

Chiral plasmonics: Fabrication and applications

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Received 09 Jun 2015, Accepted 16 Jul 2015, Published Online 16 Jul 2015

Chiroptical effects have been a fundamentally interesting and important topic in the fields of physics and chemistry, and have also found many applications about recognizing/sensing chiral structures in chemical, biological and pharmaceutical industries. Many recent reports have shown that the chiroptical effects can be significantly enhanced via interactions of light with chiral plasmonic nanostructures. As a result, a new sub-field of plasmonics—chiral plasmonics or chiropasmonics—emerges and progresses rapidly. In this review article, we will focus on advanced fabrication techniques and some promising applications of chiral plasmonics. Our perspective on the upcoming challenges and opportunities in this emerging field is also provided.

1. INTRODUCTION

Plasmonics, a burgeoning branch of photonics, has been attracting intensive attention across a broad range of research fields over the past two decades [1–6]. The root of this field lies in the surface-plasmon-enhanced light-matter interactions at the nanoscale [7,8]. With the capability of concentrating and transporting photons at the deep subwavelength scale on noble metallic nanostructures, surface plasmons—coherent oscillations of free electrons excited by incident light that are confined at the metal/dielectric interfaces—have paved a new way for light control and subsequent applications. An emerging sub-field of plasmonics, so-called chiral plasmonics or chiropasmonics, has garnered increasing attention recently. The word “chirality” derives from the Greek *χειρ* (*kheir*) meaning “hand”. A chiral object is said to have left or right handedness. It is distinguishable from its mirror image (enantiomer); that is, it cannot be superposed onto it. Thus far, various chiral plasmonic designs have been experimentally demonstrated, thereby triggering extensive applications. Referring to left and right handedness, a chiral structure is expected to generate chiroptical effects (i.e., enantiomeric excess or chiral purity) under the illumination of an electromagnetic wave. When light passes through a chiral structure which has two enantiomers, interesting phenomena occur. For instance, chiral structures can present different colors under light illumination with different circular polarizations (left or right) [9].

In life science, chirality seems to be a basic but extremely important characteristic of living matter. For instance, all the essential amino acids (except glycine) are chiral and all of them have the same handedness. In pharmaceutical industries, chirality has become highly important since chiral molecules in medicine often have different

physiological effects, such as pharmacological activity, toxicity, taste and smell between enantiomers. Well-known examples are thalidomide and ethambutol; their respective “evil twin” can cause the birth defects [10] and blindness [11], respectively. This highlights the need for optically pure (i.e., containing only a single enantiomer) molecular compounds and methods for precise chirality determination. Although crucial, chirality is a difficult and subtle property that is not easy to be determined and quantified since chiroptical effects are very weak in all natural materials. The root reason for such weak chiroptical effect lies in the mismatch between the chiral length scale of light (set by the wavelength of light) and molecules, which is typically orders of magnitude smaller. Recently, it has been shown that the plasmonic metal nanostructures can lead to giant chiroptical effects [12–20] and hence breach this natural ceiling to chiroptical sensitivity.

In view of the importance and impact of this emerging chiral plasmonics field, it will be extremely helpful to have a timely review article that is able to guide those who are new to this field, reveal current limitations and challenges, and direct future research efforts. In this review, we will give a brief introduction of chiral plasmonics and summarize the recent progress in terms of fabrication and applications. At the end we will also give our prospective view of future directions.

2. BASICS OF CHIRAL PLASMONICS

2.1. Surface plasmons

Surface plasmons arise from the interaction of light with the electron plasma at the interface of metal and dielectric medium [21, 22]. This interaction couples photon energy to the surface plasma, hence oscillating at the frequency below the plasma frequency. Surface

plasmons exist in two forms, namely: propagating surface plasmon polariton and the localized surface plasmon resonance [23–25]. Propagating surface plasmon polaritons are mostly observed at the metal-dielectric interface for waveguiding and surface plasmon sources [26]. Localized surface plasmon resonances are typically observed in nanostructures such as nanoparticles and nanorods [27–29]. Localized surface plasmon resonance (LSPR) plays a major role in confining light to produce local field enhancement for applications such as sensing and detection. The energy transfer from photon causes the surface electron plasma to oscillate coherently and depending on the size of nanostructures, shape and their surroundings, a very strong resonance can be obtained for a particular wavelength of light incident onto the metal surface. At the resonance wavelength, the electric field is significantly enhanced. This indicates strong absorption and scattering of the light from nanostructures. From Mie's Theory, a spherical nanoparticle with radius R , such that $R/\lambda \ll 1$, the extinction coefficient for the light-matter interaction is given as [30]

$$C_{\text{ext}} = \frac{24\pi^2 R^3 \epsilon_m^{3/2} N}{\lambda \ln(10)} \frac{\epsilon_i}{(\epsilon_r + 2\epsilon_m)^2 + \epsilon_i^2} \quad (1)$$

where N is the electron density, ϵ_m is the dielectric constant of surrounding medium, $\epsilon = \epsilon_r + \epsilon_i$ is the dielectric constant of the bulk metal, and λ is the wavelength of light. The resonance can be obtained when the extinction coefficient is solely dependent on the imaginary dielectric constant of the bulk metal. For Eq. (1), the resonance is achieved when $\epsilon_r = -2\epsilon_m$.

2.2. Optical activity and chirality

All molecules synthesized by man are optically active [31,32]. The optical activities of these molecules are the result of asymmetry, mainly from the presence of asymmetric carbon atoms and interaction of asymmetric atoms on adjacent chromophores [33]. The asymmetric atoms affect the conformation of macromolecules, which in turn affects the properties of the light transmitted, leading to observance of an optical activity. Optically active samples contain macromolecules that come in a pair of non-superimposable mirrored image enantiomers. These non-superimposable mirrored image enantiomers are chiral and chirality plays a major role in optical activity.

