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RESEARCH ARTICLE

Single Crystal and Pentatwinned Gold Nanorods Result in Chiral Nanocrystals with Reverse Handedness

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Dedicated to Professor Alexander Eychmüller on the occasion of his retirement.

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Supporting information for this article is given via a link at the end of the document.

Abstract: Handedness is an essential attribute of chiral nanocrystals, having a major influence on their properties. During chemical growth, the handedness of nanocrystals is usually tuned by selecting the corresponding enantiomer of chiral molecules involved in asymmetric growth, often known as chiral inducers. We report that, even using the same chiral inducer enantiomer, the handedness of chiral gold nanocrystals can be reversed by using Au nanorod seeds with either single crystalline or pentatwinned structure. This effect holds for chiral growth induced both by amino acids (*e.g.* cystine) and by chiral micelles (comprising cetyltrimethylammonium chloride and 1,1'-binaphthyl-2,2-diamine). Although it was challenging to discern the morphological handedness for *L*-cystine-directed particles, even using electron tomography, both cases showed circular dichroism bands of opposite sign, with nearly mirrored chiroptical signatures for chiral micelle-directed growth, along with quasi-helical wrinkles of inverted handedness. These results expand the chiral growth toolbox with an effect that might be exploited to yield a host of interesting morphologies with tunable optical properties.

Introduction

Chirality can be transferred from organic to inorganic substances, *via* assembly of achiral building blocks into a chiral arrangement, or by the preparation of nanostructures with chiral morphology.[1] This has been historically accomplished by directing amino acids or peptides to systems such as $CaCO_3$,[2-3] Au,[4-7] Ag,[8] HgS,[9] or Te,[10] with more recent studies applying DNA or even circularly-polarized light to these systems, yielding a host of novel structures with interesting optical properties.[11] These processes, which enable new approaches to control the structure of nanomaterials,[12-15] crucially depend on the inherent properties of the inorganic crystals, such as the crystal lattice,[9] stabilization of certain chiral kinks,[2] or the presence of crystalline defects such as screw dislocations.[10] In the case of Au nanocrystals, a few synthetic strategies for chirality transfer have been successfully applied, including: removing mirror planes from the geometry of achiral nanoparticle seeds in the presence of small chiral molecules such as amino acids (chemically-induced);[4] using

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chiral micelles to wrap around nanocrystal seeds and template further growth (micelle-directed);[16] and irradiation of nanocrystal seeds by circularly polarized light to induce asymmetric hot spots and thereby favor chiral growth (CPL-induced).[17-18] In all cases, the crystal properties of the achiral seeds have been reported to influence the morphology and handedness of the final chiral products. For example, Nam and colleagues obtained helicoid particles with 432 symmetry from cubic or octahedral seeds.[4, 19] However, comparison of the optical response from helicoids obtained with the same amino acid enantiomer was opposite in both cases, as indicated by the sign of the bands in circular dichroism (CD) spectra.[20] Although the mechanisms related to such geometrical and optical differences remain largely unknown, it is quite clear that morphological/crystalline details in the seeds play a crucial role during crystal growth. From the reported observations, it remains unclear whether it is the seed morphology or other structural aspects, like the crystalline index of surface facets, the presence of twin boundaries, or other crystalline defects, that determine the resulting chiral morphology. In this context, Au nanorods (NRs) are a particularly interesting system, not only because of their well-defined crystallinity, but also because differences in certain synthetic details are known to lead to crucial differences in geometrical and crystalline features. It is well known that the choice of single-crystalline (SC) or penta-twinned (PT) Au nanocrystal seeds determines the growth of either single-crystal Au NRs (grown from SC seeds in the presence of Ag^+ ions) with an octagonal cross section, or pentagonal prisms (from PT seeds and Ag-free).[21] Consequently, the crystallographic surface facets for both Au NR types are different, with SC-Au NRs displaying {520} lateral facets capped by {110} and {100} tips[22-23] and PT-Au NRs yielding {100} sides and {111} tip facets.[24] The symmetry corresponding to the morphology of a SC-Au NR is described by the 4/mmm point group, whereas for a PT-Au NR it corresponds to the $(\bar{1}0)m2$ point group (**Figure S1**). Since chiral growth in the presence of small chiral inducers depends on the type of crystal facet exposed at the surface of the seed,[25] we hypothesized that the use of PT-Au NRs *vs*. SC-Au NRs would lead to different chiral morphologies and potentially different optical activity.

