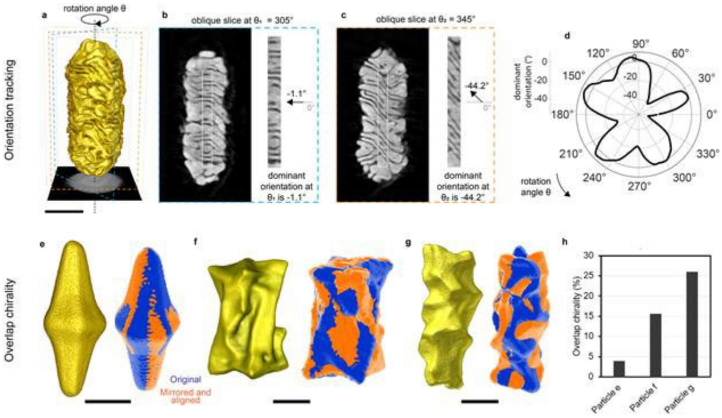
We first investigated how to obtain local analysis of the orientation of chiral features. Typically, chirality measures provide summary data, with a single metric indicating the degree of chirality and/or the handedness. Here, the orientation of chiral features on Au NRs was tracked and analyzed with spatial accuracy around the NR, evidencing local variations that were not visible when analyzing helicity (Figure, a-d).

To further quantify the chirality of non-helical structures, we investigated methods based on the calculation of the difference between a reconstruction and its mirror image. Such a descriptor effectively quantifies asymmetry, without considerations of handedness, and the difference is typically evaluated on the basis the Hausdorff distance, yielding the Hausdorff chirality measure. We found that optimizing for the minimum Hausdorff distance as required to calculate the measure requires long computation times if the full surface is used, limiting the applicability to simple shapes. As an alternative, we used a shape overlap measure (Figure, e-g), which can be calculated at a fraction of the cost. This method provided results similar to the Hausdorff chirality measure for classifying particles on the basis of their asymmetry and demonstrated that the morphology of non-helical structures could still be highly chiral (Figure, g-h), thus complementing helicity and orientation-based analyses.

Although powerful because of their simple interpretation, orientation, helicity and chiral distances are descriptors that provide part of the information only. We finally investigated if a combination, rather than a single descriptor, can predict optical properties from morphological data. Given the vast amount of data accumulated by our lab in the recent years, we will present how such combination could be learned statistically from ET reconstructions and the corresponding optical spectra.

Conclusion.
Beyond helicity, orientation tracking and asymmetry quantification provide insights into different aspects of morphological chirality. The key towards fully characterizing chirality might be in their adequate combination. Focusing on interpretable descriptors, this work expands the toolbox for microscopists to quantify chirality from ET reconstructions and paves the way towards establishing quantitative relationships between the morphology of chiral nanomaterials and their optical properties.

Graphic:



Keywords:

ET, tomography, plasmonics, chirality, descriptors

Reference:

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