By definition, optical activity refers to the interaction that occurs when plane polarized light is transmitted through an optically active sample [34]. This interaction results in the change of plane polarized light, such as the rotation of linear polarized light as it is transmitted through the optically active sample. Optically active samples have the same physical and chemical properties but have exceptions upon the interaction with lightwaves [35]. There are four different terms to characterize the chiroptical properties of optically active samples: optical rotation, ellipticity, circular dichroism (CD), and circular birefringence [35]. Among them, CD is most commonly used as it is simple to be applied to any optically active samples.

CD refers to the absorption difference between left and right circular polarized light in optically active samples. Equation 2 shows the mathematical expression for CD

$$CD = A_{\text{LCP}} - A_{\text{RCP}} \quad (2)$$

where A_{LCP} and A_{RCP} refers to the absorption coefficient of the left and right circular polarized light. The absorption difference arises from the chirality of the molecules in optically active samples. From CD values, we can deduce which conformation the samples are dominantly orientated. There are a few reasons why CD is preferred compared to the other manifestations: First, it is easy to apply across all optically active samples. Second, CD results are easy to analyse. Third, CD results can be obtained quickly. Lastly, we can obtain the ellipticity, optical rotation and

circular birefringence from CD by using mathematical transformations such as the Kronig-Kramers transformation.

2.3. Chiral plasmonics or chiropasmonics

The measurement of CD from experiments is relatively straightforward and quick. However, the CD signals obtained from the direct application of light to the molecules are very weak, often in the range of 10^{-10} [36]. This absorption difference range is very weak and often undetectable if the surrounding noise is strong. In addition, the results may not be conclusive or accurate for a robust systems measurement. The weak CD signal poses a challenge for the detection of chiral molecules or optically active samples. The reason for the poor CD results observed in most optically active samples is due to the very short time interaction between the chiral molecules and propagating light in the sample. One effective solution to increase the interaction time is to use localized lightwaves.

Extensive efforts have been spent on research to improve CD results via increasing the interaction time. Other solutions exist to strengthen the CD signal for sensing chiral molecules and optically active samples. One example is the use of fluorescent or radioactive tags attached to biomolecules to strengthen CD signal with polarized light [37,38]. However, these methods are not recommended in real applications because it degrades the sample molecules. Several undesired effects such as photo-bleaching of fluorescent molecules and blocking of the active site of target chiral molecules affect CD results. Another alternative is to use plasmon resonances [39–42], which is the main subject discussed in this review article. At the suitable resonance wavelength, surface plasmon enhanced fields are generated in the nanostructure. The enhanced light has much stronger electromagnetic field and it is localized within the vicinity of the nanostructures, hence trapping and allowing longer interaction time with the chiral molecules in optically active samples. This extended interaction time allows better absorption of light energy into the molecules, enhancing the CD results. For optically active samples, the chiral molecules have refractive index and absorption coefficient that are different for left and right handed circular polarized light.

3. FABRICATION OF CHIRAL PLASMONIC STRUCTURES

A number of innovative techniques have been used in the literature to fabricate different types of chiral plasmonic structures. In general, these techniques can be divided into top-down and bottom-up methods. Top-down fabrication are generally template-free, while bottom-up fabrication typically need chiral templates or chiral constituent elements to grow the desired chiral structures. In the following, various fabrication/growth methods will be reviewed and articulated.

3.1. Bottom-Up fabrication

Bottom-up methods generally refer to chemical synthesis and self-assembly, which offer scalable routes for fabricating chiral structures [43,44]. A grand challenge is to assemble and position nanoparticles at desired locations to build large-scale nanostructured materials. A self-assembly method is highly desirable due to its simplicity and compatibility with multicomponent integration processes, and research into efficient self-assembly protocols to manipulate nanoscale building blocks into functional nanomaterials has created enormous excitement in this emerging chiral plasmonic field.

3.1.1. DNA-Directed assembly

DNA-based nanotechnology is a fast growing field, where DNA molecules are exploited as the building blocks for constructing designed nanostructures with specific geometry and connectivity. The capability of being programmable and the feasibility of diverse functionalization have made DNA a versatile construction material. Over the years, there have

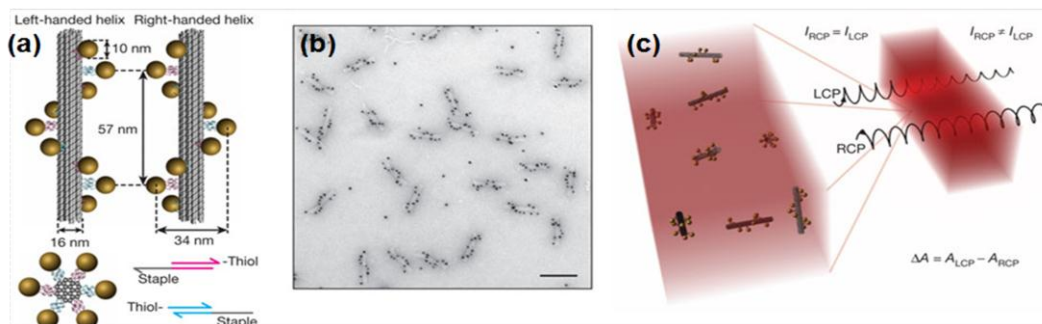


Figure 1. Assembly of DNA origami gold nanoparticle helices and principle of circular dichroism. (a) Left- and right-handed nanohelices are formed by attaching gold nanoparticles to the surface of DNA origami bundles. (b) TEM image of assembled left-handed gold nanohelices (scale bar, 100nm). (c) CD is measured as the difference in absorbance $\Delta A = A_{LCP} - A_{RCP}$ of left-hand-circularly polarized (LCP) and right-hand-circularly polarized (RCP) light as a function of wavelength. Adapted from Ref. [49] with permission.