Therefore, achiral SC- and PT-Au NR seeds with similar sizes (**Figure S2**) were subjected to both the chemically-induced[26] and the micelle-directed[16] chiral growth approaches. Given the radically different morphological features (twisted *vs*. wrinkled) that lead to chiroptical activity in each of these methods, the effects of varying the crystal habit from SC to PT were also expected to be significantly different. As previously reported, the complex morphological details of chiral Au NRs require high resolution characterization in three dimensions (3D) that could only be achieved by means of state-of-the-art electron tomography methods, which also allow quantification of the chiral structure at the nm scale.[27] Correlation between morphological and optical features is not straightforward, but the handedness of chiral structures within twisted or wrinkled nanocrystals are expected to correlate with the sign of CD bands in the corresponding spectra.[28]

Results and Discussion

The first step in the preparation of rod-like chiral particles comprises the synthesis of monodisperse SC- and PT-Au NRs. Among various methods in the literature, we selected those recently reported by us, which provide high quality and reliability. In both cases, a high aspect ratio was sought because it was found in previous work to be more efficient in terms of chiral NR growth and optical activity. In the case of SC-Au NRs, the use of small NRs (minirods) as seeds has been shown to provide access to a wider range of SC-Au NR dimensions and thus high aspect ratios can be achieved without sacrificing monodispersity.[29] For PT-Au NRs, thermal treatment of the initial seeds is effective toward enriching the population of PT nanocrystal seeds, which in turn leads to a much higher yield during seeded growth.[30] It should be noted however, that a small fraction of quasi-spherical particles may remain in the PT-Au NR dispersion (**Figure S2e**).

We initially explored the chemically-induced protocol, using *L*-cystine (*L*-2cys) as the chiral inducer. *L*-cystine is a dimer formed upon oxidation of the amino acid *L*-cysteine, which we found to lead to more reproducible results than the monomer, for chiral growth experiments. From our previous work,[26] we learnt that multistep seeded growth leads to better-defined twisted morphologies than those obtained when the total amount of growth solution would be added in a single step. Therefore, we implemented a multi-step protocol, including nine chiral growth steps, using both SC- and PT-Au NR seeds. The linear optical spectra of the respective final products (**Figure 1a**) reveal significant differences. Two well-defined extinction bands of similar intensity, centered at 591 nm and 754 nm, were recorded for the particles obtained from SC-Au NRs, whereas growth on PT-Au NRs led to a double band at shorter wavelengths (ranging from *ca*. 550 to 750 nm) and an intense band around 1050 nm. Even more remarkable are the differences observed in the corresponding CD spectra (normalized to the *g*-factor), where the bands for SC- and PT-Au NRs seem to be inverted (opposite sign) and shifted: an intense negative peak at 590 nm (maximum *g*-factor of -0.036) and a positive plateau at longer wavelengths for SC-Au NRs, but a weak negative peak at 535 nm and a more intense positive band centered at 660 nm (peak *g*-factor value of 0.020) for the product from growth on PT-Au NRs (**Figure 1b**). A notable observation here is that, even though seeded growth was carried out in the presence of the same (*L*-2cys) chiral inducer enantiomer, the sign of CD bands was inverted for NRs evolving from SC- and PT-Au NRs. Marked differences were also observed through electron microscopy and tomography characterization. As previously reported, chiral particles grown from SC-Au NRs (in the presence of *L*-2cys) showed a right-handed 4-fold twisted structure (**Figures 1c,e** and **S3**, **S4**), in agreement with the removal of mirror planes by *L*-2cys.[26] However, when growing PT-Au NRs under similar conditions, much more intricate structures were obtained (**Figures 1d,f** and **S5**), often containing cavities within highly twisted surfaces, somewhat resembling the shape of a conch shell.[31-32] Along with differences in size (length of PT-Au NRs: 179.5 ± 20.1 nm *vs*. 109.2 ± 7.5 nm for SC-Au NRs), these major morphological differences are likely responsible for the observed discrepancies in the extinction

