

REVIEW

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in their synthesis and applications

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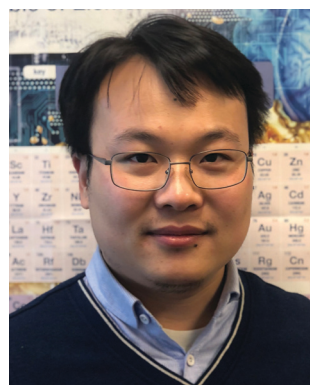
Chirality describes the geometric property of an object that is not superimposable on its mirror image and has been a pivotal concept in chemistry and biology since the 19th century. Chiral plasmonics has attracted increasing attention over the past years as modern nanofabrication techniques and soft-chemistry synthesis and assembly approaches have allowed the preparation of complex and well-controlled chiral metallic nanostructures with promising applications in fields such as molecular sensing and chiral separation and synthesis, or as optical polarizing elements. This review covers the main techniques employed to construct chiral plasmonic materials, in particular using soft-chemistry approaches, and discusses some applications of these nanostructures on the basis of recent examples drawn from the literature.

1. Introduction

Chirality is the geometrical property of an object lacking any planes of symmetry or inversion centers which distinguishes the original object from its non-superimposable mirror image – a chiral object and its mirror image are called enantiomorphs, or when referring to molecules, enantiomers.¹ Human hands are the most explicit illustration of this concept, and the word

“chirality” is derived from the word “hand” ($\chi\epsilon\iota\rho$ or $k\eta\epsilon\iota\rho$) in ancient Greek.

It was Lord Kelvin who coined the term in 1893:² “I call any geometrical figure, or group of points, ‘chiral’, and say that it has chirality if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself”, although the concept of molecular chirality had already been discovered by Louis Pasteur in 1848, while investigating the enantiomers of a tartaric acid salt,^{3,4} and described as “dissymmetry” at the time. It was not until 25 years later that Le Bel⁵ and van’t Hoff⁶ established the basis of molecular stereochemistry by formulating the notion of asymmetrical tetrahedral carbon atoms.



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Beyond its purely geometrical description, chirality also manifests itself through specific optical properties. Indeed, different enantiomers have different complex refractive indices for right- and left-handed circularly polarized (RCP and LCP) light, which can be described as “chiral light”. The difference in the imaginary part of the refractive index results in circular dichroism (CD), *i.e.*, a different absorption of RCP and LCP light, while the difference in the real part leads to circular birefringence (CB), which causes the rotation of a linearly polarized light field from its original orientation while traveling through a chiral medium. The upper scale where chirality emerges and chiroptical phenomena can be detected is of the order of the wavelength of the light used to probe the optical activity. The chiroptical properties of (bio)molecules, which arise on the molecular scale, manifest themselves in the UV-visible range and this mismatch makes the optical activity inherently weak. Surface plasmon resonances, which arise due to the coherent collective excitation of free electrons at the interface between two materials with opposite permittivities (typically a metal and a dielectric), result in the confinement of light on the nanoscale and have thus been used to boost various optical phenomena including chiroptical effects.^{24,25}

In this review, we will focus on the fabrication and applications of plasmonic chiral systems. We will first briefly present some examples of the top-down methods used to build chiral plasmonic nano-objects, before discussing the bottom-up approaches in more detail. We will in particular introduce recent examples of the synthesis of chiral nanoparticles and the different routes explored to build chiral assemblies of non-chiral nanoparticles. In the last section, various applications of such nanostructures will be discussed on the basis of recent examples drawn from the literature.

The top-down approach²⁶ involves the local elimination of material from a larger object or film in order to obtain the desired shape, layout and properties, using technologies such as direct laser writing (DLW), focused ion beam etching, and optical or electron-beam lithography. The gammadion is an archetypal “planar” chiral shape that has been widely studied.^{27–33} The optical chirality in such a planar structure arises not only from its “2D chiral” shape (any 2D structure is intrinsically mirror-symmetric and thus inherently achiral in 3D space), but also from the difference between the air-sample and sample-substrate interfaces that is required to break the symmetry.²⁸ On the contrary, the helix shape is a typical chiral structure and the top-down fabrication of metallic helices, especially gold and silver, has been extensively studied.^{34–37} For example, J. K. Gansel *et al.*³⁸ obtained gold helix arrays by DLW, which display a different transmittance for LCP and RCP light in the mid-infrared regime (Fig. 1A). In a positive photoresist, two-photon direct laser writing was used to produce helical pores, which were then filled with gold by electrochemical deposition. A free-standing array of gold helices was thus obtained by eliminating the residual polymer mold by plasma etching. This work largely extended the spectral width of plasmonic chiroptical effects and exhibited potential for controlling these effects by tuning the structural parameters including the pitch and diameter of the helices.³⁹ More complex metallic helical nanostructures were reported several years later by A. Radke *et al.* (Fig. 1B).⁴⁰ These authors combined DLW with electroless silver plating, an autocatalytic process allowing the deposition of silver in the helical voids

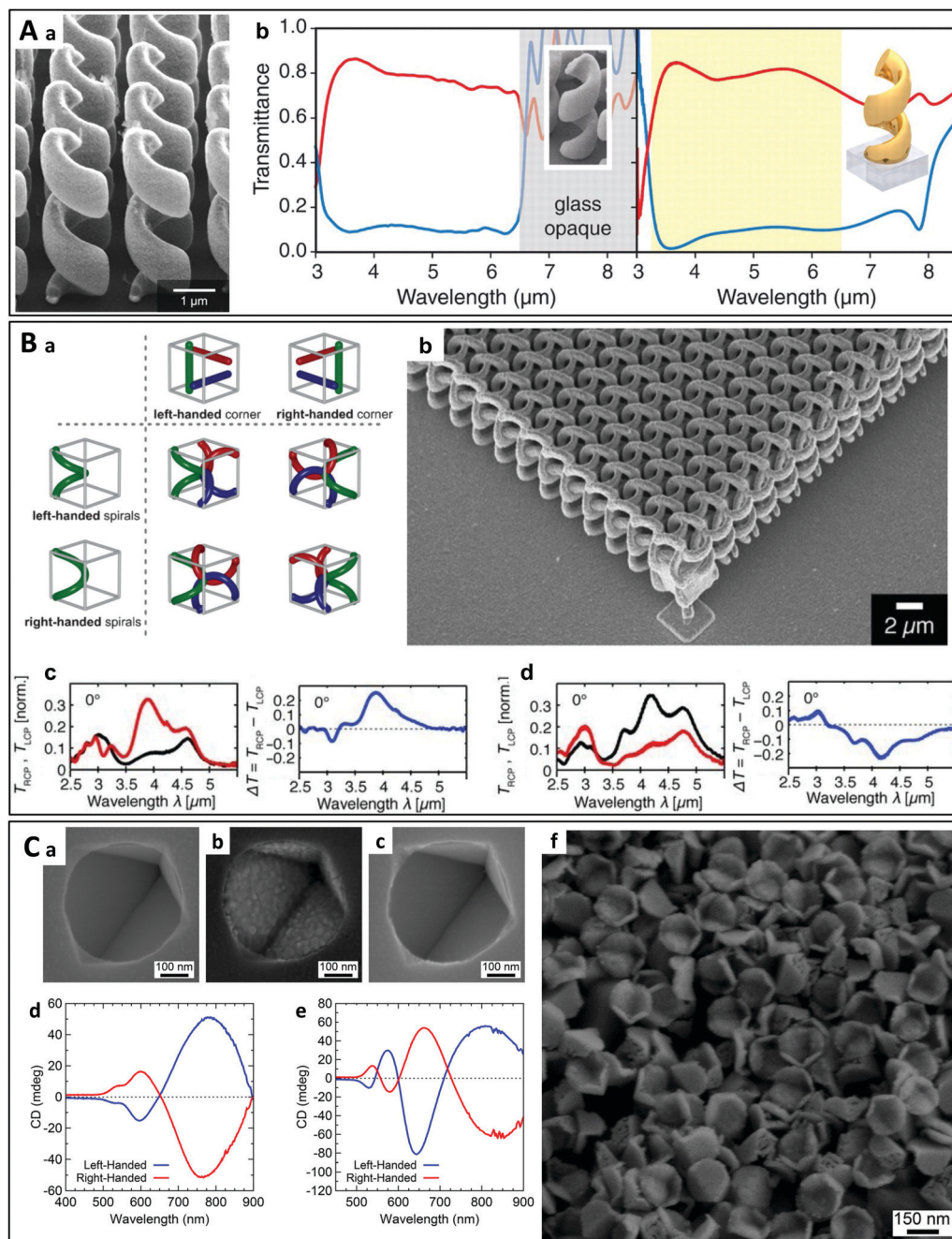


Fig. 1 (A) (a) Oblique view of an array of left-handed gold helices. (b) Experimental and modeled transmittance spectra of right-handed helices for LCP (blue lines) and RCP (red lines) light.³⁸ Copyright 2009 American Association for the Advancement of Science. (B) (a) The four possible combinations of chiral helices and corners.⁴¹ Copyright 2009 John Wiley and Sons. (b) Oblique view of a bichiral crystal with right-handed corners and helices. (c) and (d) Transmittance spectra of a bichiral crystal with left-handed corners and helices (c) and right-handed corners and helices (d) for LCP (black lines) and RCP (red lines) light at an incident angle of 0° (left spectra), and the corresponding difference in transmittance (right spectra).⁴⁰ Copyright 2011 John Wiley and Sons. (C) SEM images of (a) a left-handed etch pit formed by anisotropic etching of [111] Si, (b) the same pit with a 50 nm deposit of Au and (c) the left-handed Au nanopryramid extracted from the pit. Experimental CD spectra of left- and right-handed chiral Au nanopryramids deposited (d) with the wafer tilted and rotated during deposition and (e) with the wafer normal to the incident flux. (f) SEM image of left-handed gold nanoparticles.⁴⁵ Copyright 2014 American Chemical Society.

previously obtained by DLW. Both left- and right-handed helices were constructed ("chiral helices"). The helices were arranged in a cubic lattice with their axes ordered in both left- and right-handed fashions ("chiral corners"). The structures obtained were therefore referred to as bichiral⁴¹ crystals, which

have four possible combinations stemming from their two levels of chirality. The chiroptical effects were found to be enhanced for combinations of helices and corners with the same handedness and reduced for those with different handedness. Meanwhile, metallic crystals have shown much



Top-down approaches are suitable for the fabrication of nanoparticles or nanocrystals with a chiral geometry as any shape can be designed at will (the only limit being the size of the structure). However, most studies have focused on assemblies of similar nano-objects placed in a 2D plane either at random positions or ordered on a regular 2D array.^{24,50}

While well-defined nanostructures can be produced by lithographic techniques (and more generally top-down approaches), they often require multistep processes and expensive vacuum-based equipment. In particular, the building blocks need to have subwavelength dimensions, *i.e.*, of the order of tens of nanometers for applications in the visible and UV range, which is challenging, even for e-beam lithography. Obtaining well-defined nanostructures over large areas is also difficult, although some top-down approaches like colloidal lithography can face up to this challenge.²⁵ The problem is even greater in the case of “3D” multilayer nanostructures which require precise alignment of the individual building blocks in each layer. These technologies are also inherently restricted to small areas, which limits our capacity to produce macroscopic-scale materials.⁶³ Bottom-up techniques have thus been proposed in recent years as an alternative approach to address these issues.