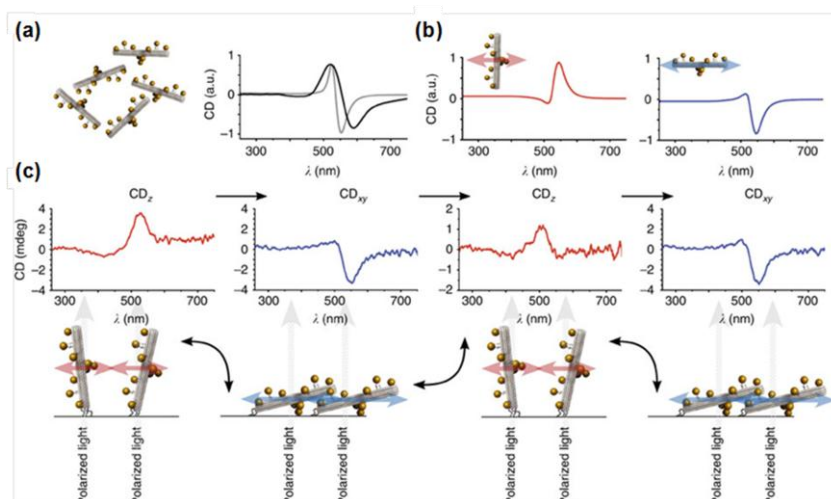


Figure 2. Dynamic material with switchable CD. (a) Theoretical (grey curve) and experimental (black curve) CD spectra for L-NHs dispersed in solution. (b) Theoretical CD spectra of L-NHs oriented parallel (red curve) and perpendicular (blue curve) to the incident beam. (c) Experimental CD spectra (top) and scheme of orientation state (bottom) of the L-NHs. Adapted from Ref. [50] with permission.

been tremendous progresses of designing and constructing DNA architectures with ever growing dimensions and increased complexity [45–47]. The nature of DNA enables DNA to direct the assembly of plasmonic nanoparticles in a chiral arrangement, hence providing a strong CD effect. In 2011, Shen and co-workers have demonstrated a distinct CD effect by organizing AuNPs in a helical fashion [48]. Kuzyk *et al.* demonstrated DNA origami based assembly of gold nanoparticle helices and their CD [49]. As illustrated in Figure 1(a), either left- or right-handed helices can be constructed by using plasmonic nanoparticles with the diameter of 10 nm. Figure 1(b) shows the transmission electron microscopy (TEM) image of the fabricated assemblies. One can see that gold particles are mostly attached to the surface of DNA origami bundles. Figure 1(c) shows CD measurements that are performed on solutions comprising of left- or right-handed nanohelices. Both right- and left-handed assemblies demonstrated strong CD that matches quite well with the theoretical predictions. They also showed that varying the nanoparticle sizes affects CD signal greatly due to the change in surface-to-surface distance between adjacent nanoparticles that subsequently affects near-field plasmonic coupling. For example, when 16 nm nanoparticles were used, more red shifted and stronger CD signal was achieved compared to that using 10 nm AuNPs.

The same group later showed that the optical response between two circular dichroism spectra can be reversibly switched by altering the helix orientation [50], as shown in Figure 2. By functionalizing a quartz

surface with biolinkers (BSA-biotin-neutravidin), the gold nanoparticle nanohelices can stand upright in a buffer solution. Upon drying, the nanohelices will fall down, resulting in an alignment parallel to the quartz surface. Through this repeatable process, the alignment of the nanohelices can be reversibly switched, resulting in a reversible switch of the CD signal. Another advantage is that the alignment process leads to a multi-fold increased CD signal over signals resulting from randomly oriented samples at equal concentrations. Such switchable chiral nanostructures could find many potential applications in sensing and data storage.

3.1.2. Cholesteric liquid crystal (CLC)-directed assembly

Cholesteric liquid crystals (also known as chiral nematic liquid crystals) are chiral materials with strong optical selection of either LCP or RCP light. They are organized in layers with no positional ordering within layers but has a director axis which varies with layers. The variation of the director axis tends to be periodic in nature. The period of this variation (the distance over which a full rotation of 360° is completed) is known as the pitch, p . The pitch determines the wavelength of light that is reflected and this phenomenon is called Bragg Reflection. The CLC structure is omnipresent in living matter and concerns many applications in optics because of its selective light reflection property. CLCs are also excellent candidates for matrix-guided self-assembly because the CLC state combines order and mobility at the molecular (nanoscale) level. The coupling of nanoparticles with the orientational order of the CLC phase

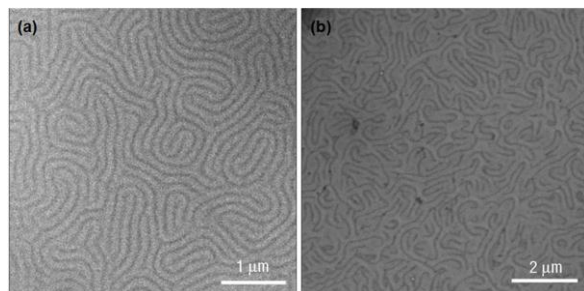


Figure 3. Transmission electron micrographs of liquid crystalline materials. (a) Micrograph showing the fingerprint cholesteric texture for the pure liquid crystalline material. (b) Micrograph of cholesteric liquid crystal material doped with nanoparticles. Nanoparticles are assembled into ribbons that mimic the fingerprint texture. Adapted from Ref. [51] with permission.

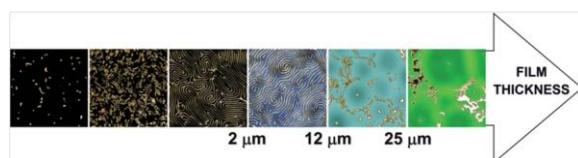


Figure 4. Scheme to summarize the thickness-dependent gold nanoparticle patterns. Adapted from Ref. [52] with permission.