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spectra. These images also demonstrate strong inter-particle variability within the same batch, which hinders the interpretation of the growth process. It should be noted that, even if at a lower extent of complexity, similar results were obtained when a single-step growth protocol was employed (see description in the Supporting Information and **Figure S6**).

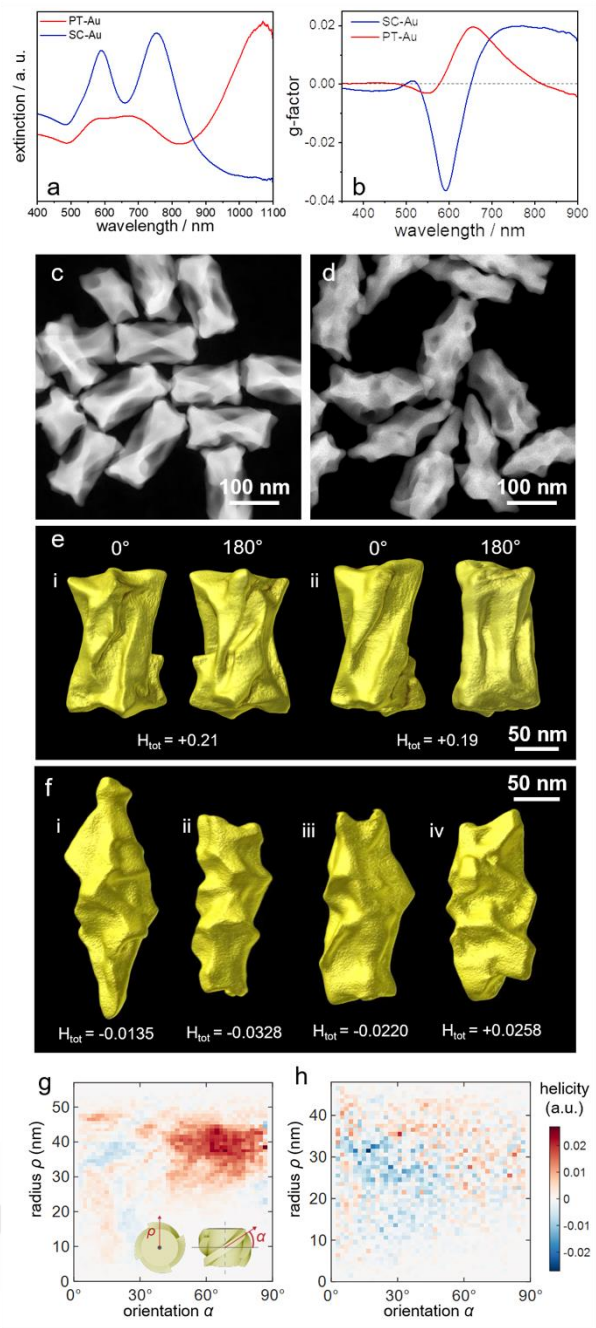

Figure 1. Characterization of chiral products using *L*-2cys as the chiral inducer. (a,b) Extinction and *g*-factor spectra for the chiral particles obtained from SC- and PT-AuNR seeds, using an identical multi-step protocol. (c,d) Representative high angle annular dark field scanning transmission electron microscopy (HAADF STEM) images of chiral SC-Au NRs (c) and of PT-Au NRs (d). (e,f) Isosurface renderings of electron tomography reconstructions for typical chiral SC-Au NRs (e) and PT-Au NRs (f). The particle in e-i is shown at two different orientations (0° and 180°), revealing a 4-fold symmetry. The total helicity value (H_{tot}) is indicated for each particle. (g,h) Helicity plots for the particles shown in e-i (g) and in f-ii (h). Insets in g show the definition of the orientation *α* and of the radius *ρ* (distance from central rotation axis) for a simple helix. Red dots indicate dominantly right-handed features, blue dots indicate dominantly left-handed features, the intensity scales with the number of similarly oriented surface elements (see Materials and Methods in the SI).