As opposed to top-down methods, the bottom-up approach^{26,63–65} involves arranging small particles into more sophisticated hierarchical structures and assemblies, in which the material properties attained go beyond the sum of the properties of the individual building blocks. Chiral plasmonic nanostructures can be synthesized using various techniques, the chirality being obtained either through chiral arrangement of the particles by controlling the external constraints during

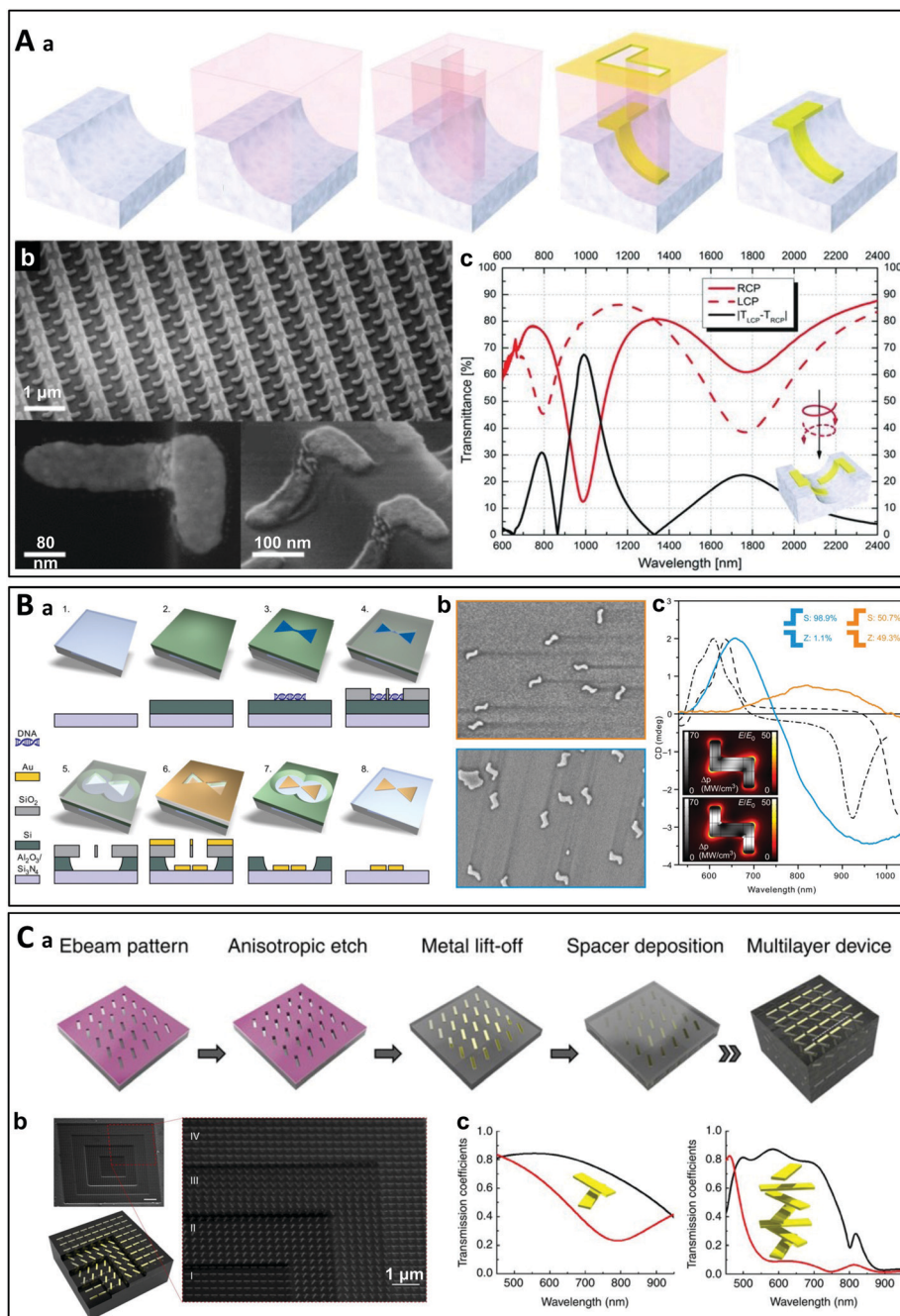


Fig. 2 (A) (a) Schematic representation of the on-edge lithography method, where L-shaped gold particles are deposited by e-beam lithography on the edge of the stripes of a pre-patterned substrate. (b) SEM images of the resultant chiral nanomaterial array. (c) Simulated transmittance spectra of a 3D L-particle array for RCP and LCP light and their intensity difference.⁴⁶ Copyright 2012 John Wiley and Sons. (B) (a) Schematic representation of the lithography process in which DNA origami nanostructures are used as a mask (the bow-tie shape shown here is non-chiral). (b) SEM images of samples containing a 50:50% (racemic) distribution of S- and Z-shaped nanostructures (top) and ~99% S-shaped nanostructures (bottom). (c) Measured CD spectra of the samples shown in (b) and simulated CD responses for symmetric (dashed) and slightly asymmetric (dash-dotted) S-shaped chiral nanoparticles.⁴⁷ Reproduced under the terms and conditions of the CC-BY license. (C) (a) Schematic representation of the lithographic fabrication of a multilayered chiral nanostructure. (b) SEM images of a four-layer device using samples prepared by focused ion beam milling to reveal each layer. (c) Transmittance spectra of a two-layer and a four-layer device for LCP and RCP light.⁵⁴ Copyright 2012 Springer Nature.

assembly (for instance using shear forces that induce a linear anisotropy to build oriented layers of 1D nanoobjects that can be stacked into a Bouligand structure) or by means of chiral

templates. As compared to top-down methods, bottom-up approaches are often faster, less expensive and more adaptable to prepare arbitrary structural geometries over a larger range of scales.⁶⁶



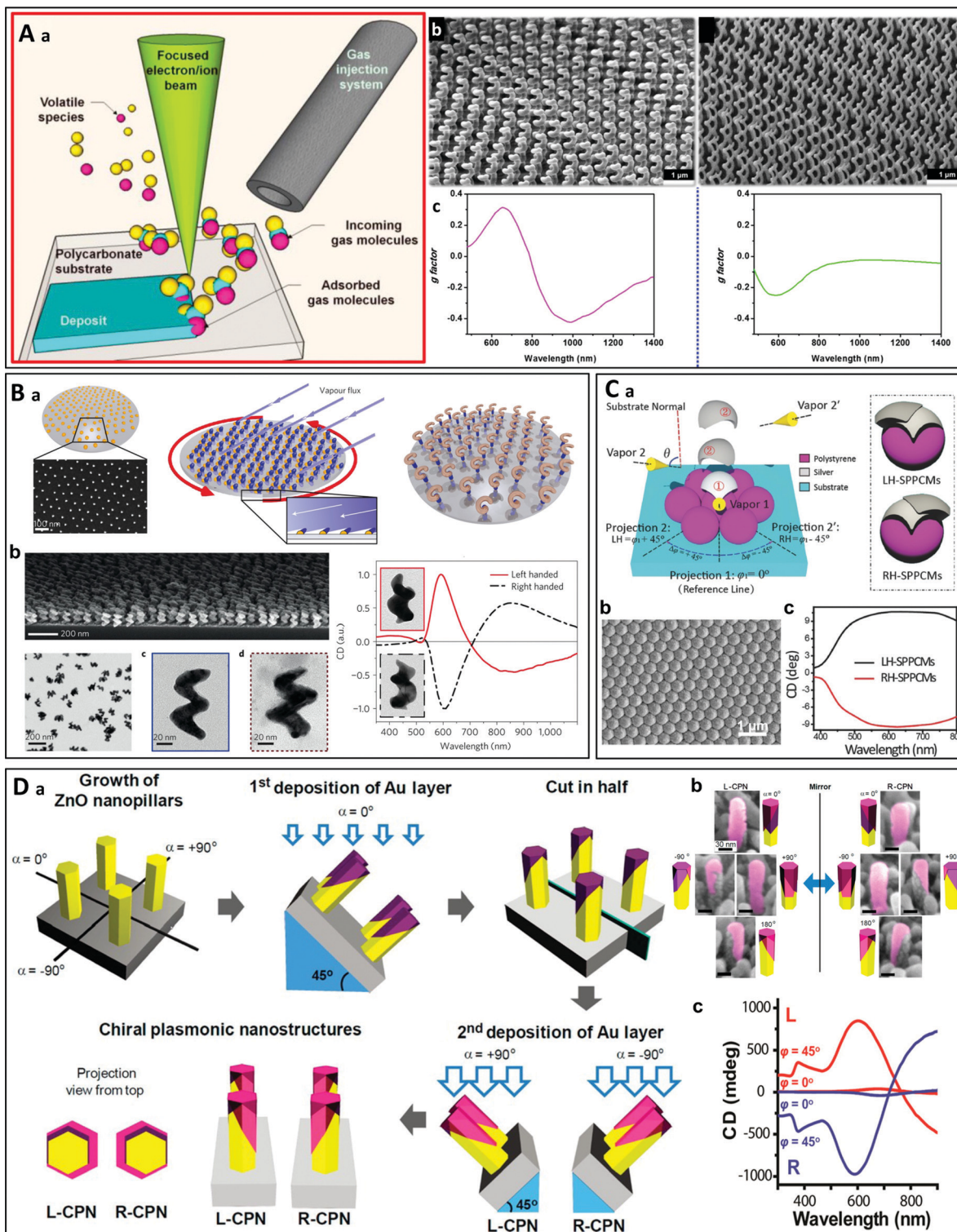


Fig. 3 (A) (a) Schematic principle of FIBID/FEBID on a flexible substrate.⁷⁰ Copyright 2015 American Chemical Society. (b) Arrays of chiral platinum nanohelices with different pitches prepared by FIBID (left) and FEBID (right) and (c) their experimental g -factor spectra.⁷¹ Copyright 2015 American Chemical Society. (B) (a) Schematic principle of glancing angle deposition (GLAD). (b) SEM images of Au:Cu (65:35) nanohelices obtained by GLAD. (c) CD spectra of left- and right-handed Au helices.⁷³ Copyright 2013 Springer Nature. (C) (a) Schematic representation of two-step GLAD on a self-assembled microsphere monolayer (left) and the resultant LH and RH stacked-patch plasmonic chiral metamaterials (SPPCMs). (b) Top-view SEM image of a 90 nm-thick LH SPPCM. (c) CD spectra of LH and RH SPPCMs.⁸¹ Copyright 2016 John Wiley and Sons. (D) (a) Schematic principle of the synthesis of chiral plasmonic nanoshells (CPNs) by vacuum evaporation. (b) SEM images of the left- and right-handed nanostructures at different angles (Au layers were artificially colored for clarity) and (c) experimental CD spectra of an L-CPN and an R-CPN at normal ($\phi = 0^\circ$) and inclined light incidence ($\phi = 45^\circ$).⁸² Copyright 2013 American Chemical Society.



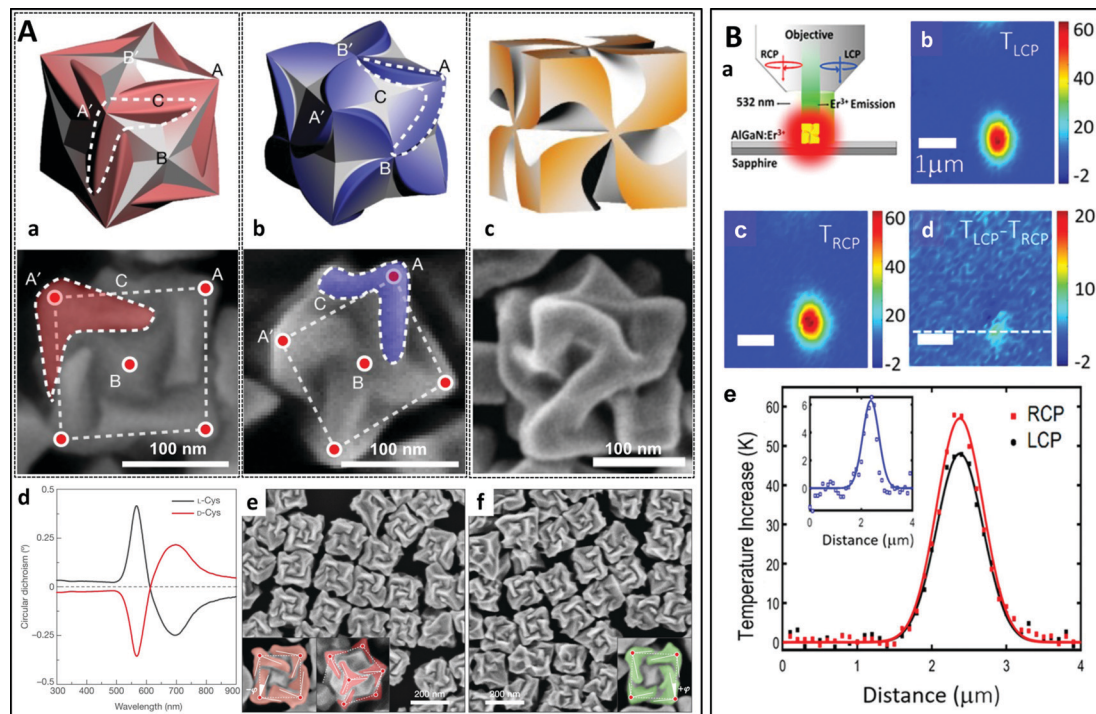


Fig. 4 (A) Chiral gold helicoids obtained by amino-acid- or peptide-directed growth. (a) 432 helicoid I, grown on a cubic seed under L-cysteine-control. (b) 432 helicoid II, grown on a cubic seed under L-glutathione-control. (c) 432 helicoid III, grown on an octahedral seed under L-glutathione-control. (d)–(f) CD spectra (d) and SEM images of the left-handed (e) and right-handed (f) 432 helicoid I.⁸⁷ Copyright 2018 Springer Nature. (B) (a) Schematic diagram of photothermal circular dichroism under RCP/LCP light. (b)–(d) Thermal image of a small cluster of chiral helicoid under LCP (b) and RCP (c) light, and the difference between LCP and RCP individual images obtained from luminescence ratio thermometry (d). (e) Thermal profiles under LCP and RCP illumination. The inset shows the thermal profile from panel (d) along the white dashed line.⁸⁹ Copyright 2020 American Chemical Society.