may give rise to hybrid materials with enhanced chiroptical properties. In an early work, Mitov and co-workers have demonstrated the long range ordering of platinum nanoparticle assemblies that adopt the helical configuration of the cholesteric liquid crystalline phase [51]. The platinum nanoparticles form periodic ribbons that mimic the well-known “fingerprint” cholesteric texture, as shown in Figure 3. More importantly, the nanoparticles do not simply decorate the original cholesteric texture but create a novel helical structure with a larger helical pitch. This gives one great freedom to control different parameters to tune the structuring of nanoparticles. In a following work, Mitov group has attempted to organize the gold nanoparticles using CLC template [52]. They found that CLC film thickness plays a crucial role for the nanoparticles pattern formation, as shown in Figure 4. Depending on the film thickness, different patterns could be formed. For very thin films (<2 μm), the full development of helical twist is restricted. The helical structure has to adapt to the geometrical frustration. Due to the symbiotic association of gold nanoparticles with the CLC structure, only ribbon nuclei are observed for the thinnest films. By increasing the thickness of the film, the geometrical frustration relaxes and ribbon nuclei will grow to be longer chains. A very regular network of periodic lines (known as the fingerprint texture) appears with an increase of the film thickness (near 2 μm). In the thickness range of 2–12 μm, the gold nanoparticles will self-assemble into a network of double spirals. In the thickness range of 12–25 μm, the gold nanoparticles will then self-assemble as targets (i.e., a ring with a spot in the center). For films with the thickness larger than 25 μm, the gold nanoparticles will aggregate to form nanoparticle clusters.

An effective way to evaluate the impact of gold nanoparticles in CLC materials is the measurement of optical reflection properties. The central reflection wavelength λ_0 of a CLC structure is directly related to its helical pitch p by Bragg's law: $\lambda_0 = np \cos \theta$, where n is the average refractive index and θ is the angle between the direction of light propagation and the helix axis [53]. Figure 5 shows the change of transmittance spectra of cholesteric films with and without gold nanoparticles before and after annealing process. Before annealing, the presence of gold nanoparticles do not significantly modify the Bragg band. After annealing, the pure CLC film is much more blueshifted than the one with the presence of gold nanoparticles. This shift lag is mainly

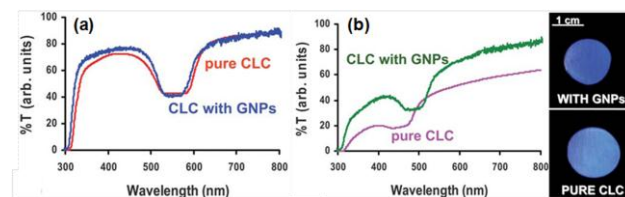


Figure 5. Transmittance spectra of cholesteric films with and without gold nanoparticles (a) before and (b) after annealing (18 h). Inset shows images of experimental cells after annealing with and without gold nanoparticles. Film thickness was 13 nm. Adapted from Ref. [52] with permission.

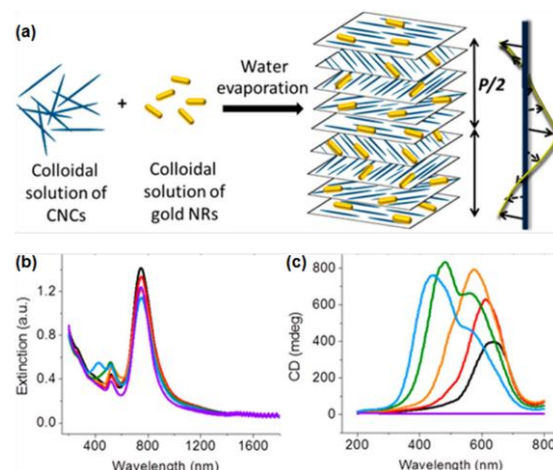


Figure 6. (a) Schematic of the preparation of the composite chiroptical plasmonic film by mixing aqueous suspensions of CNCs and gold NRs. (b-c) Tunable chiroptical activity of the NR-CNC composite films by adding NaCl into the mixed NR-CNC suspensions with $C_{NR} = 0.47$ wt%. (b) Extinction and (c) CD spectra of the NR-CNC films at NaCl of 0 (black color), 0.02 (red color), 0.06 (orange color), 0.13 (green color), 0.22 (blue color), and 2.13 (violet color) wt%. Adapted from Ref. [65] with permission.

attributed to the change of anchoring properties at both the nano- and mesoscale caused by the gold nanoparticles. The CLC template-induced self-assembly/organization of nanoparticles with versatile patterns is a promising approach toward an inexpensive bottom-up technique for on-demand selective positioning and patterning of nanoparticles over large areas.

3.1.3. Cellulose nanocrystal(CNC)-directed assembly

Analogous to the molecular orientation in CLC phases, there is another well-studied chiral film that is made of cellulose nanocrystals (CNCs). In relatively concentrated aqueous CNC colloidal suspensions, phase separation can take place: an isotropic and a cholesteric liquid crystalline phases can be formed by whisker-like CNCs [54]. The chiral nematic order of the latter can be also largely preserved in dry films [55], where adjacent CNC layers have an anticlockwise rotation with respect to each other and hence forming a left-handed helical structure [56–58]. Such CNC films can demonstrate strong chiroptical properties [55]. In addition, the responsive wavelength range for the CNC film can be conveniently tuned from the visible to the nearinfrared by changing the experimental conditions of film preparation [56,57,59,60]. The CNC-based CLC phase has also been used as a template to synthesize chiral mesoporous silica [61] and carbon [62], which were subsequently decorated with metal NPs [63,64]. Very recently, a direct use of CNC films as a host for the organization of metal NPs, and especially, of plasmonic NRs has been reported [65]. Figure 6(a) shows the schematic

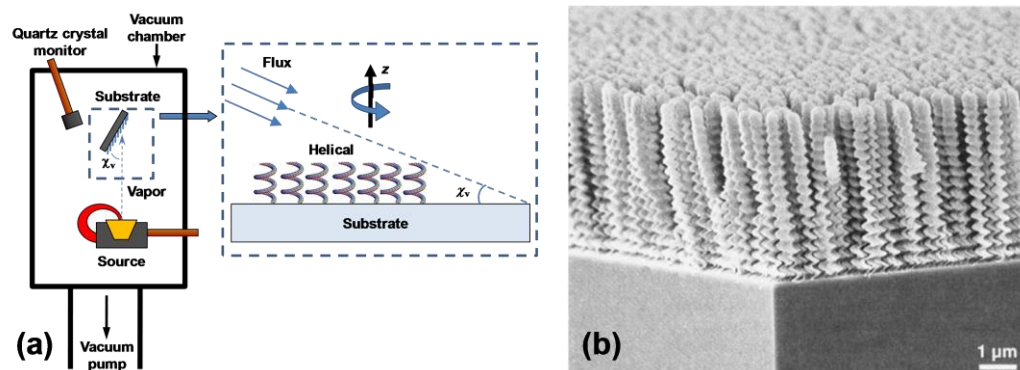


Figure 7. (a) Schematic of the oblique angle deposition process. (b) A typical chiral thin film on a glass substrate with 17.3 helical turns of pitch 360 nm. Adapted from Ref. [68] (a) and Ref. [72] (b) with permission.

