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Single-crystal and pentatwinned nanorods reverse the handedness of chiral plasmonic nanocrystals: an electron tomography study

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Background and aims.

Nanomaterials with chiroptical properties absorb differently left- and right-handed light, an asymmetry that is reinforced by the local surface plasmon resonance of metallic nanoparticles. The synthesis of such chiral particles with controlled shapes and optical properties is of major interest for a host of potential applications including bio-sensing, therapeutics or catalysis, and can be realized by transferring chirality from an organic inducer to the inorganic material in seed-mediated colloidal synthesis [1,2]. Usually, the handedness of the inducer is thought to be transferred to the product [1]. However, recent studies showed that the geometry of the achiral seeds can also influence handedness, even if the same inducer is used [3], and it remains unclear if such effect is related to morphological or structural (surface facets, twin boundaries, defects, …) properties.

Here, we aimed to understand the effect of the seeds on the growth of chiral features. Specifically, we investigated the growth starting on well-defined single-crystal (SC) or penta-twinned (PT) gold nanorod (NR) seeds. To uncover the complex morphological changes at the nanoscale, we used electron tomography (ET), a method that enables three-dimensional (3D) reconstructions down to the atomic scale. In two different synthesis protocols, micelle-templated or chemically induced, 3D reconstructions and nanoscale morphological analysis showed that the final products had reverse handedness and strong morphological differences when using PT or SC seeds [4].

Methods.

We studied the growth of chiral features on well-controlled achiral gold seeds synthesized by wet chemistry. The two systems investigated here were PT NRs featuring five {100} lateral facets and caped by {111} facets at the tips, and SC NRs with an octagonal cross-section, {520} lateral facets and {110} and {100} tips. Chiral features were grown by two protocols. The chemically induced pathway used the chiral L-cystine (L-cys) amino-acid, which was previously reported to yield highly twisted structures on SC seeds [2]. The micelle-templated protocol used chiral, worm-like micelles formed by (S)-1,1'-binaphthyl-2,2-diamine (S-BINAMINE) and cetyltrimethylammonium chloride (CTAC), that are known to yield wrinkled, helical, NRs [1]. The optical properties of the seeds and of the products were characterized by extinction spectroscopy and circular dichroism (CD) measurements.

To characterize the morphology and structure of the final products, we used ET, whereby projection images acquired at incremental tilt-angles are used to compute a 3D reconstruction of the object. Tilt-series were acquired in 2-3° increments and in scanning transmission electron microscopy (STEM) high angle annular dark field (HAADF) mode to provide mass-thickness contrast and meet the requirements for accurate reconstructions. The reconstructions were computed using an expected maximization (EM) algorithm or a constraint SIRT approach developed in-house and implemented in Matlab with the ASTRA toolbox. Morphological analyses included helicity measurements and orientation tracking. Helicity uses a surface mesh extracted from reconstructions to compute a pseudoscalar metric indicating how close to a perfect helix the shape is and its handedness (positive helicity means right-handed, negative means left-handed) [5]. Orientation tracking reveals the dominant orientation of features around a NR to study the local variations of chirality and was implemented using a combination of the ImageJ OrientationJ plugin and in-house code.

Results.

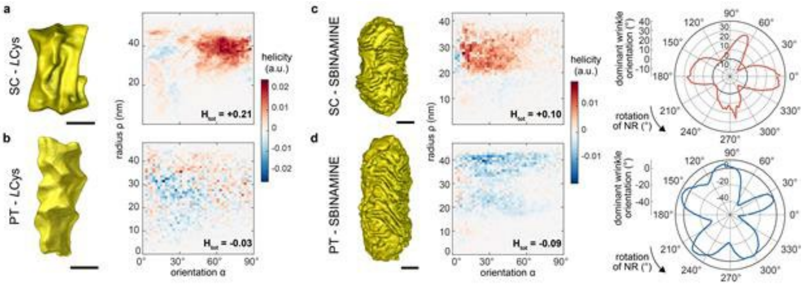
Regardless of the synthetic pathway, starting from PT or SC seeds resulted in products with opposite signs in CD spectra, indicating a reverse handedness. Strong discrepancies were further seen in the morphology of the particles, as reconstructed in ET. With the L-Cys protocol, SC seeds resulted in strongly twisted NRs with clear right-handed morphology (Figure, a). This observation was supported by helicity measurements, showing strongly positive values. On the other hand, PT seeds resulted in poorly defined, highly complex shapes with no obvious handedness (Figure, b). Helicity measurements were typically weak, with a complex combination of right and left-handed features in each particle leading to some NRs exhibiting a dominantly left handedness and others with right handedness (Figure, b). This observation suggests that optical handedness is not limited to helical features. Overall, a strong influence from the seed crystal structure was expected in this growth protocol, as chirality emerges through the preferential growth of chiral facets stabilized by the chiral inducer. More surprisingly, micelle-templated NRs grown from PT seeds also had an opposite sign in CD spectra as compared to their SC counterpart. ET reconstructions showed closely resembling wrinkled morphologies in both cases, with a major difference in the orientation of the wrinkles (Figure, c, d). PT NRs showed left-handed wrinkles, coherently with positive g-factor plots, while SC NRs showed right-handed features. Helicity measurements confirmed this observation by showing close absolute values but opposite signs.

To further probe how the morphology of the seeds was impacting the final micelle-templated products, we assessed if the presence of corners and lateral facets influenced the wrinkle morphology beyond the global particle handedness. Notably, the tips featured better aligned wrinkles on SC NRs, and wrinkles on the lateral facets grew at different angles. Tracking the dominant orientation of wrinkles around the particles also revealed that PT NRs retained a 5-fold symmetry with alternating areas of flat and oriented wrinkles (Figure, c, d). In contrast, SC NRs had a 4-fold symmetry with similarly alternating flat and oriented wrinkles, coherent with an intermediate with square cross-section we previously identified. These observations confirm that the way micelles adsorb on the seeds’ surface is influenced by geometrical (angles, number of facets) or crystallographic (facet index) consideration, in turn impacting the orientation of wrinkle growth and, likely, the handedness of the particle.

Conclusion.

We used ET and detailed nanoscale morphological analyses to show that the nature of the achiral seed in chiral seeded growth has a major influence on the handedness of the products and on their chiroptical properties. Furthermore, this observation in micelle-templated growth shows that wrinkle growth is not random but influenced by geometrical or crystallographic factors. This work enhances the toolbox for controlling chirality at the nanoscale and demonstrates the benefits of ET in linking morphology and optical properties, supporting the development of novel optical nanomaterials.

Graphic:



Keywords:

TEM, tomography, chirality, plasmonics, nanorods

Reference:

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