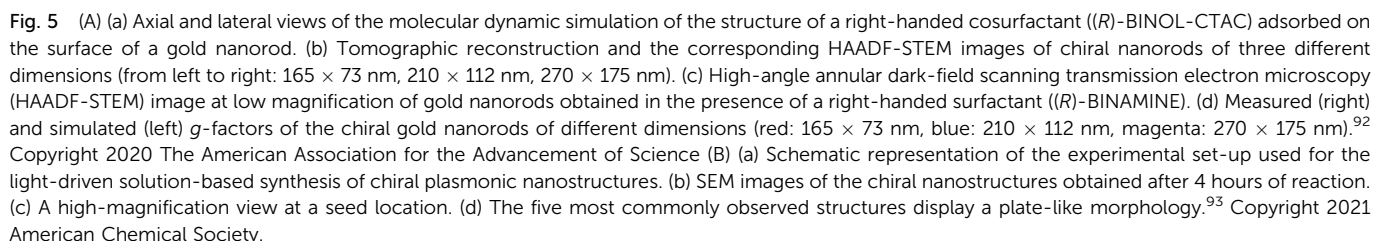
decaying within about 10 nm of the surface of the islands (Fig. 6A).⁹⁸ In more recent work,¹⁰⁰ non-chiral chromophores were hybridized with double-stranded DNA, which induced bisignate CD signals at the absorbance band of the chromophores (Fig. 6B). Interestingly, after coupling to a plasmonic resonance mode of gold nanorods, the CD signals were reversed and enhanced by one order of magnitude.

Beyond the transfer of chirality to a single nanoparticle, placing a chiral molecule in the gap between two plasmonic nanoparticles can significantly enhance the chiroptical effect due to the stronger electromagnetic field in the gap, also known as a “hotspot”. This important enhancement has seen applications in the sensitive detection of chiral molecules, especially biomolecules (see Section 4.5.1). For example, X. Wu *et al.* reported the ultra-sensitive sensing of a protein by encapsulating the molecule in the gap of a heterodimer of gold and silver nanoparticles (Fig. 6C).¹⁰² Although the geometry was not chiral, the presence of the chiral biomolecule in the plasmonic hotspot led to remarkable plasmonic CD. Recently, L. Tian *et al.* synthesized plasmonic homodimers and heterodimers with a metal–organic molecular cage (MOC) in the hotspot, which then served as a receiver of (chiral) molecules. The authors demonstrated interesting interaction phenomena including enhanced chirality (Fig. 6D), as well as surface-enhanced Raman scattering and plasmonic tuning.¹⁰³ L. M. Kneer *et al.* prepared a two-layer sheet (2LS) DNA origami supporting single-stranded DNA-coated gold nanospheres or nanorods.¹⁰⁴ Transfer of

chirality from the DNA origamis located in the hotspots to the nanoparticles resulted in enhanced CD signals at the plasmonic resonances. Finally, Severoni *et al.* placed chiral molecules at the tip of gold nanorods assembled into chains, leading to plasmon-enhanced circular dichroism.¹⁰⁵ The role of optical hotspots at the gaps of linear tip-to-tip nanorod assemblies is shown to be the origin of enhancement in the dichroism from chiral molecules. Furthermore, the refractive index rather than the absorption-mediated chiral response of the molecules is responsible for the dichroism in the visible-NIR plasmonic regime, far from the molecule UV absorption resonances.

3.2.3. Self-assembly. The self-assembly^{106–109} of nano-objects into functional superstructures has been a dynamic field of research in recent years. Self-assembly methods, which use chemical or physical forces to arrange individual building blocks in well-defined hierarchical ensembles, represent an important component of the bottom-up strategies to fabricate chiral plasmonic nanostructures.^{66,110–112} Indeed, self-assembly can be used to arrange non-chiral plasmonic particles in a chiral pattern, where the interactions of the dipole moments of the individual nanoparticles give rise to coupled collective modes with different responses to LCP and RCP light.^{66,113–117} Numerous modes can exist in a complex structure and they can be excited and spectrally overlap with one another, producing the complicated CD spectra of chiral plasmonic nano-assemblies. Self-assembly methods nevertheless





3.2.3.1. Nanoparticle assembly on pre-formed chiral templates. Conventional templates for chiral plasmonic assemblies include thin films patterned by e-beam-lithography,¹¹⁸ polymers,^{119,120} nanofibers,^{121,122} DNA^{98,123–129} and other biomolecules.^{130,131} For example, chiral assemblies have been synthesized in aqueous suspensions of plasmonic nanorods using chiral supramolecular nanofibers as templates (Fig. 7A).¹²¹ Jung *et al.* employed a gelator template moiety in combination with specific helicity-directing molecular

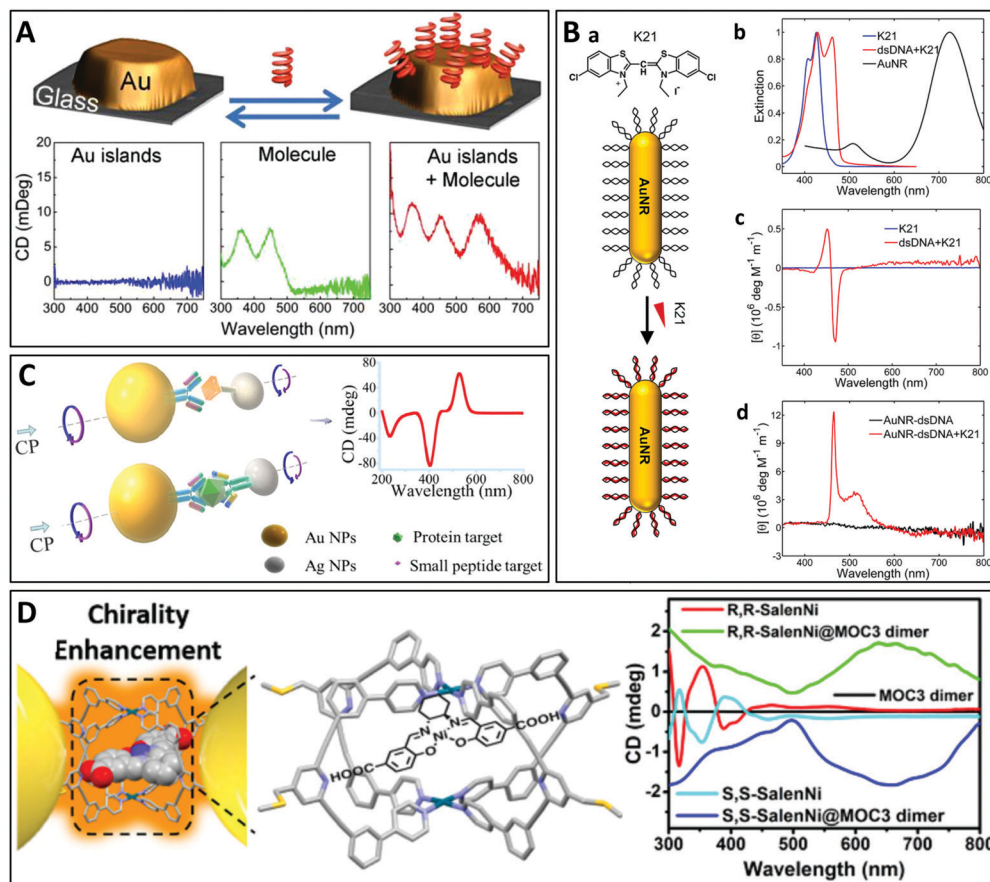


Fig. 6 (A) Chiroptical activity induced by interaction with riboflavin placed close to a non-chiral gold nanoparticle (AuNP). CD emerges at the plasmonic resonance of the AuNP while the CD of the biomolecule is also enhanced.⁹⁸ Copyright 2013 American Chemical Society. (B) (a) Schematic representation of the assembly of the chromophore molecule K21 with a gold nanorod (AuNR) conjugated to double-stranded DNA (dsDNA). (b) Normalized extinction spectra of aqueous solutions of K21 before (blue) and after (red) binding to dsDNA and of AuNRs alone (black). (c) CD spectra of K21 before and after binding to dsDNA. (d) CD spectra of AuNRs conjugated to dsDNA before and after self-assembly of K21 on the DNA templates.¹⁰⁰ Copyright 2019 American Chemical Society. (C) Schematic illustration of the assembly of NP heterodimers and their use for biological analyses.¹⁰² Copyright 2013 American Chemical Society. (D) Chirality enhancement of chiral molecules encapsulated in the MOC located in the gap of a plasmonic dimer.¹⁰³ Copyright 2021 American Chemical Society.

components to produce long helical nanofibers, on which the controlled growth of gold nanoparticles at spatially arranged locations along the fibers was achieved by UV reduction of Au(I) ions on the supramolecular templates.¹³² Chemical reduction of Au(I) has also been performed on the supramolecular fibers of chiral peptides.^{133–136} In two recent reports, Oda *et al.* described the assembly of gold nanospheres on silica helices through hydrostatic interactions¹³⁷ and covalent binding¹³⁸ (Fig. 7B). The chiroptical properties arose from anisotropic coupling between the nanoparticles arranged on the helices. This was further evidenced by the fact that the chiral character of the material vanished in a multilayer film of aligned helices when the helices were close enough to interact with each other.¹³⁸ Multilayer films of oriented nanoparticle-grafted helices have been aligned using grazing incidence spraying (GIS).^{139–143} The multilayer structure was obtained through layer-by-layer (LbL) assembly,^{144,145} whereby the interlayer spacing can be finely tuned. When the spacing between the helices is small, non-chiral interactions between nanoparticles

on neighboring helices dominate the chiral interactions between nanoparticles on the same helix, causing loss of the chiroptical properties. This work is one of the examples demonstrating that chiroptical properties can be modulated not only in the individual chiral building blocks but also through hierarchical arrangement using self-assembly methods.

Another strategy employs cellulose nanocrystals which naturally form cholesteric phases. Upon evaporation of a mixed suspension of cellulose and gold nanorods/nanoparticles^{131,146–150} or silver nanowires,¹⁵¹ the nano-objects are embedded during evaporation (Fig. 7C). Chiral soft liquid crystals may also be used to template the assembly of plasmonic nanoparticles.^{152–155} These templates can enable the efficient assembly of larger amounts of nano-objects but lack tunability, which is limited by their structure.