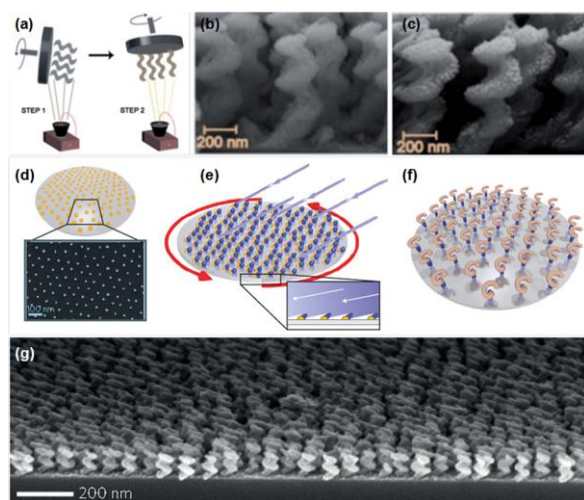


Figure 8. (a) Schematic of the two-step fabrication method, where conventional GLAD is used to fabricate the dielectric 3D scaffold followed by an evaporation of metallic islands. SEM images of the nanostructured surfaces without (b) and with (c) the Ag metallic islands; (d-f) Fabrication process using seed layer: (d) gold nanodots patterned by micellar nanolithography (bottom, SEM image of patterned wafer) act as nucleation sites (e) during subsequent shadow growth. (f) Manipulation of the substrate angle and deposition material creates complex 3D structures. (g) SEM image showing Ag:Cu (65:35) alloy helices array grown on the wafer. Adapted from Ref. [76] (a-c) and Ref. [77] (d-g) with permission.

approach of preparing the chiral plasmonic cellulose films that is based on the co-assembly of CNCs and gold NRs. The underlying physical mechanism of the co-assembly is that the anionic CNCs and cationic NRs carry opposite electrostatic charges carried and prefer to attract each other in the mixed suspension, hence inducing the chiral assembly of the NRs in the host cellulose films. A distinctive advantage of such chiral composite films is that their chiral plasmonic properties can be easily tuned by adding a varying amount of electrolyte (NaCl) to the mixed NR-CNC suspensions. The tuning mechanism is ascribed to the reduction in electrostatic repulsion between the CNCs in the presence of salts, which changes the helical pitch of the CNC matrix [59,60]. Figure 6(b) and (c) show the tunable chiroptical activity of the NR-CNC composite films by adding different amounts of NaCl into the mixed NR-CNC suspensions. The composite films show typical characteristic plasmonic peaks independent of the concentration of the NaCl. Contrastly, they exhibit concentration-dependent CD spectra, which are associated with both the CNC host and plasmonic chiroptical activity of the NRs. Such tunable

chiroptical characteristics can benefit many potential applications. The ease and robustness of film preparation is also very attractive for large scale production.

3.1.4. Glancing angle deposition (GLAD)

GLAD is another promising bottom-up method for the fabrication of chiral plasmonic structures. It is a simple and scalable physical vapor deposition method based on geometric shadowing effect [66–69], which allows the fabrication of highly porous thin films with columnar microstructure controllable on the sub-micrometer scale. GLAD uses highly oblique or glancing angle deposition [the substrate was tilted at an angle of $<15^\circ$ measured between the direction of the impinging vapor flux and the substrate plane; this angle is denoted by χ_v in Figure 7(a)] to accentuate the atomic shadowing effects, leading to thin films with porosities tunable from 10% to 90% [70,71]. By periodically rotating the substrate 180° about the substrate normal [the z -axis in Figure 7(a)] during the deposition process, a chiral thin film with desired helical morphology can be obtained. The pitch of the helical nanowires in the chiral thin film is defined as the width of one complete turn along the axis. The void region between the helical nanowires and the volume fraction of the deposited material can be experimentally controlled. Figure 7(b) shows a typical chiral thin film using GLAD [72]. Each chiral thin film is an array of helical nanowires that are parallel and nominally identical to each other, providing the thin film a distinct axis of chirality that is aligned normal to the substrate. This helical morphology gives rise to a resonance for either LCP or RCP light, which is so-called the circular Bragg regime [73–75]. Most importantly, when the incident CP light has a wave vector parallel to the axis of chirality and the CSTF is sufficiently thick, CP light of the same handedness as the chiral thin film is highly reflected, but CP light of the other handedness is much less reflected, in the circular Bragg regime.

The nature of the chiral thin films gives inspiration for the creation of metallic helices, which will have chiral plasmonic properties associated with the strong resonances of localized surface plasmons of noble metals, especially gold and silver. However, due to the 3D shape and requisite small feature sizes, fabrication of plasmonic helices still remains a big challenge. Recently, there are two different reported methods that can use GLAD techniques to fabricate plasmonic helices. One method uses GLAD dielectric helices as scaffolds for subsequent GLAD noble metal coatings [76], as shown in Figure 8(a)–(c), and the other one uses a combination of Au nanodot seeding and low temperature (liquid nitrogen substrate cooling) GLAD deposition [77], as shown in Figure 8(d)–(g). GLAD has a distinct advantage of being scalable and provides great freedom to engineer the chiral structure. For example, both wafer scale fabrication and gradually changed helix have been experimentally demonstrated [78]. However, both methods have obvious limitations: the vapour deposition of noble metals onto the helical dielectric scaffolds results in a non-continuous, nanoparticle-like coating,

