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Chiral nanomaterials: evolving rapidly from concepts to applications

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Chiral nanostructures is one of the most rapidly developing research fields encompassing chemistry, physics, and biology. The rise to academic prominence of chiral nanostructures was fueled by their giant optical activity and the fundamental structural parallels between biotic and abiotic structures with mirror asymmetry. Our introduction and the themed collection provide both a timely snapshot and comprehensive overview of concepts being developed by a diverse spectrum of scientists around the world working in in chiral nanostructures from metals, semiconductors and ceramics. Many fundamental discoveries in this area are expected that are likely to encompass multiscale chirality transfer, chiral surfaces, biological signaling, and circularly polarized emitters. Technological applications being pursued along the way of fundamental studies include biosensing, healthcare, chiral photonics, and sustainable catalysis.

Chirality, also known as mirror asymmetry, is a geometrical property describing the fact that an object and its mirror image are not identical to each other. One of the most characteristic examples of a three-dimensional chiral object is a helix that changes the direction of the twist from left to right when reflected in the mirror. In the realm of chemistry, chirality emerges when the chemical structures contain four or more atoms with non-planar geometry. Chirality has profound consequences for biology and optics because both biomolecules and photons can possess the same geometrical quality. The left- and right-versions of the chemical structures seem to behave identically in most of their properties, but they do not when interacting with other chiral structures.

Nanoparticles (NPs) are composed of a number of atoms that is of the same order of magnitude as that of proteins and, thus, must be able to exhibit chirality too.[1] For a long time, NPs have been pictured and described as simple spherical (or other symmetrical) objects but at the atomic scale, and even larger scales, they have complex features that display mirror asymmetry. This is the fundamental reason why a rapid development of chiral inorganic nanomaterials has occurred over the last two decades.[2–5] This themed collection in *Materials Advances* contains recent reviews and original papers that show the exciting research directions that chiral nanoscale structures have followed in optics, with some inroads also in biology and chiral chemistry.

A wide variety of chiral inorganic nanostructures and superstructures thereof have been synthesized and assembled. Many past and ongoing studies in chiral nanostructures are centered on metallic NPs and their assemblies. The avalanche of studies in this area has been motivated by the exceptionally strong circular polarization of photons when interacting with the plasmonic states of nanoscale matter that has become chiral at the molecular or nanometer scale,[6,7] arising from the chirality of DNA, the particles themselves, or their three-dimensional assembled structures.[8,9] Such a strong polarization rotation also indicates the possible biomedical qualities, such as the ability to detect the biomarkers of neurodegenerative diseases, which also display distinct nanoscale chirality.[10]

This themed collection of articles highlights the progress in the field, which is mostly related to metal nanostructures, but also includes semiconductor NPs. Wu and Pauly review the techniques employed to construct chiral plasmonic materials, and in particular the chemical methods of soft matter (DOI: 10.1039/D1MA00915J). The paper details various methodologies for the engineering of nanoscale chiral materials, based on lithography and self-assembly. To this spectrum of methods, they introduce the layered stacking of plasmonic nanowires, which display exceptionally high polarization rotation due to the cross-finger arrangements of the nanowires.

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Mondal *et al.* continue this topic and discuss both metal and semiconductor chiral inorganic nanostructures from the perspective of chirality transfer from organic molecules to the inorganic components of these materials (DOI: 10.1039/D1MA00846C). In particular, they point out the significance of chiral nanomaterials for optoelectronics and bio-applications. They additionally highlight in the review the technologies suitable for complementary metal-oxide semiconductor (CMOS) device processing as a manufacturing pathway to next-generation chiroptical devices. The authors also discuss approaches to resolve compatibility issues between CMOS processing and the self-assembly of nanomaterials.

From the onset of the field of chiral inorganic nanostructures, engineering of their three-dimensional geometry with DNA remains one of the most active areas of research. Yang *et al.* (DOI: 10.1039/D1MA00781E) review recent developments in the DNA programming of chiroplasmonic nanostructures, based on natural and artificial DNA segments. The authors point to the amazing variety of chiral geometries that are possible for materials based on DNA origami, spanning from individual NP–molecule hybrids to the hierarchical chiral superstructures of NPs with different complexities. The applications of DNA-programmed chiral plasmonic nanostructures, including in biodetection, metamaterials, and DNA computers, will inspire future studies in chiral materials at the convergence of DNA nanotechnology and chiral plasmonics.