The DNA origami represents another very popular template allowing the synthesis of reconfigurable chiral nanostructures.^{156–158} This involves the folding of long DNA strands into 2D and 3D nanostructures by hybridizing them with so-called staple oligonucleotides. The staple oligonucleotides are connected with the



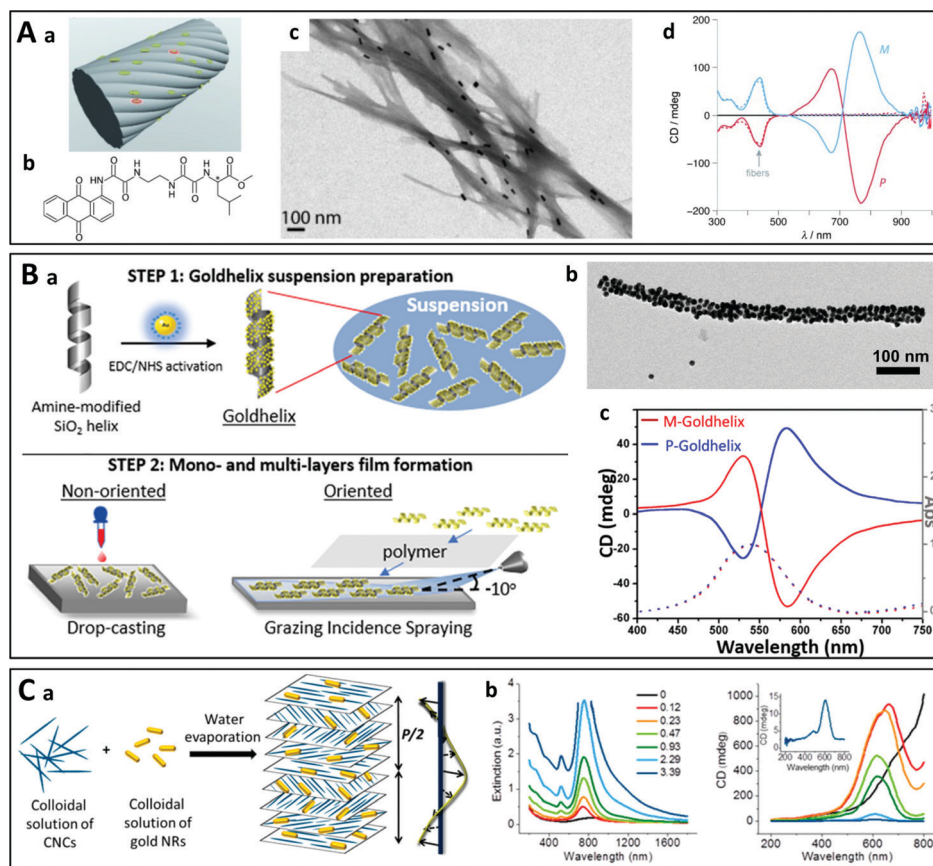


Fig. 7 (A) (a) Schematic representation of the nanoparticles on the supramolecular fibers prepared from anthraquinone-based oxalamide (b). (c) TEM image of gold nanorods adsorbed on twisted supramolecular *M*-fibers. (d) Experimental CD spectra of right- (*P*) and left-handed (*M*) fibers.¹²¹ Copyright 2011 John Wiley and Sons. (B) (a) Schematic principle of the assembly of gold nanoparticles on silica helices and their incorporation into multilayer thin films by LbL assembly. (b) TEM image of a gold-nanoparticle-coated silica helix. (c) CD (solid line) and absorbance (dashed line) of a *P*- and *M*-silica helix coated with gold nanoparticles.¹³⁸ Copyright 2020 American Chemical Society. (C) Liquid crystal-like chiral nanostructures obtained by self-assembly of gold nanorods (NRs) and cellulose nanocrystals (CNCs) as the template. Upon slow evaporation of water from an aqueous suspension of a mixture of CNCs and gold NRs, the CNCs form a left-handed liquid crystalline cholesteric phase and the NRs embedded in the cholesteric solid film align with the orientation of the cellulose nanofibers. (b) Extinction (left) and CD spectra (right) with increasing concentration of NRs in the film.¹³¹ Copyright 2014 American Chemical Society.

DNA through Watson–Crick base pairing and their positions are predetermined, which dictates the shape of the DNA origami structures. When used as template for the self-assembly of chiral plasmonic nanostructures,^{66,159,160} the DNA origami acts as a scaffold on which the nanoparticles are grafted and is the origin of the chirality.¹⁶¹ For example, in pioneering work in 2012, long DNA strands bearing hundreds of specifically designed staple oligonucleotides were assembled in a DNA origami containing 24-helix bundles offering nine attachment sites for single-stranded DNA-coated gold nanoparticles.¹²⁶ Left-handed and right-handed self-assembled gold helices were thus obtained, leading to a CD close to the resonance wavelength of the individual particles (Fig. 8A). Lan *et al.* used bifacial origamis and gold nanorods (AuNRs) to construct discrete 3D anisotropic plasmonic dimer nanoarchitectures with a precisely modulable spatial configuration.¹⁶² The same group further prepared AuNR helical superstructures with predetermined chirality where the origami was intercalated between neighboring AuNRs.¹⁶³

This approach allowed precise control of the inter-rod distance and angle as well as the average number of nanorods in the helices (Fig. 8B).

Diverse chiral architectures based on DNA origami have been prepared, including gold nanorod dimers^{164–167} and trimers,^{165,168} gold–silver core–shell nanorod dimers,¹⁶⁹ micrometer-long plasmonic polymers,¹⁷⁰ spherical AuNP tetrahedron architectures.¹⁷¹ Very recently, Martens *et al.* studied the long- and short-range chiral interactions in DNA-assembled plasmonic chains where the coupling was ensured by an achiral nanosphere situated between a pair of gold nanorods arranged far apart but in a chiral fashion using a DNA origami.¹⁷² The transmitter particle caused strong enhancement of the CD response with the emergence of an additional chiral feature at the resonance frequency of the nanosphere. Lan *et al.* have developed an approach for the tunable self-assembly of chiral DNA supramolecular architectures using a versatile DNA origami adapter.¹⁷³ The configurational handedness of self-assembled metastructures of plasmonic nanorods can be



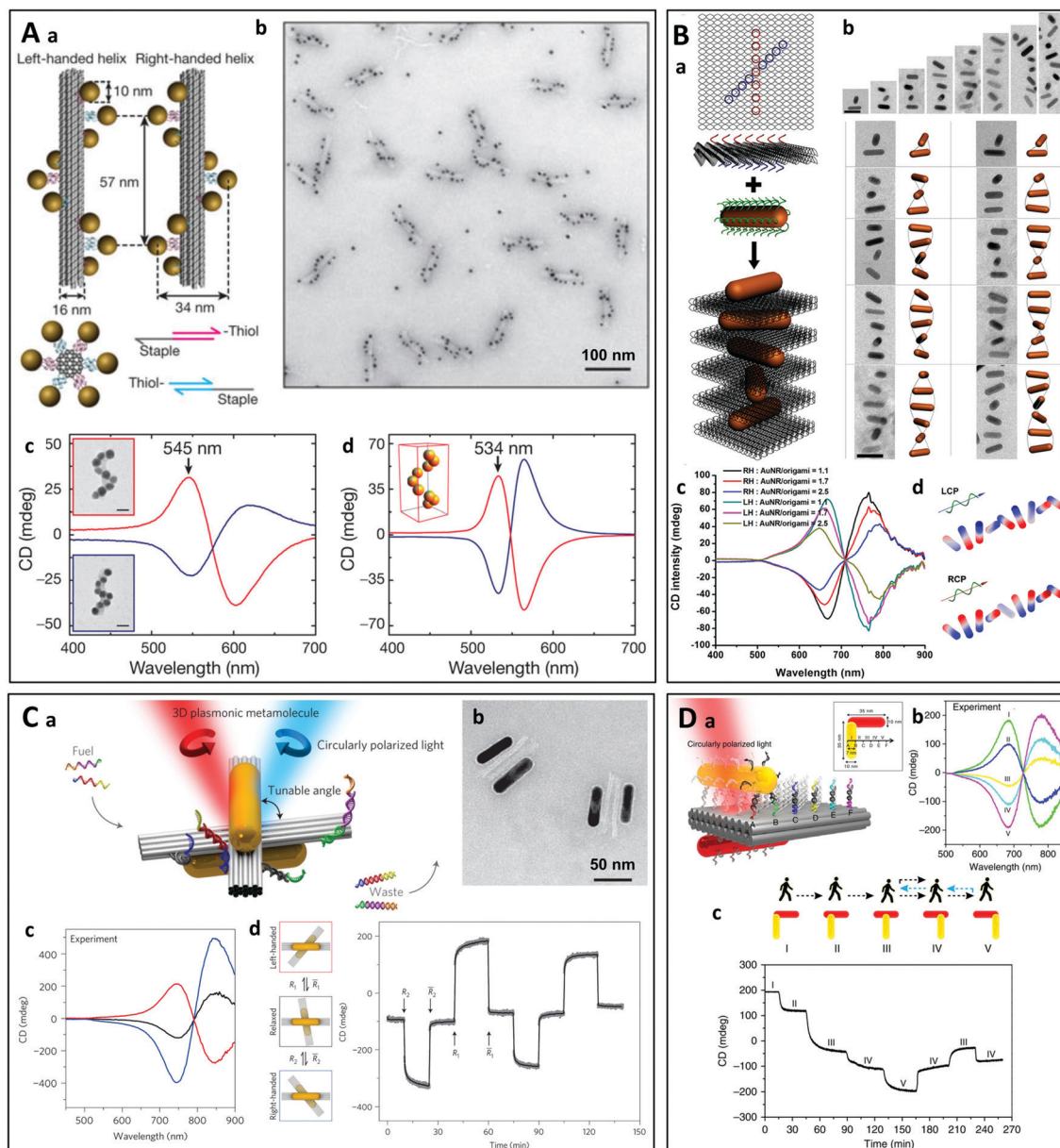


Fig. 8 (A) (a) Schematic representation of left-handed and right-handed gold helices assembled on DNA bundles. (b) TEM image of assembled left-handed gold nanohelices. (c) and (d) Measured (c) and modeled (d) CD spectra of left-handed (red lines) and right-handed (blue lines) helices that are made from 16 nm gold nanoparticles.¹²⁶ Copyright 2012 Springer Nature. (B) (a) Schematic representation of the self-assembly of right-handed AuNR helices using a DNA origami. (b) Cryo-TEM images of the assembled AuNR helices containing varying numbers of AuNRs and the corresponding reconstructed models. (c) CD spectra of right-handed and left-handed helices containing varying number of AuNRs. (d) Calculated surface charge distribution profile of a right-handed helix upon induced by the illumination with LCP and RCP light.¹⁶³ Copyright 2015 American Chemical Society. (C) (a) Schematic representation of a gold nanorod dimer attached to two DNA bundles at a tunable angle. The CD of the structure can be modulated by adding specific DNA strands to change the angle between the two nanorods. (b) TEM images of the plasmonic metamolecules in the right-handed state. (c) CD spectra measured in the left-handed (red line), relaxed (black line) and right-handed (blue line) states. (d) The plasmonic metamolecules can be driven to either the left- or right-handed state by adding specific DNA strands (R_1 and R_2). The CD signal was monitored over time at a fixed wavelength of 725 nm.¹⁷⁷ Copyright 2014 Springer Nature. (D) (a) Schematic of the plasmonic walker. Two gold nanorods (AuNRs) are assembled perpendicularly to one another on a double-layer DNA origami template, and the walking track comprises six rows of footholds (A–F) to define five walking stations (I–V). (b) Measured CD spectra at different stations. (c) Directional (forward and reverse) nanoscale “walking” of a nanorod on a DNA sheet leads to a change in the CD of the nanorod dimer.¹⁷⁸ Reproduced under the terms and conditions of the CC-BY license.

modulated with the DNA origami adapter to produce stair-like and coil-like metastructures.

Many efforts have been made to design DNA origami-based chiral nanostructures responding to external stimuli,^{115,174}

which may be employed for the sensitive detection of (bio)molecular species in solution.¹⁷⁵ Thanks to the reversible binding of the DNA strands, actively tunable chiral plasmonic nanostructures can be obtained using DNA origami templates.¹⁷⁶



Single-stranded DNA (ssDNA) chains are widely used to functionalize nanoparticles on account of their ability to bind very specifically to their complementary ssDNA through DNA hybridization. For example, chiral pyramids^{182–184} have been obtained using ssDNA scaffolds (Fig. 9A). Gold nanoparticles of two different sizes were synthesized and functionalized with four different ssDNA strands constituting two complementary pairs. Asymmetric pyramids composed of two large and two small gold nanoparticles were produced by hybridizing the two kinds of functionalized nanoparticles. The same group has prepared gold nanorod dimers as well as twisted assemblies with multiple nanorods in both side-by-side and end-to-end configurations using a DNA polymerase chain reaction.¹⁸⁵ Due to the heat sensitivity of the reaction, similar structures have been shown to respond to temperature changes (Fig. 9B).¹⁸⁶

Peptides are also frequently employed to stabilize nanoparticles.^{87,199–202} The assembly of the nanoparticles is