To further probe the morphology of these particles and the relationship to their chiroptical properties, we conducted helicity analysis through a method specifically designed to quantify the handedness of surface features in electron tomography reconstructions.[27] The resulting helicity plots (**Figure 1g**,**h** and methods for computational details in the SI) show the histogram of right-handed (positive helicity values) or left-handed (negative helicity values) surface elements, their orientation angle (*α*, X-axis) and their distance from the central rotation axis of the particle (radius *ρ*, Y-axis). As shown in **Figures 1g** and **S4**, twisted SC-Au NRs had mostly right-handed features and positive helicity values, as previously reported.[26] In contrast, particles grown from PT-Au NRs systematically showed a mixture of right- and left-handed orientations, reflecting their complex and varied features (**Figures 1h** and **S5**). The mixed (right- and left-handed) orientations of chiral features in PT-Au NRs, combined with the greater polydispersity of the initial (PT NR) seeds, are likely to contribute to the lower *g*-factor recorded for these particles.

To investigate a possible cause of the inverted CD spectra, we further calculated the total helicity (H_{tot}) by integrating the helicity plots. This metric quantifies how close to a perfect helix a given geometry is, with the ideal case having a helicity of ± 1, depending on handedness. We systematically obtained small values for PT-derived particles (**Figure 1f**), typically in a range of ±0.03. With six particles reconstructed from this sample, the averaged total helicity was -0.0127±0.0480, again showing strong interparticle variability. It is therefore difficult, due to the limited sample size and despite the negative sign of the average value, to attribute a dominant morphological handedness to the PT-Au NRs and to explain the sign of the CD spectra based on this analysis. Interestingly, this also suggests that the nature of chirality in SC- and PT-Au NRs is fundamentally different, with PT-Au NRs corresponding to particles with a poorly defined structural helicity and nonobvious morphological handedness, despite their clear chiroptical properties.

Given the unexpected morphology obtained from chiral growth using PT-Au NRs, we tracked the morphological evolution upon various additions of growth solution (**Figures S7** and **S8**). Electron tomography and helicity analysis revealed a considerably roughened surface with numerous left- and right-handed features, already after the first chiral growth step (**Figure S8a,b**). After 9 dissymmetric growth steps, the surface exhibited even more pronounced irregularities. Overall, these results show that, at any stage of growth, the use of PT-Au NR seeds leads to roughened surfaces with both left- and right-handed tilted ridges. These observations are significantly different compared to growth starting from SC-Au NR seeds, where smooth surfaces can be identified at early stages and well-defined handedness is observed in the final stage.[26]

When using SC-Au NR seeds, cysteine-mediated chiral growth has been reported to proceed via a facet-driven mechanism, in which {521} chiral facets are formed in the presence of chirality-inducing molecules of matching handedness.[26] To assess if this

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mechanism also applies to PT-Au NR seeds, we conducted atomic resolution tomography on a PT-Au NR after the first growth step (**Figure S9**). Although the obtained reconstruction allowed us to identify crystallographic orientations (**Figure S9c**), indexing the surface proved difficult because of its continuously varying curvature. This observation shows that PT-based particles have less well-defined surface facets than their SC counterparts. Close inspection of the images also revealed that the five-fold twinning of the Au NR seed was preserved in the overgrown particle (**Figure S9b,c**), even though the C5 morphological symmetry was not.

