NANOPARTICLE SELF-ASSEMBLY

Enantioselective photoactivation

Circularly polarized light actualizes the formation of chiral twisted ribbons from achiral semiconductor nanoparticles.

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Advances in lithography and in the development of metamaterials have invigorated the two-centuries-old study of chiroptics — the differential absorption or refraction of circularly polarized light (CPL) by matter. Indeed, such advances have led to the fabrication of chiral sculpted films and other helicoidal nano- and microstructured architectures, and promise negative-index materials, enantiosensitive plasmonic sensors and circularly polarized lasers, among other inventions[1]. However, fabricating thin films of chiral helicoidal metals and semiconductors is a sophisticated process involving physical vapour deposition under high vacuum onto tilted, precisely rotating, substrates. Writing in *Nature Materials*, Nicholas Kotov and colleagues now demonstrate that the chirality of self-assembled, micrometres-long twisted ribbons of cadmium chalcogenide nanoparticles can be controlled by the handedness of CPL[2]. Such light-driven enantioselection of twisted ribbons promises to make these chiral micromaterials available to the average wet-bench chemist.

Twisted single crystals and polycrystalline objects can be found in all manner of materials, including elements, minerals, simple salts, organic molecular crystals and polymers of high molecular weight[3]. A persistent debate running through the discussion of the formation of many of these materials has focused on the dichotomy between twisting from the bottom up (helical associations of straight crystallites) and twisting from the top down (stress-relieving distortions of single crystals). The difference between these two classes is sometimes hard to establish because oriented attachment of tiny crystallites can result in the formation of common crystal lattices[4], whereas strong internal stresses produce dislocation ensembles and eventually grain boundaries that lead to polycrystallinity. It is however conceivable that the understanding of the nanoparticle-association mechanism may be refined through high-resolution transmission-electron-microscopy imaging of crystal growth by oriented attachment, as recently described[5,6].

Kotov and co-authors show that the light-induced self-assembly of CdTe nanoparticles begins with a ‘transmutation’ of elements, in which tellurium is reduced and replaced by sulphur ions stripped from sulphur-rich CdTe capping ligands. The twisted ribbons that result are made almost entirely from CdS nanoparticles. In previous work, some of the authors showed that left- and right-handed CdS nanoribbons form with equal probability when illuminated with unpolarized light[7]. Now they demonstrate that, by irradiating the samples with CPL, excesses of one handedness over the other — that is, ((left – right)/(left + right)) × 100 — can be as great as 30%. As the configurations of the chiral ribbons are fixed once formed, the authors conclude that the spin angular momentum of light is transferred to the helicoidal structures (which show pitches of the order of the wavelength of light). This is unexpected, as it has long been known that enantioselective photochemistry