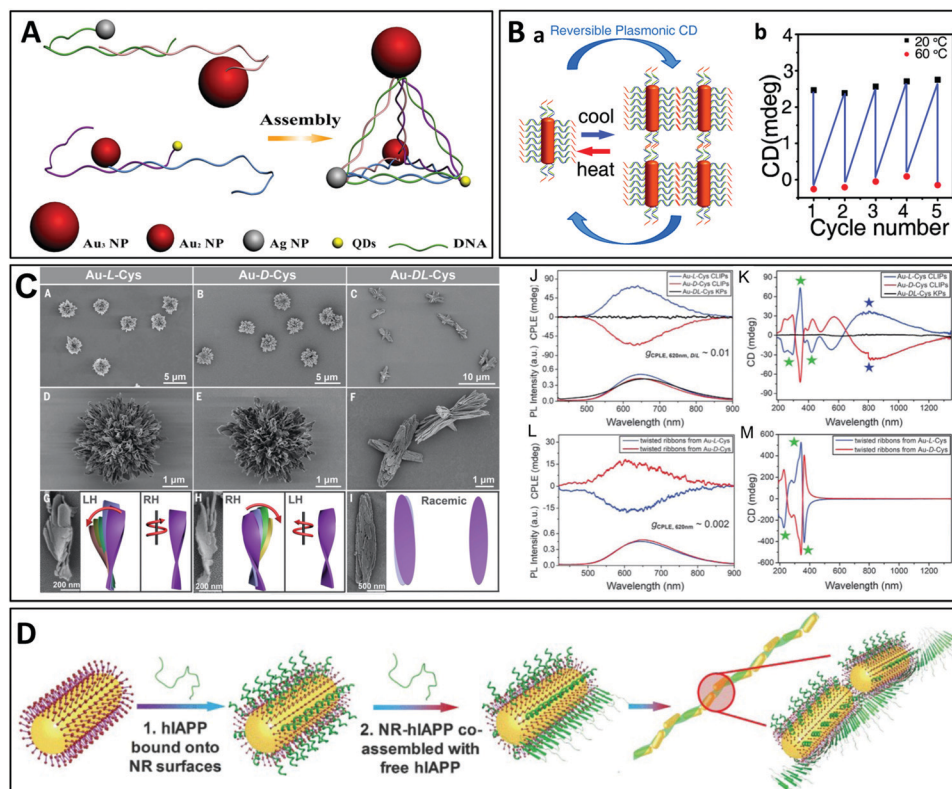


Fig. 9 (A) Nanoparticles functionalized with ssDNA strands are assembled into chiral pyramids by DNA hybridization.¹⁸³ Copyright 2012 American Chemical Society. (B) Assembly and disassembly of gold nanorod dimers functionalized with ssDNA strands upon cooling and heating.¹⁸⁶ Copyright 2012 American Chemical Society. (C) Low magnification SEM images of hierarchically organized gold nanoparticles coated with cysteine surface ligands, which formed left- or right-handed coccolith-like particles (CLIPs) [(A) and (B)], or kayak particles (C) when a racemic mixture of D- and L-cysteine was used. (D to F) Enlarged SEM images of Au-L-Cys and Au-D-Cys CLIPs [(D) and (E)] and Au-DL-Cys kayak particles (F). (G to I) SEM images and the corresponding schematic illustrations of the individual twisted ribbons constituting the CLIPs. (J) Circularly polarized light emission (CPLE) and (K) CD spectra of Au-L-Cys CLIPs (blue), Au-D-Cys CLIPs (red) and Au-DL-Cys kayak particles (black). (L) CPLE and (M) CD spectra of Au-L-Cys (blue) and Au-D-Cys (red) twisted ribbons.¹⁹⁰ Copyright 2020 The American Association for the Advancement of Science. (D) Liquid crystal-like helices with a long-range order obtained by assembly of the human islet amyloid polypeptide (hIAPP) with NRs.¹⁹⁹ Copyright 2021 The American Association for the Advancement of Science.

achieved through polymerization of the peptides anchored on the particle surface. In a recent study, J. Lu *et al.* used the human islet amyloid polypeptide (hIAPP) for the helical assembly of gold nanorods (Fig. 9D).¹⁹⁹ The hIAPP is the hormone that regulates physiological glucose concentrations and is responsible for fiber formation in the human brain. Its secondary structure forms a β -sheet which assembles into long tape-like helical structures with a regular pitch. These authors conjugated gold nanorods with hIAPP and obtained liquid crystal-like helices through self-assembly of the peptide β -sheets. The helical assemblies with long range organization displayed a g -factor of up to 0.12, which was 4600 times higher than that of the individual nanorods functionalized with hIAPP. The enhanced optical asymmetry stemmed from the long-range coupling of the longitudinal plasmons, while unfavorable scattering was reduced by antiparallel orientation of the dipoles. In addition, geometrical factors such as the nanorod size, helical pitch, distance between the nanorods and number of nanorods could be finely tuned, allowing for tunability of the optical asymmetry. In another recent report, Bhat *et al.* described the synthesis of monodisperse gold nanoparticles

coated with liquid crystalline dimer-like arylamines, which spontaneously assembled into a fluid/frozen lamellar structure exhibiting CD activity.²⁰³ The similar hierarchical, cooperative self-assembly/self-organization of gold nanorods, a micelle-forming surfactant and bilayer-forming amphiphilic phospholipids led to the formation of a chiral liquid crystal-like mesophase.²⁰⁴ Finally, dual thermal- and photo-switchable plasmonic chiral assemblies have been prepared using a supramolecular approach with gold nanorods modified with guanosine, deoxyguanosine and boric acid, which form a chiral gel upon mixing. Upon heating, the chiral nanofibers disassemble and the chiroptical properties vanish.²⁰⁵ In another study, chiral cholesterol-capped gold nanoparticles were mixed with two nematic liquid crystal hosts, forming chiral nematic phases.²⁰⁶ The helical pitch was shown to depend on the nanoparticle size and the number of chiral ligands bound to the nanoparticle surface. Finally, Cheng *et al.* recently showed that gold nanorods can be co-assembled with chiral polymers to form side-by-side helical assemblies.²⁰⁷

Although it was not performed with plasmonic particles, a unique example of the light-induced chiral self-assembly of



nanoparticles was reported by J. Yeom *et al.*²⁰⁸ The authors used circularly polarized light as a “template” for the chiral self-assembly of CdTe nanoparticles. CdTe nanoparticles may be stabilized with thioglycolic acid (TGA) and are themselves chiral. A racemic dispersion containing equal numbers of left- and right-handed CdTe–TGA nanoparticles was illuminated with chiral light. The left-handed (respectively right-handed) nanoparticles more efficiently absorbed left-handed (respectively right-handed) photons, which caused the photooxidation of TGA and its decomposition. As a result, illumination of the racemic dispersion with circularly polarized light led to an excess of unprotected nanoparticles of the same handedness and their selective assembly into twisted nanoribbons with an enantiomeric excess exceeding 30%. This is one of the rare examples of the translation of chirality from chiral photons to matter and may be an indication of the origin of homochirality on Earth. A similar strategy was applied to gold nanoparticles, but realization of the light-driven synthesis of chiral nanostructures turned out to be more difficult for plasmonic nanoparticles than for the semiconductor due to the short lifetime of the plasmonic states. Illumination of gold salt solutions with circularly polarized light was nevertheless shown to induce the formation of nanoparticles and their subsequent assembly into chiral nanostructures.²⁰⁹ Despite their seemingly irregular shape, the resulting nanocolloids exhibited CD spectra with opposite polarity upon exposure to photons with left or right circular polarization. In another example, Horrer *et al.* showed that a perfectly achiral nanostructure exhibits a near-field response that is sensitive to the handedness of light due to near-field interference between the different plasmonic modes sustained by the plasmonic metamolecule under circularly polarized light excitation.²¹⁰ The local near-field chirality could be imprinted into a photosensitive polymer film, efficiently transforming the optical chirality into geometrical chirality, the initially achiral structure becoming chiral after interaction with chiral light. Finally, Morisawa *et al.* irradiated gold nanorods supported on TiO₂ with RCP or LCP light to generate electric fields with a chiral distribution around each nanorod.²¹¹ A photoinduced reversible redox reaction (site-selective oxidation due to plasmon-induced charge separation and reduction by UV-induced TiO₂ photocatalysis) was used to selectively deposit PbO₂ around the nanorods with a chiral geometry.

The self-assembly approaches described above may potentially be scaled-up to produce chiral nanostructures in large amounts, although they are sometimes based on expensive reagents such as long synthetic DNA strands. Furthermore, the tunability is often limited by the molecular template as this dictates the scale on which chirality emerges. Finally, the transfer of these chiral building blocks from suspensions to complex multimaterial metadvice remains a challenge. The use of external forces to synthesize template-free chiral thin films over macroscopic areas has thus been proposed.

3.2.4. Directed self-assembly. An emerging strategy which ensures both tunability and scalability of the targeted nanostructures is to use self-assembly techniques that are already well established for non-chiral systems in combination with an

external force. Nanoparticles can be deposited in patterns over large areas using various approaches which do not inherently induce a chiral pattern, but where an external force can be exerted during or after the assembly to break the symmetry.

For example, Choi *et al.* showed that herringbone-patterned plasmonic sheets with periodic kirigami cuts allowed modulation of the polarization of terahertz radiation in the presence of a mechanical strain (Fig. 10A).²¹² The micrometer-scale dimensions of the nanostructure led to chiroptical properties in the terahertz range, but a similar pattern on the nanoscale would lead to chiroptical activity in the visible range.⁴⁸ Such kirigami modulators have a huge potential for applications in numerous domains, including polarization-based terahertz imaging, line-of-sight telecommunication, encryption of information and space exploration.²¹² In addition, the intensity and handedness of the CD can be actively tuned and/or reversed by mechanical deformation of the kirigami templates. These reconfigurable chiral nanostructures¹¹⁵ have attracted increasing interest in recent years as they offer dynamic and/or reversible control of the chiroptical properties which can be used in smart nanooptic metamaterials as likewise in molecular motors and open the way to a better understanding of the dynamics of light–matter interaction. Kim *et al.* reported another example where chirality was induced by application of a mechanical torque during the assembly of achiral gold nanoparticles (Fig. 10B).²¹³ Gold nanoparticle multilayers were deposited by LbL assembly on a flexible substrate which was mechanically twisted during deposition. This approach is extremely simple as the handedness can be conveniently controlled on the nanoscale in a top-down fashion using macroscale deformation, and the chirality is retained even after releasing the torsion. In addition, the CD of the samples can be reversibly tuned by stretching and releasing the substrates. In another work, thermomechanical strain in a multilayer assembly of spherical gold nanoparticles on a Ti layer patterned by nanoimprint lithography was used to prepare large-area surface-bound 3D chiral meta-atoms arrays.²¹⁴ Another example makes use of a helical magnetic field to assemble magnetoplasmonic Ag@Fe₃O₄ core-shell nanoparticles into chains stacked in a chiral nematic-like superstructure that can be dynamically modulated at the millisecond time scale.²¹⁵

Chirality can also be obtained by stacking layers of in-plane oriented 1D nano-objects or 1D assemblies with a twist, leading to so-called Bouligand structures. Using a very elegant and simple approach, Probst *et al.* have recently shown that twisted chiral assemblies can be prepared from spherical gold nanoparticles (Fig. 11B).²¹⁶ The nanoparticles were arranged in a striped pattern by capillary-assisted assembly^{217–219} using nanochannel templates made by lithography. Parallel arrays of gold nanoparticles on two substrates were stacked face-to-face with a twist, the handedness of the structure being determined by the angle of twist which could be selected at will. Interestingly, the two substrates could be separated and repositioned, while the CD of the structure could be actively modulated by compression of the film. A similar multilayer