The above results suggest that, chiral growth using PT-Au NR seeds yields chiral nanostructures with opposite optical handedness to that for chiral NRs grown from SC-Au NR seeds. However, the wide variety of morphologies obtained using PT-Au NR seeds, largely complicates the analysis and discussion of this observation. The inverted CD signal may arise from a predominance of optically-active left-handed features that helicity cannot account for, *i.e.* a weakly helical yet chiral morphology.[33] In the future, this type of chirality could be revealed using a measure of asymmetry such as the Hausdorff distance between a particle and its mirror image.[17]

Next, we proceeded to perform a similar study based on the alternative, micelle-induced chiral growth method, using 1,1'-binaphthyl-2,2-diamine (BINAMINE) as the chiral co-surfactant, together with cetyltrimethylammonium chloride (CTAC) as surfactant. The mechanism behind micelle-induced chiral growth is considered to involve the formation of helical micelles around the Au NR seed, subsequently templating the growth of quasi-helical features.[16] Detailed helicity analysis in previous works revealed the complexity of such surface features, containing both left- and right-handed helical wrinkles at the nm scale. However, one handedness was consistently found to dominate, in agreement with the handedness of the chiral co-surfactant used in the synthesis.[27] In this context, we hypothesized that the growth on PT- rather than SC-Au NR seeds under identical conditions might also lead to an inversion in optical activity and in the predominant wrinkle handedness. Characterization of the obtained chiral products revealed similar extinction spectra and wrinkled morphologies (see **Figure 2** for *S*-BINAMINE and **Figure S10** for *R*-BINAMINE), regardless of the crystallinity of the achiral Au NR seed employed in the synthesis. Extinction spectra for both chiral products feature a band peaking at 570 nm, which tails off into the NIR region (**Figures 2a** and **S10a**). However, the chiroptical (CD/*g*-factor) signature of NRs grown from PT-Au NR seeds was found to be nearly perfectly inverted (**Figures 2b** and **S10b**). In contrast to the observations for chiral Au NRs grown using *L*-2cys, electron tomography reconstructions for several NRs grown from PT- and SC-Au NR seeds consistently revealed features of opposite morphological handedness for both samples (**Figures 2c,d** and **S11**). Even though *S*-BINAMINE was used in both syntheses as the chiral inducer, wrinkled SC-Au NRs exhibited preferentially right-handed helicity, whereas wrinkles grown on PT-Au NRs were preferentially tilting to the left. Quantification provided by helicity calculations (**Figure 2e,f**) confirmed this observation, yielding a total helicity of -0.09 for wrinkled PT-Au NRs, *i.e.*, an overall left-handed helical structure, whereas a total helicity of +0.10 was determined for wrinkled SC-Au NRs, as expected for a right-handed structure.

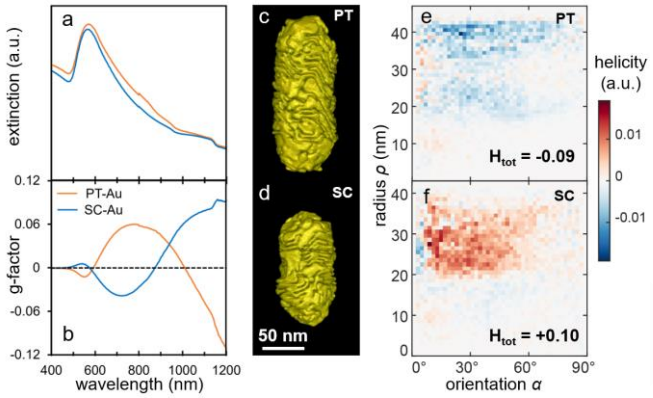

Figure 2. Characterization of chiral wrinkled Au NRs synthesized using pentatwinned or single-crystal achiral seeds, in the presence of S-BINAMINE/CTAC mixtures. (a,b) Extinction (a) and chiroptical (b) spectra of chiral nanoparticles in aqueous colloidal dispersions. (c,d) Isosurface rendering from electron tomography reconstructions of a representative PT-Au NR (c) and a SC-Au NR (d). Scale bar is valid for both images. (e, f) helicity characterization of the particles in (c) and (d), respectively.