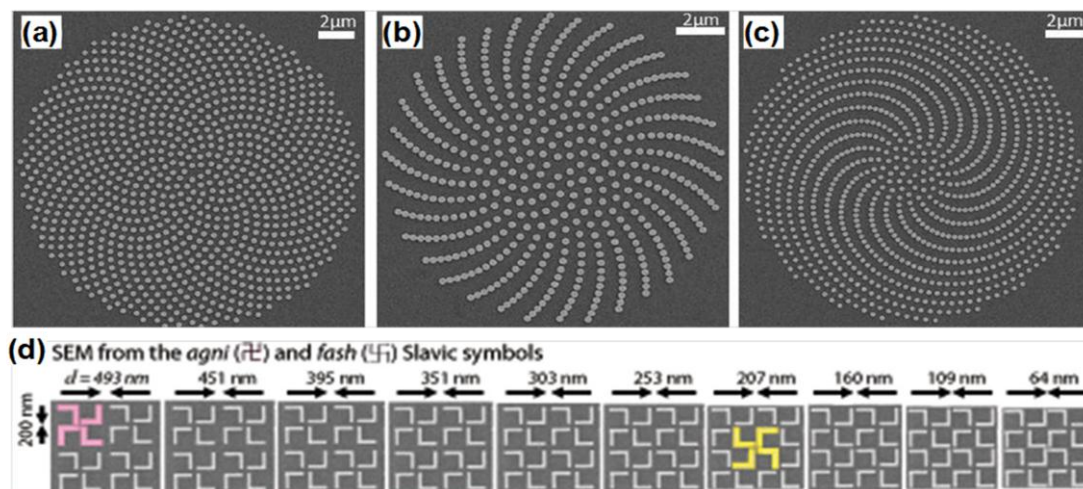


Figure 9. SEM images of (a) g-spiral, (b) α_2 -spiral, (c) α_1 -spiral and (d) gammadion Au nanostructures. Adapted from Ref. [85] (a-c) and Ref. [86] (d) with permission.

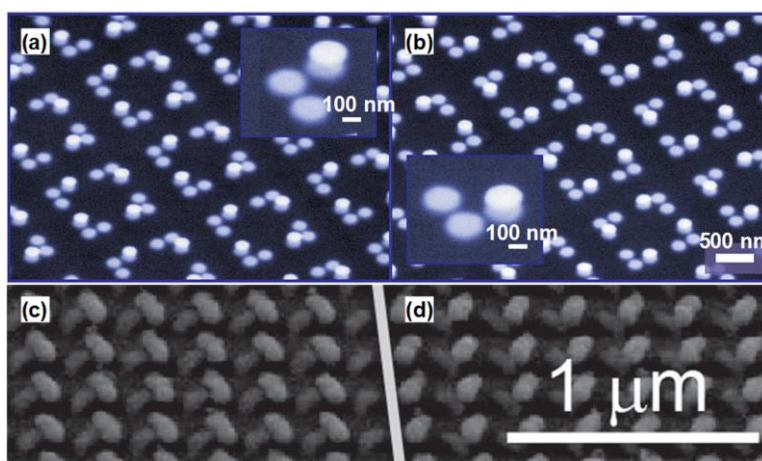


Figure 10. (a,b) Tilted SEM images of chiral plasmonic molecules arranged in C_4 symmetry with the first layer consisting of three particles and the second layer containing a single dot. Tilted SEM images of twisted arcs of chiral enantiomer (c) (right) and (d) (left). Adapted from Ref. [89] (a&b) and Ref. [90] (c&d) with permission.

which makes differential absorbance poorer than a continuous layer. Moreover, the response wavelength range depends greatly on by both the topological parameters of the helix and nanoparticle geometries, making the final structures less repeatable. On the other hand, the low temperature GLAD with nanodot seeding can produce continuous small size metal helices, but the liquid nitrogen cooling adds too much complexity.

3.2. Top-Down fabrication

Top-down fabrication usually refers to those sophisticated and expensive techniques, which offer high resolution and accurate fabrication. The widely used top-down fabrication are electron beam lithography (EBL) and focused ion beam (FIB) lithography. Both techniques are capable of creating arbitrary and complex shapes in two dimensions at the nanometer scale [79–84]. However, the top-down writing is a planar patterning method, which increases the difficulty of fabricating 3D structures using EBL or FIB.

3.2.1. Electron-Beam Lithography (EBL)

EBL is the most frequently used fabrication technique for plasmonic nanostructures. Since EBL can only define patterns in electron resists, a combination of EBL and lift-off or etching process is required to transfer structures to achieve plasmonic nanostructures. EBL provides the

user with a very high resolution of the designed structures but is time-consuming, particularly for large-area fabrication. Various 2D (planar) chiral plasmonic structures have been successfully demonstrated based on EBL [85,86], as shown in Figure 9. Among all the fabrication techniques, EBL provides the most accurate, definitive, and flexible fabrication with nearly arbitrary designs. However, it is still a challenging task to fabricate 3D chiral structures. To create 3D structures using EBL, since E-beam can only write the pattern on a single surface at one time exposure, it usually requires multiple lithographic steps for each layer and additional planarization layer. This will increase the fabrication complexity and inaccuracy. Intensive efforts have been made to realize the 3D chiral plasmonic nanostructures. Thus far, different groups have successfully demonstrated 3D structures with strong chiroptical properties [87–91], as shown in Figure 10.