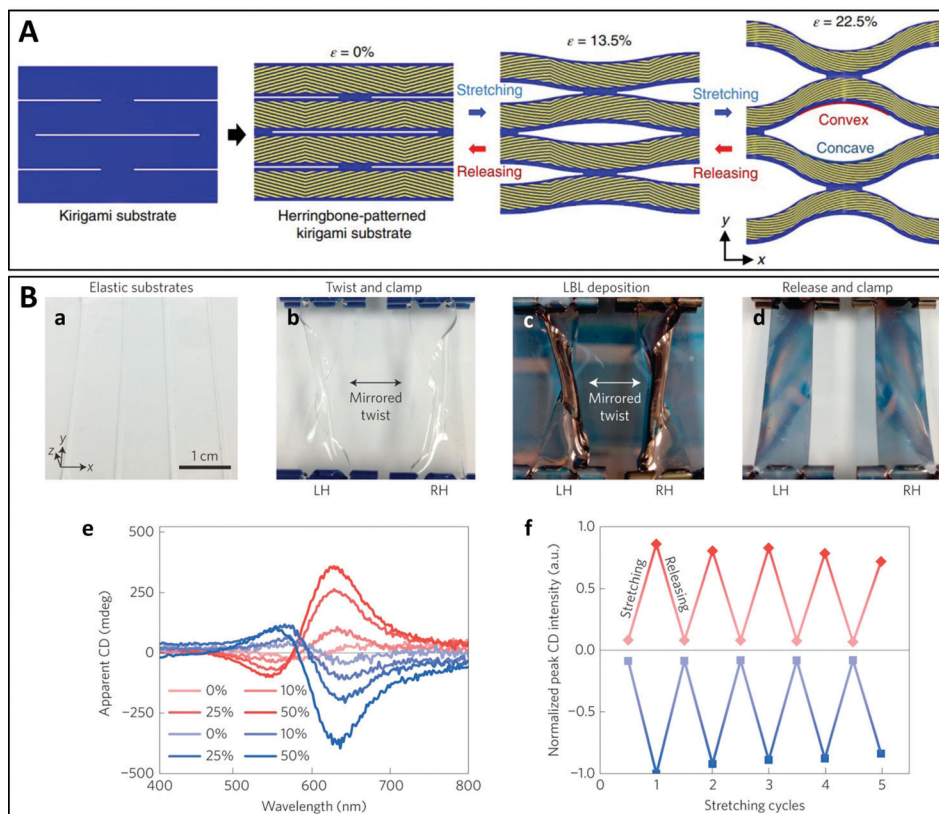


Fig. 10 (A) Schematic representation of a kirigami reconfigurable chiral plasmonic structure: herringbone-patterned gold strips are deposited on the kirigami substrate which can be stretched to modulate the polarization rotation angle and ellipticity.²¹² Copyright 2019 Springer Nature. (B) Reconfigurable mechano-tunable chiral metasurfaces obtained by colloidal assembly of spherical gold nanoparticles on a twisted flexible substrate. (a) PDMS substrates. (b) PDMS substrates twisted in opposite directions. (c) LbL deposition of AuNPs on the twisted substrates. (d) Relaxed substrates coated with AuNP multilayers. (e) CD spectra of LH (red) and RH (blue) samples under stretching (from 0% to 50%). (f) Peak CD values of LH and RH samples during five cycles of reversible stretching from 0 to 50%.²¹³ Copyright 2016 Springer Nature.

twisted architecture was obtained by Hu *et al.*²²⁰ using grazing incidence spraying, a versatile and efficient technique for the alignment of 1D nano-objects in monolayer thin films, which has previously been used to align silver nanowires,^{140,142} gold nanorods,¹⁴¹ cellulose nanofibers,¹³⁹ or semiconducting oxide nanowires.¹⁴³ Layers of oriented silver nanowires and gold nanorods were incorporated into twisted 2- and 3-layer films using LbL assembly (Fig. 11B).²²⁰ The advantages of this approach are that the number of oriented plasmonic layers, their composition and the angle between them can be freely chosen, and the interlayer spacing may be finely tuned.²²¹ The thin films displayed broadband CD extending over the UV, visible and near-infrared ranges and reaching extremely high *g*-factors. Finally, Lv *et al.* reported the fabrication of biomimetic chiral photonic crystals (Fig. 11C) consisting of a multilayer twisted stack of aligned inorganic nanowires.²²² This structure mimics the cuticle of many scarabaeoid beetles that are able to selectively reflect left circularly polarized light. The individual layers were oriented and deposited using the Langmuir-Schaefer technique and the multilayer structure was obtained by LbL assembly. The high *g*-factors could be modulated by controlling structural parameters of the crystals, including the number of layers, the pitch and the twisting angle.

4. Applications

Chiral plasmonic metamaterials have unique polarization-dependent optical properties that are potentially tunable, which opens up perspectives for applications in polarization-sensitive optical devices such as chiroptical detectors and filters, in 3D displays or to induce chiral forces.^{25,63,111} However, it is the possibility of coupling chiral surface plasmons to the metamaterial environment that has driven the research to find applications mostly in molecular sensing,^{223,224} enhanced spectroscopies,²²⁵ non-linear chiroptics and chiral catalysis.²²⁶

4.1. Chiral forces

The interaction of chiral particles with light (which may be chiral or not) can result in a force that depends on the particle handedness and can therefore be used to manipulate and sort the particles. For instance, Wang and Chan predicted that an electromagnetic plane wave should exert a lateral optical force on a chiral particle above a reflective surface, which will emerge as the particle interacts with the reflection of its scattered field.²²⁷ Interestingly, this force acts in a direction where there is neither wave propagation nor an intensity gradient, and deflects particles with opposite helicities towards opposite sides.



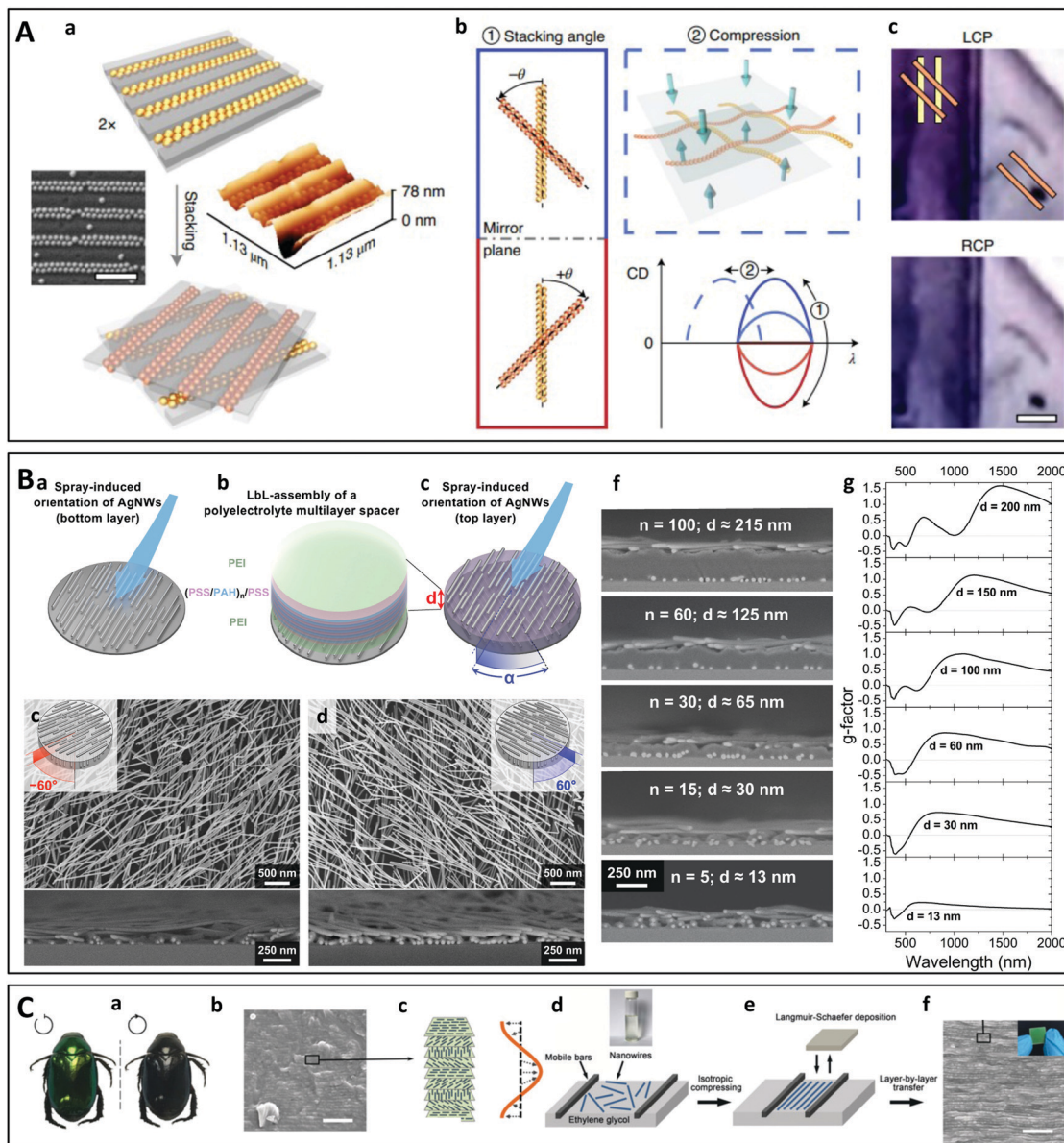


Fig. 11 (A) Schematic principle of chiral assembly through macroscopic stacking of achiral linear arrays of spherical gold nanoparticles. (a) The gold particles are assembled into dimer chains in nanochannels. (b) The CD can be dynamically controlled by changing the stacking angle and compression. (c) Photograph demonstrating the polarization-sensitive transmission of LCP or RCP light through a sample stacked at -45° .²¹⁶ Copyright 2021 Springer Nature. (B) Twisted multilayer films of oriented silver nanowires (AgNWs). (a) A first layer of oriented AgNWs is deposited by grazing incidence spraying on the substrate, before (b) depositing a multilayer polyelectrolyte dielectric spacer of precisely tunable thickness d by LbL assembly. (c) The next AgNW layer is deposited after rotating the sample through an arbitrary angle. (d) and (e) Top-view and cross-section SEM images of left- and right-handed 2-layer films. (f) The interlayer spacing d can be finely tuned and (g) the corresponding broadband chiroptical properties depend strongly on this spacing.^{220,221} Copyright 2021 American Chemical Society. (C) Biomimetic Bouligand nanostructure with modulable chirality obtained by Langmuir–Schaefer deposition of inorganic nanowires and LbL assembly. (a) Photographs of *Anomala corpulenta* Motschulsky taken under LCP or RCP light. (b) Cross-section SEM image of the cuticle of *Anomala corpulenta* Motschulsky showing a layered structure. (c) Schema of a chiral photonic crystal with a helical arrangement of layers of aligned $\text{NiMoO}_4 \cdot x\text{H}_2\text{O}$ nanowires. (d) and (e) Schematic principle of the Langmuir–Schaefer deposition of a layer of aligned nanowires. (f) Cross-section SEM image and photograph (inset) of the chiral photonic crystal film obtained by LbL transfer with a predetermined twisting angle.²²² Copyright 2019 John Wiley and Sons.

Hayat *et al.* later showed that lateral forces can be produced by direct interaction of the optical spin angular momentum with chiral particles, pushing them in opposite directions depending on their helicity.²²⁸ This was also investigated in a Kretschmann configuration by Zhang *et al.*²²⁹

Canaguier-Durand *et al.* have proposed a systematic description of the forces and torques that chiral light fields can exert on chiral objects.²³⁰ In particular, they showed that the chiral force components are directly related to the optical rotation and circular dichroism, and hence that the resulting



4.2. Polarization photodetectors

4.3. Non-linear chiroptical properties

While the non-linear optical anisotropy is pronounced in such plasmonic metasurfaces, the intensity of the non-linear optical response is still quite low. This challenge was taken up by Kim *et al.* in recent work using a polaritonic chiral plasmonic cavity coupled with the intersubband transitions of semiconducting heterostructures designed to have giant second and third order non-linear responses.²⁵⁶ A non-linear circular dichroism of close to unity and conversion efficiencies of over $10^{-4}\%$ for SHG- and THG-CD were achieved simultaneously on a single chip. Similarly, coupling of a 2D van der Waals semiconductor (tungsten disulfide) with an aluminum vortex metalens led to high SHG-CD.²⁵⁷ THG-CD