Detailed analysis of selected reconstructions revealed additional differences in the morphologies of wrinkled Au NRs obtained from SC- and PT-achiral seeds. Whereas the latter particles typically featured blunt tips (**Figure S11a,c**), SC-Au NRs typically contained well-defined wrinkles, suggesting an influence of either the tip morphology or the type of crystal surface facets at the tips, on micelle adsorption and further growth. Notable differences were also found between wrinkles growing on the side facets of PT- or SC-Au NR seeds. For clarity, we first establish two definitions to describe the geometry of wrinkles on rods, as modelled in **Figure S12**: a wrinkle direction angle describes the angle of that wrinkle when visualized sideways or in cross-section (*e.g.* **Figure 3a,e**); a wrinkle orientation angle describes the angle of that wrinkle when visualized in a front view through isosurface rending (*e.g.* **Figure 3b,f**). On PT seeds, numerous wrinkles were seen to have a ±25-30° direction angle with respect to the normal direction of the surface (**Figure 3a**). In contrast, most of the wrinkles on SC seeds were almost perpendicular to the lateral facets, occasionally with small but random direction angles (**Figure 3e**). Apart from the growth direction, wrinkles were also observed to have different orientations (**Figure 3b,f**). Specifically, two types of areas could be distinguished on the surfaces of wrinkled particles, in which wrinkles were either mostly flat (**Figure 3c,g**), or mostly tilted (**Figure 3d,h**). To understand the distribution of these areas at the chiral NR surface, we tracked them by measuring the dominant wrinkle orientation when the NR was rotated along its major axis (see Materials and Methods and **Figure S13**). As shown in **Figures 3i and S11d**, when rotating particles grown from PT-seeds, five areas were observed to contain mainly flat wrinkles (dominant orientation close to 0°), whereas five areas had wrinkles tilting to the left (negative orientation angle). An idealized view of this geometry is presented in **Figure S14**. Remarkably, these areas alternated, in agreement

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with the 5-fold symmetry of the achiral PT seeds being preserved. Particles grown from SC seeds also contained distinct areas of flat or tilted wrinkles (albeit with positive orientation angles, *i.e.*, to the right), but in this case with a 4-fold rotational symmetry around the major axis of the NRs (**Figures 3j and S11**). This symmetry is directly reminiscent of the intermediate morphologies that were reported to occur during achiral-to-chiral transitions, comprising a square cross-section with {110} facets.[26] Given the different geometries (number of faces and corners or angles at corners) and surface facets between PT seeds and SC intermediates, our observations at the tips and sides of the wrinkled Au NRs strongly suggest that such geometrical and crystallographic considerations influence the growth of wrinkles and/or micelle adsorption.

These observations hint at a possible factor to explain the CD sign and morphological handedness reversal in the micelle-directed synthetic pathway, but, as with the *L*-2cys induced synthesis, other effects may co-exist. These effects include differences in growth kinetics, different intermediate structures, preferential interaction of the BINAMINE chiral molecules with the surface facets of these intermediates, subtle differences in tip protrusions and anisotropy, etc. The influence of tip morphology on the chiroptical signature has been explored by Liu, et al., who showed through simulations that chiroptical spectra for nanocube models with high-Miller-index chiral facets were dramatically shifted – and inverted – compared to those from nanorod models possessing similar chiral facets.[34] In summary, numerous factors may influence the morphology of Au NRs and in turn their chiroptical response. Disentangling these effects will require additional characterization and new descriptors for complex chiral structures, as well as chemical strategies to probe the growth pathway.