3.2.2. Focused Ion Beam (FIB) lithography

FIB lithography is another classic top-down fabrication method for plasmonic devices. A big advantage of FIB is that it is a maskless lithography. One can directly mill the metal films to create the nanostructures and hence, an efficient way to validate proof-of-concepts. However, it is still time-consuming for large-area fabrication. Another issue associated with FIB is that redeposition of the removed metals

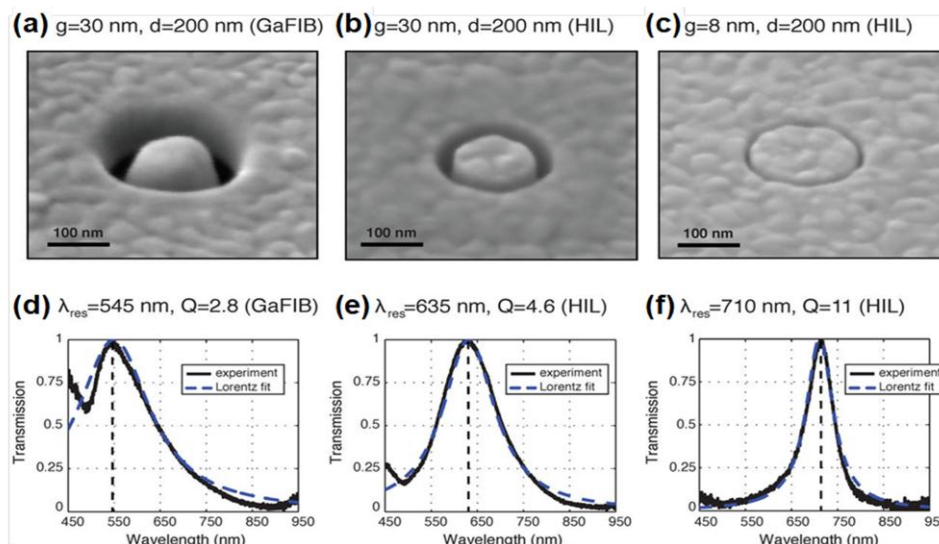


Figure 11. (a–c) SEM images of coaxial apertures with 200 nm diameter in a 100 nm thick gold film made with Ga-FIB and HIL, respectively and their corresponding transmission spectra (d–f). Adapted from Ref. [92] with permission.

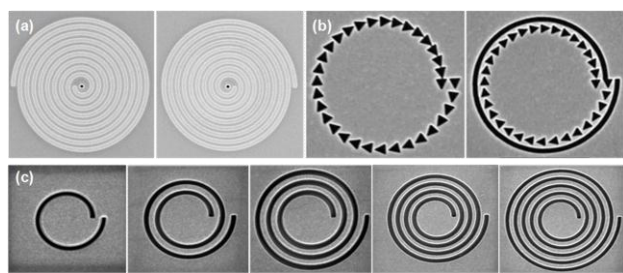


Figure 12. SEM images of (a) the left (left) and right (right) handed enantiomer (mirror image) planar chiral structures, (b) a spiral triangular sub-aperture array (left) and a hybrid spiral lens (right), (c) a right handed spiral structure with an increasing number of turns from 1 to 5 (left to right). Adapted from Ref. [95] (a), Ref. [96] (b) and Ref. [97] (c) with permission.

during the milling process, which may greatly affect the optical performance of the plasmonic nanostructures. Similar to EBL, FIB also provides accurate, definitive, and flexible fabrication with nearly arbitrary designs but again poses many challenges in fabricating 3D structures. For FIB lithography, Ga, Ne and He ions are widely used for milling the noble metals. Comparatively, Ne and He ions have much lower mass than Ga ions, hence allowing for precise and controlled milling, while Ga ions have a greater mass that allows for rapid material removal. Melli and co-workers have shown coaxial optical antennae with sub-10-nanometer critical dimensions using helium ion lithography (HIL), which nearly reach the theoretical resonance quality factor limit [92]. Figure 11 illustrates the coaxial optical antennae showing much enhanced fabrication resolution of HIL [Figure 11(b)] versus Ga-FIB [Figure 11(a)] with the same nominal dimensions. The coax fabricated via HIL also have a much higher Q-factor of 4.6 than those fabricated by Ga-FIB with Q-factor of 2.8 [see Figure 11(d)&(e)]. The Q-factor is determined by fitting the transmission peaks with a Lorentz function. By reducing the gap size to 8 nm [Figure 11(c)], the Q-factor can be further increased to 11 [Figure 11(f)]. As the gap size is reduced, the plasmon resonance wavelength becomes shorter [93], enhancing the contribution of the retardation effect to improve the Q-factor [94].

FIB provides a convenient way to create various chiral structures for proof-of-concept demonstration. For example, various left-

and right-handed spiral (LHS and RHS) apertures have been demonstrated in metallic films by FIB [95–97], as shown in Figure 12.

4. Applications

4.1. Light rendering

Light is essentially an electromagnetic wave that consists of electric and magnetic fields oscillating perpendicular to each other and to the propagating direction as well. Light properties can be strongly altered when light interacts with ordered micro/nanostructures with special shapes. The chiral plasmonic nanostructures described in this review article can therefore modify the light polarizations according to the chirality due to the strong photon-plasmon interactions, which gives a strong optical activity or CD. Based on this chirality-induced light modification, many photonic applications have been demonstrated.

4.1.1. Chiral plasmonic lenses

Chen and co-workers have demonstrated a very simple chiral structure, which they called spiral plasmonic lens [98], as shown in Figure 13. The plasmonic field at the focus of a spiral lens strongly depends on the handedness of the circularly polarized incident light [99–101]. It has been demonstrated analytically and numerically that a spiral plasmonic lens can focus circular polarization of a given handedness into a solid spot and defocus circular polarization of the opposite chirality into a doughnut shape with a dark center [99]. However, since the plasmonic focal field is essentially TM-polarized (perpendicular to the surface), it is much more difficult to couple the longitudinal component into the apertures of NSOM probe than the transverse components for extremely small aperture size. As a result, it is expected that a doughnut spot with a dark center should be experimentally observed for both LHC and RHC illuminations due to NSOM detection mechanism. However, the mapped peak intensity will show a distinct difference (> 2 times intensity difference) for the same illumination power with different handedness, as shown in Figure 13. Therefore, one can still utilize the intensity difference to differentiate the handedness of polarizations even though the shapes of the NSOM images look similar for LHC and RHC illumination.