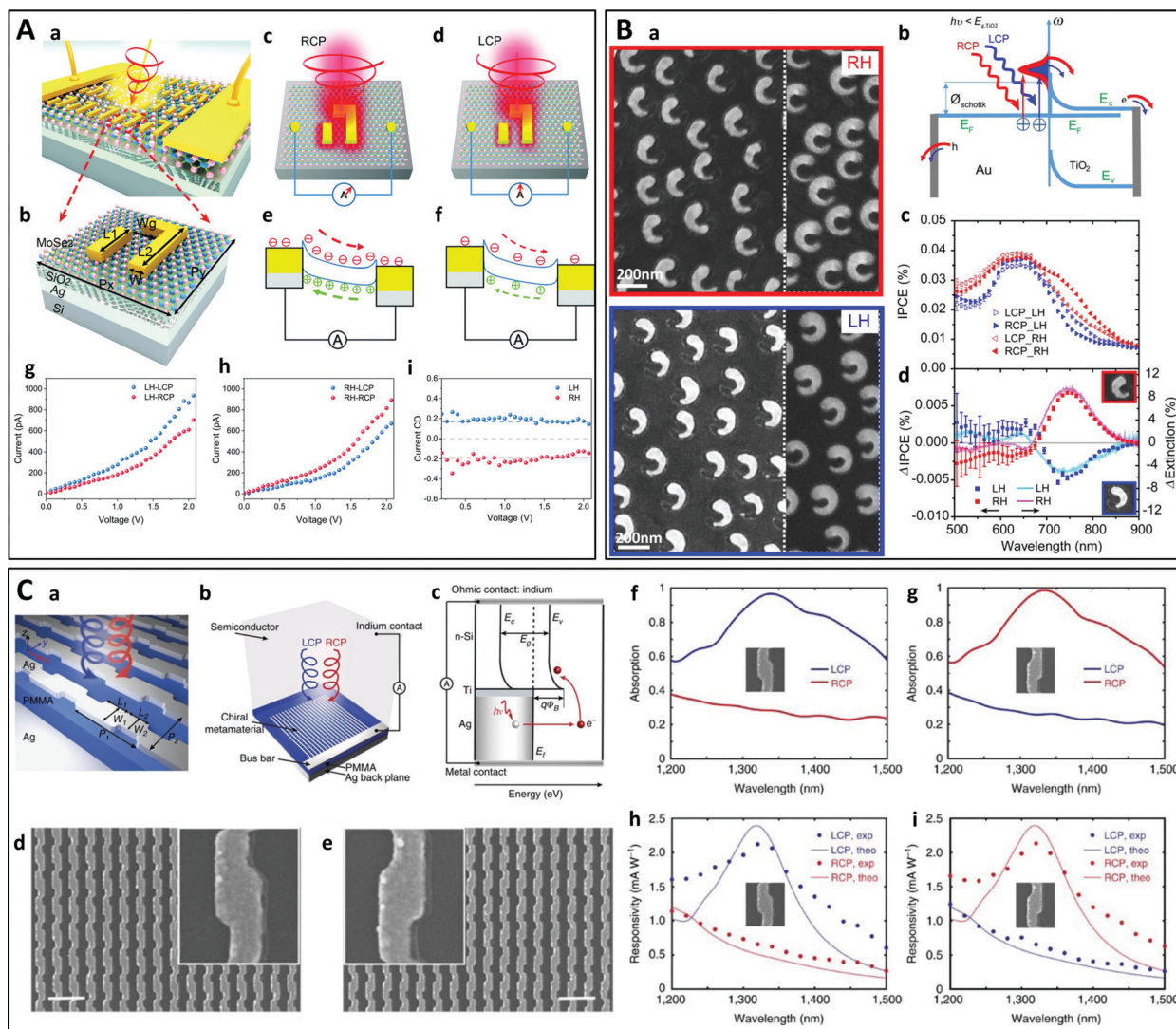


Fig. 12 (A) Chiral plasmonic metasurface on a MoSe₂ monolayer. (a) Schematic of the hybrid structure. (b) A unit cell of the chiral plasmonic metasurface. (c) and (d) Schematic of the selective enhancement of electromagnetic field for the RH plasmonic metasurface under illumination of RCP (c) and LCP (d) light. (e) and (f) Energy band diagrams of the device for the RH plasmonic metasurface under illumination of RCP (e) and LCP (f) light, respectively. (g) and (h) Measured I - V responses for LH (g) and RH (h) metasurfaces under circularly polarized light illumination. (i) Photocurrent CD vs. bias voltage for both handedness.²⁴⁰ Copyright 2020 The Royal Society of Chemistry. (B) Hot electron generation from chiral gold split-ring-resonators (SRRs) on TiO₂. (a) SEM images of SRRs of opposite handedness on TiO₂. (b) Schematic illustration of the hot electron transfer process from the chiral SRRs to the TiO₂ layer: RCP or LCP light with photon energy below the TiO₂ band gap excite plasmons in the chiral SRRs with different efficiency. (c) Incident photon to charge conversion efficiency (IPCE) spectra for RH and LH samples under LCP and RCP illumination. (d) IPCE response difference between RCP and LCP light (Δ IPCE, squares) compared to the circular dichroism (Δ Extinction, full lines) measured for the same samples.²⁴¹ Copyright 2016 American Chemical Society. (C) Silver chiral metasurface on a silver backplane separated by a dielectric spacer. (a) Schematic of the device. (b) Schematic of the CPL detector consisting of a chiral metamaterial integrated with a semiconductor that serves as a hot electron acceptor. A Schottky barrier is formed between Si and the Ti interfacial layer. The hot electrons that are photo-generated in the Ag metamaterial are then injected over this barrier into the Si. (d) and (e) SEM images of the LH (d) and RH (e) metamaterial. (f) and (g) Measured optical absorption spectra under LCP (blue) and RCP (red) illumination for LH (f) and RH (g) metamaterials. (h) and (i) Measured (dots) and theoretically calculated (solid curve) photoresponsivity spectra under LCP (blue) and RCP (red) illumination for LH (h) and RH (i) metamaterials.²⁴⁴ Reproduced under the terms and conditions of the CC-BY license.

with more than an order of magnitude variation between RCP and LCP excitation was also obtained by coupling chiral plasmons to the photonic waveguide mode of a Si layer device.²⁵⁸

4.4. Chiral catalysis

Metallic particles are often used as catalysts for chemical reactions,^{259,260} but obtaining asymmetric catalysis with

molecular species remains a challenge.²⁶¹ Several attempts have been made over the last years to use chiral plasmonic nanoparticles or chiral assemblies of plasmonic particles as enantioselective catalysts.²⁶² A first approach consisted of templating metal films that are commonly used as electrocatalysts with chiral molecules to produce mesoporous chiral surfaces.²⁶³ Such films were later used by the same group to induce



asymmetry in the electrochemical synthesis of mandelic acid.²⁶⁴ Starting from a prochiral compound, an excess of the (*R*)-enantiomer when using platinum electrodes templated with (*R*)-molecules was obtained and *vice versa*, while the enantioselectivity could be tuned by changing the number of chiral cavities in the material. A similar approach was employed using nickel electrodes for the discriminatory electro-oxidation of the two phenylethanol enantiomers²⁶⁵ or using silver electrodes for the electro-oxidation of amino acids.²⁶⁶ Liu *et al.* prepared Au/Ag alloyed nanotubes coated with cysteine which served as electrodes in an electrochemical cell.²⁶⁷ Depending on the handedness of the cysteine coat, selective electro-oxidation of tyrosine enantiomers was observed.

Very recently, it was shown that photoinduced reactions performed on chiral plasmonic particles could also result in chiral products.²⁶⁸ A prochiral molecule, 2-anthracenecarboxylic acid, was stereoselectively adsorbed on Ag and Cu nanohelices as enantiomorphous anti-head-to-head dimers. The dimers displayed either *Si-Si* or *Re-Re* facial stacking depending on the handedness of the nanohelices, which led to a specific enantiopreference during their photoinduced cyclodimerization.

One more example of photoinduced asymmetric synthesis is the crystallization of sodium chlorate. It was initially demonstrated that circularly polarized light could induce a bias during the chiral crystallization of NaClO₃.²⁶⁹ A few years later, Chen *et al.* used non-chiral gold triangle trimers in a saturated solution of sodium chlorate illuminated with RCP or LCP light to obtain a crystalline enantiomeric excess of more than 50%.²⁷⁰ In a follow-up paper, the same group explained this result by modeling the plasmonic near-field during illumination and showing that the large enantiomeric excess previously observed arose from a difference in the frequency of attachment of chiral crystalline clusters to crystal nuclei, or in the local concentration of NaClO₃ due to chirally biased diffusion, rather than from enantioselective optical trapping.²⁷¹ A similar light polarization-dependent chiral synthesis was documented using chiral metallic particles, which exhibited a different photocatalytic activity depending on the helicity of the illuminating light.²⁷² These observations may be explained by considering the different emission rates of hot electrons in chiral plasmonic particles upon illumination with circularly polarized light,^{273–275} as experimentally measured by Fang *et al.* in split ring resonators deposited on a semiconductor.²⁴¹

The above studies employed chiral plasmonic systems weakly interacting with their target molecules. It was however recently shown^{276–280} that chemical reactions can be controlled through strong light-matter coupling by putting the molecules in cavities.²⁸¹ Use of plasmonic chiral cavities²⁸² could potentially pave the way to enantioselectivity in chemical reactions.

4.5. Sensing

Chiral sensing techniques, in particular CD spectroscopy, have been extensively used to acquire information on biomolecular structures, arrangements and conformations.²²³ Although CD is a low-cost and non-invasive approach, the chiroptical signals

of biomolecules are usually very weak due to the small characteristic size at which chirality arises as compared to the wavelength of UV or visible light. Various strategies based on plasmonic systems have thus been explored over the last years to enhance the chiroptical signals and the sensitivity of the related biosensing methods.^{223,225,283}

4.5.1. Enhancement of the CD of chiral molecules by coupling with non-chiral particles and metasurfaces. The CD of chiral molecules is inherently small due to the different scales of the chiral arrangement of atoms in a molecule and the wavelength of UV or visible light. The use of non-chiral particles or metasurfaces (either metallic^{98,101,284} or dielectric,^{283,285–287} or a combination of both^{288,289}) has been proposed to enhance the local electric field and thereby increase the measured chiroptical signal. In a seminal paper, Govorov *et al.* demonstrated that a non-chiral nanoparticle can modify the CD of a chiral molecule through Coulomb dipole and multipole coupling, resulting in the resonant enhancement of the CD signals of the molecule and also the appearance of new spectral features.²⁸⁴ A few years later, Maoz *et al.* found that the adsorption of riboflavin or poly-lysine on achiral gold islands induced a CD signal at the wavelength of the surface plasmon resonance.⁹⁸ This induction decayed within about 10 nm of the surface of the islands. Nesterov *et al.* investigated numerically the role of plasmon-generated near fields in the enhancement of the CD of chiral molecules placed in the vicinity of plasmonic particles.¹⁰¹ These authors showed that the relative orientation between the incident light and plasmonic modes played a crucial role and that surprisingly, achiral structures led to greater enhancement than their chiral equivalents.

Another strategy based on the formation of nanoparticle dimers has been described by Xu *et al.*²⁹⁰ Gold nanoparticles were functionalized with L- or D-cysteine molecules, inducing the formation of nanoparticle dimers with a plasmonic CD signal that depended on the cysteine concentration, reaching a detection limit of 20 pM.

4.5.2. Surface-enhanced Raman optical activity (SEROA) and enantiomer-resolved surface-enhanced Raman scattering (SERS). Raman optical activity (ROA), which measures the difference between the Raman scattering of right- and left-circularly polarized light, was discovered in the early 1970's.^{291,292} A big drawback of ROA spectroscopy is the weakness of the signal, the Raman intensity ratio of both circular polarizations being typically of the order of 10^{−4}. Similarly as for surface-enhanced Raman scattering (SERS), it was predicted that the ROA signals of chiral molecules adsorbed on metal surfaces should be strongly increased.^{293,294} The experimental proof of this enhancement was only obtained in the 2000's,^{295,296} despite the interest of ROA for investigating the structure of biomolecules.²⁹⁷ Theoretical models were developed to calculate the enhancement of ROA in the case of (off-resonant) chiral molecules placed near plasmonic spherical nanoparticles,^{298,299} and it was even predicted that it should be possible to increase the sensitivity of SEROA down to the single-molecule limit on well-designed plasmonic nanostructures.³⁰⁰ In spite of these predictions and



exciting possibilities, the enhancement achieved in practice by coupling molecules close to plasmonic particles is much weaker.^{301–306} Furthermore, Ren *et al.* have shown that depending on the way the molecules adsorb on the metallic particles, all the vibrational modes are not equally enhanced.³⁰²

An alternative approach employs nanoparticles with a chiral surface or functionalized with chiral linker molecules. For instance, silver colloids functionalized with aromatic linkers were found to form chiral aggregates in the presence of chiral acids, allowing their detection by SEROA.³⁰³ Sun *et al.* used “classical” Raman spectroscopy with chiral gold nanoparticles to detect specific cystine enantiomers.³⁰⁷ In another study, the surface of a gold grate was functionalized with enantiopure helicene molecules, leading to different SERS signals when it was exposed to L- or D-dihydroxyphenylalanine.³⁰⁸ Similarly, Liu *et al.* described a chiral plasmonic surface consisting of helical gold fibers which displayed selective SERS factors for different enantiomers.³⁰⁹

4.5.3. CD-based sensing using chiral particles and meta-surfaces. Chiral plasmonic metasurfaces have been employed to detect chiral^{27,77,310–315} and non-chiral^{314,316} molecules.