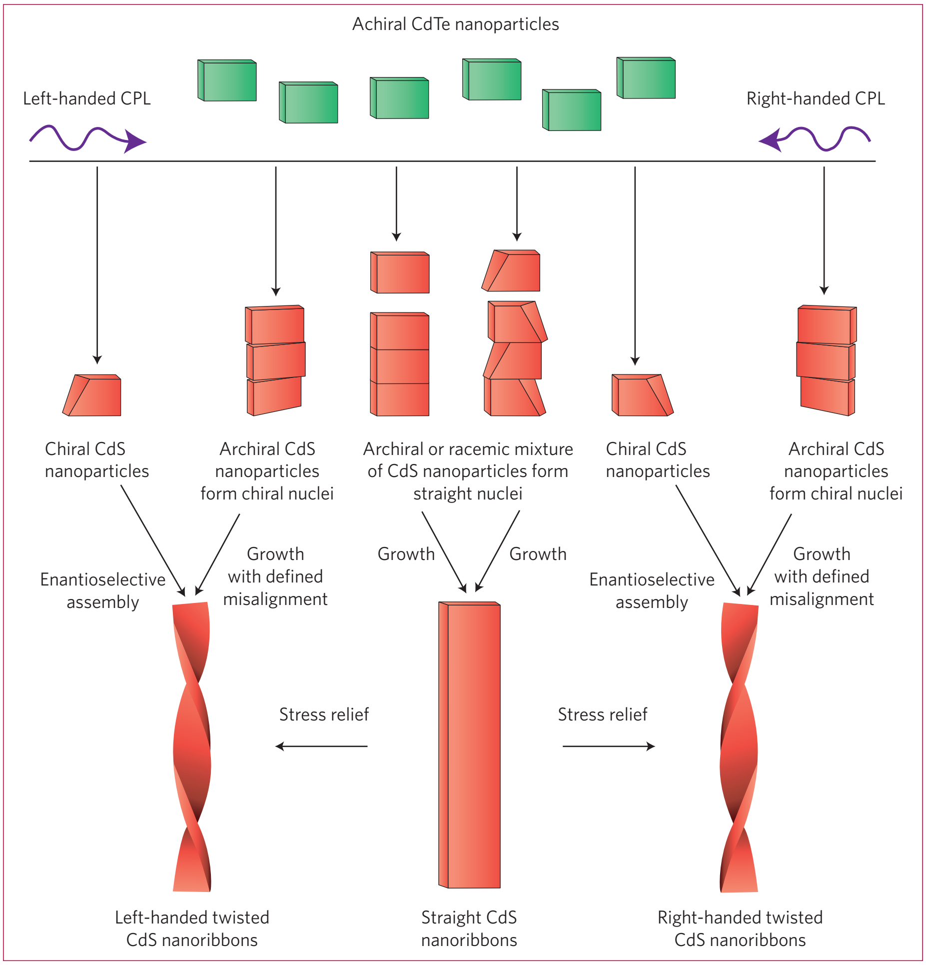

Figure 1 | Competing mechanisms for the formation of twisted CdS ribbons with pitches of ~1 μm by photoactivation of thioglycolic-acid-capped ~5-nm achiral CdTe nanoparticles[2]. CPL may produce enantiomorphous CdS nanoparticles (polyhedra with oblique faces) from achiral CdTe particles (rectilinear polyhedra), and the enantioselective associations of such particles may lead to helicoidal ribbons of opposite twist. Alternatively, the achiral CdS nanoparticles may associate with a fixed twist with left (right) handedness in left (right) CPL. Kotov and colleagues propose that racemic or achiral CdS nanoparticles assemble into straight ribbons that subsequently twist in order to relieve stresses that build up during enantioselective photooxidation[2].

is inefficient because most molecules are much smaller than the wavelength of near-ultraviolet light; in fact, the difference in the absorption coefficients for mirror-image molecules in solution is vanishingly small, leading only to minute enantioselectivities[8]. Single nanoparticles of CdTe are also only a few nanometres in size, yet the authors show that their enantioselective interactions with CPL are large. Perhaps enantioselective photoexcitation becomes more efficient and autocatalytic as the chiral ribbons grow.

Pinning down the actual mechanism of the transformation of CdTe nanoparticles into twisted CdS microribbons will require further investigation, however. At present, several distinct interpretations are credible. For instance, CPL might favour the formation of chiral nanoparticles that prefer to assemble into twisted ribbons of certain handedness. Or CPL may create a bias that directs similar, yet not necessarily chiral, nanoparticles to assemble into twisted morphologies, and such a bias (or even a stochastic excess of one chiral form over another) might be enhanced autocatalytically as twisted ribbons grow and experience differential activation by CPL. These possibilities are illustrated in Fig. 1, together with Kotov and co-authors' proposition that twisting is a consequence of stress relief in straight nanoribbons following photooxidation of the CdS nanoparticles. The authors presume that such a strain builds up from lattice mismatch of the CdS nanoparticles following their photocorrosion.

Recent studies may help to evaluate the various mechanistic possibilities. For example, it was demonstrated that abrasive grinding of a collection of right- and left-handed crystals of the simple salt $NaClO_3$ leads to deracemization[9] — the resolution of the system into all-right- or all-left-handed crystals over time. It seems that autocatalytic enantioselective recognition of microscopic or nanoscopic crystallites is necessary to move the system out of symmetric equilibrium[10] (here, light plays no role; however, the so-called Soai alkylation of aldehydes can be directed towards enantiopure products by autocatalysis with CPL[11]). The formation of twisted single crystals can also be mediated by special defects such as single dislocations[12] or low-angle boundaries[13].

The light-induced transformation of CdTe nanoparticles into twisted ribbons of CdS described by Kotov and colleagues involves many steps, including enantioselective photochemistry followed by oxidation and reduction, diffusion of Te out of the nanoparticles and S into them, nanoparticle association to build structures with longer-range order, and the process of twisting. Each of these steps, occurring at different time and length scales, will require further analysis in order to develop more efficient processes that can yield enantiopure materials. ❐

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