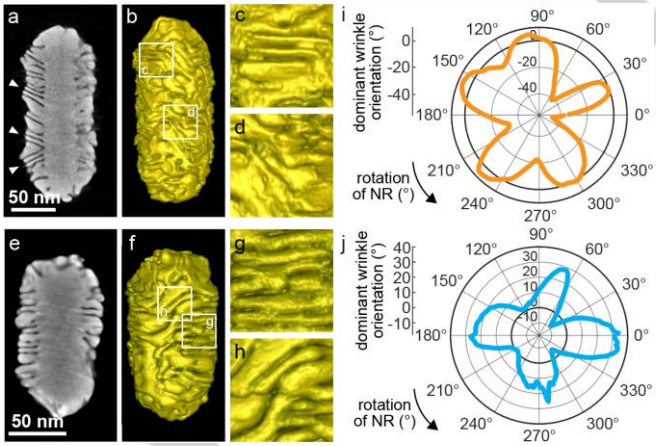

Figure 3. Morphology of wrinkles on chiral particles grown from PT- and SC-Au NRs using the micelle-templated synthesis with *S*-BINAMINE. (a-d) Central orthoslice (a) showing the direction of growth (white arrows) and isosurface visualization of the 3D reconstruction (b) of a wrinkled PT-Au NR, with close-up views of the surface (c,d) demonstrating two main orientations of the wrinkles. (e-h) Central orthoslice (e) and surface visualization (f) of a wrinkled SC-Au NR with close-up surface views (g,h). (i,j) Polar plots of the dominant wrinkle orientation in the particles shown in (b) and (f), respectively, as a function of the rotation of each particle around its major axis.

Conclusion

We have identified a major influence of the crystallinity of achiral seeds on the handedness of Au NRs obtained using two different chiral growth methods on both SC- and PT-Au NRs, but always using the same enantiomer of the corresponding chiral inducer. When small amino acids (*L*-2cys in this case) were used as chiral inducers, SC-Au NR seeds evolved into chiral NRs with a 4-fold twisted structure, whereas growth on PT-Au NR seeds led to more complex shapes. The overall optical handedness – as measured by CD spectroscopy – was inverted for these structures. However, although SC-Au NRs showed a twisted right-handed morphology, particles grown from PT-Au NRs did not display an obvious left-handed twist, which suggests that the origin of their chiroptical properties may lie in a different type of geometrical chirality. Regarding chiral micelle-templated growth, similar rod-like structures surrounded by helical wrinkles were obtained, regardless of seed morphology (and thus facet crystallinity). In this case, inversion of the handedness for wrinkled SC- and PT-Au NRs was more evident, both in the optical (CD band inversion) and morphological (tilt angle inversion) characterization. Electron tomography analysis also allowed us to determine 4-fold and 5-fold symmetries for wrinkled SC- and PT-Au NRs, respectively, even though seeds with similar sizes were subjected to identical growth conditions. These results reinforce the notion that wrinkle growth is not random but influenced by geometrical and/or crystallographic factors, thereby highlighting a previously neglected aspect of chiral syntheses that might be exploited to yield a host of interesting morphologies with tunable optical properties, depending on the choice of achiral seed.

Supporting Information

The authors have cited additional references within the Supporting Information.[35-42]

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Keywords: chirality • gold nanoparticles • plasmonics • electron tomography • chiral crystal growth

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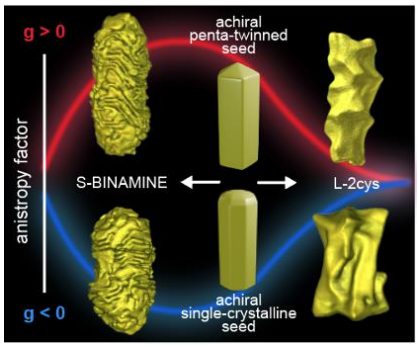

The handedness of chiral gold nanorods synthesized by seeded growth typically follows that of the organic chiral inducer, being right-handed when templated by *S*-BINAMINE micelles or induced by *L*-cystine (*L*-2cys). Our results demonstrate that a change in the achiral seed, from single crystalline to pentatwinned, can reverse the sign of circular dichroism (CD) measurements, adding a new effect to guide the chirality of gold nanoparticles.

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