The grafting of alkyl ligands on silver spirals was shown to weaken the experimental chiroptical activity without affecting the CD spectra.³¹⁶ Similarly, Jeong *et al.* used optimized AgTi alloy nanohelices to sense changes in the refractive index of the environment (Fig. 13A).³¹⁴ These authors showed that not only the amplitudes of the positive and negative maxima in the CD spectra were affected but also the positions of the maxima and the zero-crossing points. Besides this highly sensitive but non-specific detection of a change in the bulk refractive index, biotin-coated helices could also be employed for the specific sensing of avidin.³¹⁴ However, most studies of the sensing of biomolecules using chiral plasmonic metasurfaces have been based on the change in the CD spectrum induced by the adsorption of a protein on a chiral gold thin film, according to the pioneering demonstration of Hendry *et al.*²⁷ In this work, the superchiral electromagnetic fields produced upon excitation of the chiral plasmonic nanostructure were used to detect the adsorption of several proteins down to the picogram scale (Fig. 13B). The same group later demonstrated that these superchiral fields could be employed to investigate the secondary, tertiary and quaternary structure of proteins.^{31,310,313} Zhao *et al.*

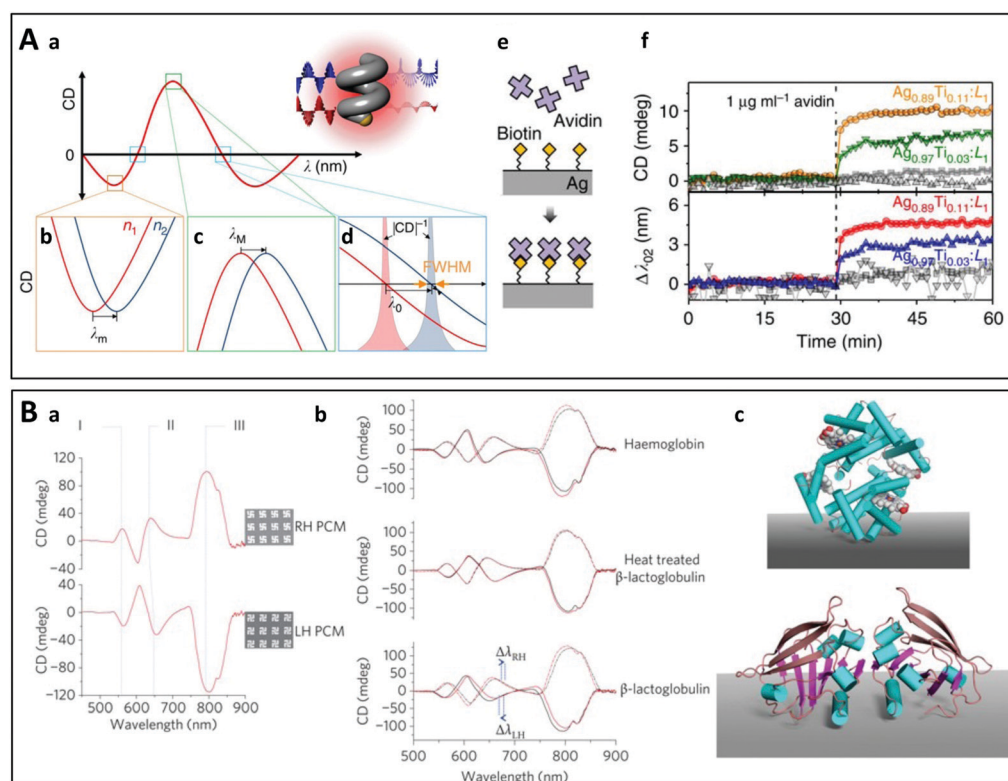


Fig. 13 (A) (a) Schematic principle of polarization-dependent chiral plasmonic sensing using shape-engineered Ag–Ti nanohelices: the CD spectrum of a plasmonic enantiomer is modified when the refractive index of the surrounding medium changes. This modification can be detected at the wavelength of minimum CD λ_m (b), of maximum CD λ_M (c) and at the wavelength at which CD equals zero λ_0 (d). (e) Schematic view of biotin–avidin interaction on the surface of a Ag–Ti nanohelix. (f) *In situ* measurements of the biotin–avidin interaction by monitoring the change of CD at λ_0 and the wavelength shift of $\Delta\lambda_0$ (lower plot) using Ag–Ti nanohelix with different compositions.³¹⁴ Reproduced under the terms and conditions of the CC-BY license. (B) (a) CD spectra of the left-handed and right-handed chiral metamaterials immersed in distilled water, and the corresponding SEM images. (b) Influence of the adsorbed proteins haemoglobin, β -lactoglobulin and thermally denatured β -lactoglobulin on the CD spectra of the metamaterials. Red spectra were collected before protein adsorption for the left-handed (solid line) and right-handed (dashed line) metamaterials, and black spectra were collected after protein adsorption. (c) Schematic representation of Haemoglobin (upper) and β -lactoglobulin (lower) shown adopting a well-defined arbitrary structure with respect to a surface.²⁷ Copyright 2010 Springer Nature.



likewise used the superchiral near-fields generated by plasmonic metasurfaces for biosensing in a flow cell mounted on top of a twisted metamaterial similar to that shown in Fig. 2C,³¹¹ or on a chiral conic nanoshell metallic nanostructure.⁷⁷

Finally, some metals such as palladium and magnesium undergo a fast and reversible phase transition when exposed to hydrogen. This has been used to determine the hydrogen content in the surrounding atmosphere by monitoring changes in the CD of palladium nanohelices³¹⁷ or of a chiral metasurface composed of magnesium and gold nanoparticles.³¹⁸

4.5.4. DNA-enabled chiral plasmonic sensing. We previously discussed the high degree of flexibility offered by DNA for the assembly of plasmonic particles into well-defined chiral structures. The unique advantage of this approach is that the DNA nanostructure can be designed to change its shape in response to a specific change in its environment. This geometrical variation can be easily detected in DNA-based chiral assemblies of plasmonic particles using CD spectroscopy,¹⁷⁵ and the highly specific binding between complementary DNA strands has been extensively used to build DNA sensors based on plasmonic DNA superstructures. Thus, chiral plasmonic multimetal nanoparticles of different sizes were functionalized with complementary DNA strands to build chiral heterodimers with a high optical activity.³¹⁹ DNA detection at the zeptomolar level was achieved by combining this approach with the exponential amplification of the polymerase chain reaction (PCR) method. Attomolar sensing of DNA without the need for PCR amplification has also been reported using DNA-functionalized nanorods arranged in a side-by-side chiral assembly¹⁸⁵ or post-assembly reconfiguration of nanoparticle pyramids.³²⁰

DNA-based chiral plasmonic assemblies can even be used for intracellular sensing. In a recent study, Hao *et al.* designed Au@AgAu yolk-shell nanorods with a chiral shape induced by the presence of D/L-penicillamine.³²¹ Two complementary single-stranded DNAs were attached to the nanorods and to spherical gold nanoparticles. The core-satellite assemblies were generated by DNA hybridization, which led to a change in the CD spectra. These structures were employed to detect Zn²⁺ ions in living cells in the presence of a Zn²⁺-specific DNA-cleaving DNase. Similarly, microRNA was monitored in living cells by Meng *et al.* using a DNA-driven two-layer core-satellite nanostructure,³²² by Xu *et al.* using side-by-side self-assembly of DNA-functionalized nanorod dimers,³²³ and by Li *et al.* using hybrid nanopyramids comprised of gold and upconversion nanoparticles, which allowed them to follow the concentration of microRNA by measuring the plasmonic CD or luminescence.³²⁴

The high level of control and flexibility offered by DNA origamis has led to their extensive use for CD-based biosensing. Kuzyk *et al.* designed a DNA origami-based reconfigurable plasmonic system which underwent DNA-regulated conformational changes on the nanoscale (Fig. 8C).¹⁷⁷ This group later adapted the same design to sense picomolar amounts of RNA³²⁵ or thrombin by grafting two thrombin-binding aptamers onto the DNA origami.³²⁶ Lan *et al.* similarly

designed a left-handed chiral superstructure using gold nanorods and V-shaped DNA origamis.¹²⁴ The DNA origamis could be dynamically converted through a toe-hold-mediated strand displacement reaction from a tightly folded state to an extended one, or to the enantiomer (inversion of handedness). The rich DNA chemistry can be used to build complex plasmonic assemblies that switch between different states with detectable changes in the CD spectra, allowing the concomitant sensing of various DNA strands.¹⁷⁸ However, the most widely studied architecture is the cross-shaped assembly of two gold nanorods, which has been employed to detect tumor-marker RNA sequences³²⁷ or different aptamers.^{180,328} Beyond its biosensing applications, the same architecture has been used to construct a DNA-based adaptative plasmonic three-state logic gate,³²⁹ with specific input DNA strands coding for three different logic outputs.

5. Conclusions and perspectives

We have outlined in this review the considerable efforts that have been invested over the last years in the design and fabrication of highly efficient chiral materials with targeted properties. Very diverse nanostructures have been prepared ranging from the most simple ones (twisted nanorod dimers) to more complex architectures such as helices, gammadions, or individual nanoparticles with complex chiral symmetries like high-Miller-index helicoid particles.

Several challenges have been at least partially addressed and continue to motivate research in the field. The first is to obtain chiral plasmonic nanostructures with the highest possible chiroptical properties, and the quest for record *g*-factors (highly asymmetric transmittance or scattering/reflectance of RCP and LCP light) is still ongoing. The second is the tunability of the optical properties, especially regarding the wavelength range in which chiroptical properties arise. This necessitates the design of nanostructures with modulable shapes and sizes. The third is the responsiveness to the chemical environment in order to construct active chiral plasmonic systems, which has notably been achieved through DNA origami technology.

Top-down techniques have proven to be particularly effective to produce complex and very well-defined metasurfaces with features of almost arbitrary shape. Unfortunately, although highly efficient to synthesize micrometric structures with chiroptical properties in the THz and infrared domains, these approaches are much more difficult to implement to prepare nanometric structures with chiroptical properties in the visible and UV ranges. The necessary equipment is expensive and the processes are complex, while the structures produced only cover small areas. On the contrary, bottom-up approaches can be easily scaled up (although they may rely on expensive reagents such as artificial DNA) to obtain chiral nanostructures in suspension or in thin films. Chirality may originate from a predesigned chiral template, from assembly/synthesis in the presence of chiral molecules, or in template-free methods from the use of external forces during or after assembly to break the symmetry.



A wide variety of potential applications have been proposed for these novel materials, in particular as optical devices and for sensing applications. Most of these applications are however limited by the high losses inherent to plasmonic nanostructures caused by the resonant excitation of the electron cloud at optical frequencies.³³⁰ These losses induce a huge photothermal effect,^{89,247} which is used in some applications such as photothermal therapy.^{331,332} This problem has been partly addressed by improving the structure and metal quality³³³ or by adding gain materials.³³⁴ However, intrinsic metal losses cannot be avoided, and the use of high-permittivity all-dielectric nanostructures that exhibit very low losses at optical frequencies has been proposed.³³⁵ Their resonances can be utilized in direct analogy to the plasmonic resonances of metallic nanoparticles to engineer their optical response towards specific applications such as sensing.^{283,285}

Other challenges in the field of chiral plasmonic metasurfaces will have to be addressed in the coming years. In particular, bridging the gap from the proof-of-concept on a laboratory scale to functional commercial devices will require the design of chiral nanostructures which can be prepared in a reproducible manner on a large scale, can be integrated into more complex multimaterial devices, and retain their properties over long periods under working conditions.

While the structure and properties of these nanomaterials are becoming increasingly well characterized, modeling the structure–property relationships is still a challenge. It is indeed possible to simulate the light–matter interaction on the single nano-object scale using for instance finite difference time domain techniques, but modeling large (chiral) arrays of interacting (chiral) nanoparticles requires powerful computing resources.

Difficulties also persist with regard to the optical characterization of the nano-objects. Far-field chiroptical properties are routinely measured using commercial CD spectrometers, but this technique suffers from many artifacts when employed to characterize anisotropic thin films. This is often neglected and more advanced methods such as Mueller matrix polarimetry are more suited to precisely investigate the intricate polarization characteristics of these complex materials with multiple anisotropies. Furthermore, measuring the chiroptical properties at the level of a single nano-object is one more challenge which should ultimately lead to a better understanding of the near- and far-field properties of these structures.

Finally, the chiral nanostructures that have been studied to date are often quite simple and composed of only one or two different materials, whereas much more complicated hierarchical chiral nanostructures containing multiple materials can be found in nature. The design, fabrication and characterization of such multimaterial hierarchical architectures with several levels of anisotropy is a future direction of investigation which will open up new perspectives for fundamental research and practical applications.

Conflicts of interest

There are no conflicts to declare.

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