Motivated by the need to engineer better sensors and metamaterials with a tunable optical response in the visible region, Dass *et al.* (DOI: 10.1039/D1MA01211H) also focus on a new development in the DNA-based methodology for the engineering of chiral nanostructures. Continuing on from prior studies in this area, they show that gold–silver core–shell NPs are suitable building blocks for plasmonic nanostructures, thereby expanding the range of attainable optical properties. The chiral arrangement of the core–shell nanorods affords a spectral tunability of chiroplasmonic resonances within a broad spectral window from 400 nm to 700 nm.

Kim *et al.* report on the variability of chiral shapes that metal NPs can acquire when grown from specific seeds in the presence of low molecular weight biomolecules (DOI: 10.1039/D1MA00783A). They show that complex chiral shapes of chiral gold NPs with characteristic sizes from 100 nm to 180 nm can be precisely adjusted by tuning the growth conditions. The presented data enabled a thorough assessment of the contributions from the electric dipole and magnetic dipole to the variation in the chiroptical response, as well as the optical asymmetry *g*-factors for chiroptical peak positions from 540 nm to 650 nm.

Fernandez-Caban *et al.* (DOI: 10.1039/D1MA00876E) describe enantioselectivity on the surfaces of chiral nanostructures, looking into the case of tartaric acid (TA) adsorbing on surfaces vicinal to Cu(111). The authors carried out comprehensive mapping of the enantiospecific surface reactivity *versus* the crystallographic orientation of the Cu surfaces. Idealized spherically shaped single crystal NPs allowed the direct measurement on 169 different Cu(hkl) surfaces of the adsorption of TA monolayers. Enantiospecificity is revealed by the dependence of the TA decomposition kinetics on the mirror asymmetry of the local arrangement of atoms. The authors found that D-TA is more reactive than L-TA on *S* surfaces, whereas L-TA is more reactive on *R* surfaces, which has connotations for the growth of chiral Cu NPs in dispersions. The most enantiospecific surface orientation was found to be Cu(754).

Although most studies of chiral inorganic nanostructures are carried out in solution, the optical response on surfaces has more nuanced optical effects. Fazel-Najafabadi and Auguie (DOI: 10.1039/D1MA00869B) show that light scattering by NP clusters varies with the spatial arrangement of the constituent particles and the orientation of the cluster with respect to the incident light. These effects must be considered in the context of chiroptical devices, which are typically based on solid surfaces. They computationally explored the angular dependence of polarization-dependent light absorption and scattering for three archetypal geometries: finger-crossed gold nanorods, a helix of gold nanospheres, and a linear chain of silicon particles. The optical effects in the far field are related to the local degree of optical chirality in the near field. Rigorous analytical solutions for fixed and orientation-averaged optical properties are offered, which may be useful for a variety of other systems.

Similar effects are described by Gilroy *et al.* (DOI: 10.1039/D1MA00831E) in the framework of chiroplasmonic structures with a gammadion shape, aiming for the ultrasensitive detection of chiral (bio)-molecules. The authors examined the formation of 'superchiral' near fields in gammadions with realistic surface roughness, which can potentially affect the local helicity of electromagnetic fields. This combined experimental and computational study shows that surface protrusions and indentations can actually be helpful toward the creation of spots with superchiral characteristics, due to the concentration of electric fields in such imperfections.

Wen *et al.* describe a relatively new area in the field of chiral inorganic nanostructures – the emission of circularly polarized luminescence from semiconductor NPs (DOI: 10.1039/D1MA00843A). The emitters in this case are achiral (to be more exact, racemic), but they are embedded in a nucleotide–amino acid hydrogel that forms twisted ribbons with a specific handedness. The helicity of the hydrogel can be controlled by the chirality of one of the components – a fluorenylmethoxycarbonyl derivative of the amino acid glutamine (Glu). The mirrored circularly polarized luminescence spectra of such nanoparticles were obtained when the gels were based on derivatives of L- or D-Glu, respectively. This study provides a convenient way to fabricate optically active devices using gels.

Overall, this collection of articles provides an excellent overview of exciting areas of research and application of chiral nanomaterials, in particular focusing on the relevance of the chiral morphology toward the optical response of such nanomaterials. The field is at an extremely active and thrilling stage, which will definitely result in the further demonstration of interesting properties and applications of chiral nanomaterials to be discovered.

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