4.1.2. Circular polarizers and filters

In bulk optics, one usually creates the circularly polarized light using a quarterwave plate in combination with a linear polarizer. In many applications, micro/nano-scale polarizing elements are highly desired. However, it is very challenging to fabricate micropolarizing structures

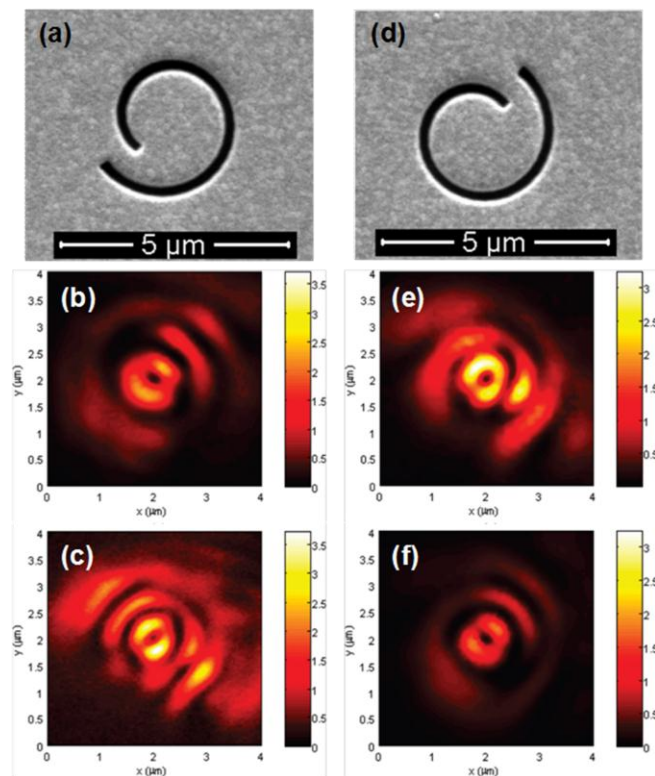


Figure 13. SEM images of a LHS (a) and RHS (d) plasmonic lenses in gold film fabricated with FIB milling and their NSOM images under LHC (b&e) and RHC(c&f) illumination. Adapted from Ref. [98] with permission.

sensitive to circular polarization. With chiral plasmonic materials and synthetic chiral metamaterials, it is possible to use a single structure that allows to transmit left-hand circular polarization but reflect/absorb left-hand circular (or vice versa). Bachman *et al.* have demonstrated such a kind of circular polarization transmission filters by using spiral plasmonic nanoantennas [102], as shown in Figure 14. Such structures can provide controllable bandwidth and peak wavelength by varying the spiral arm length. Fabrication is relatively easy since it requires only standard thin film process with three lithography levels having dimensions easily obtained with state-of-the-art photolithography systems.

Alù group have also demonstrated a broadband circular polarizer based on twisted plasmonic metasurfaces [103]. The design is based on multilayer stacked planar metasurfaces realized with conventional lithographic techniques, with a certain rotation angle from one layer to the next. By introducing a twist in the lattice orientation, they can relax the fabrication stringency to a great extent and achieve exotic optical performance. Figure 15(a)–(f) shows the evolution of the frequency response by increasing the number of stacks. It can be seen clearly that by cascading more layers, the bandwidth is gradually broadened and the extinction ratio becomes much larger. For a right-handed twist, LCP light is reflected within the bandwidth of operation, while RCP light is transmitted. Figure 15(g) shows a SEM image of the fabricated four-layer twisted structure, which is obtained by focused-ion beam milling so as to reveal the details of each cascaded layer. With such a fabrication technique, it is therefore possible to realize broadband circular polarizers at even shorter wavelengths using low-loss plasmonic metals, for example silver and aluminium, hence spanning the entire visible range.

4.1.3. Active metamaterials

Metamaterials are artificially designed optical materials that possess unique optical properties and enable novel manipulations of light

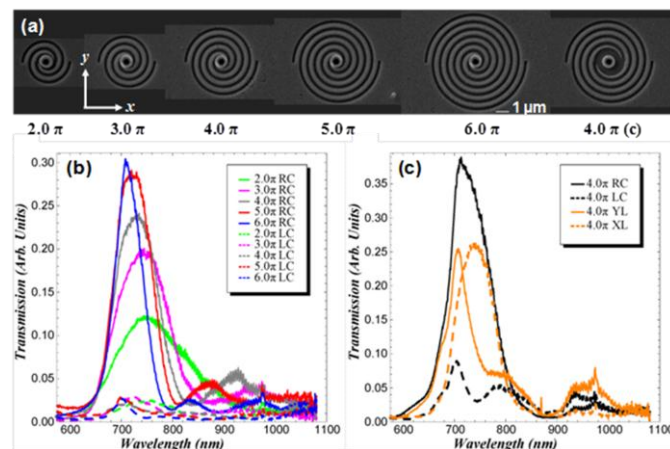


Figure 14. (a) Archimedean spiral gratings that consists of gold and silicon dioxide; (b) Transmission as a function of spiral arm length; (c) Transmission comparison for right- and left-circular, and linear (x- and y-directions) polarizations. Adapted from Ref. [102] with permission.

[104–109]. Over the past decade, there has been tremendous progress in the development of various kinds of metamaterials. While some applications can be fully accomplished with passive metamaterials that exhibit constant optical response, it is still highly desirable to have active metamaterials in developing applications that need dynamic controls, for example, switches and modulators. Many active mediums have been used to build active plasmonic and metamaterial devices, including liquid crystals [110–118], molecules [119–121], fluids [122, 123], and other active materials [124–126]. In an effort that exploits the use of DNA to functionalize plasmonic nanoparticles, Liu *et al.* found that DNA not only facilitates the assembly of the plasmonic nanoparticles but also acts as a driving force to regulate conformational changes at the nanoscale dimensions, which can be then exploited to construct reconfigurable 3D plasmonic metamolecules [127]. Figure 16 shows the concept of a reconfigurable 3D plasmonic metamolecule and preliminary experimental results. In Figure 16(a), two gold nanorods (AuNRs) are bound on a switchable DNA origami template consisting of two connected bundles, which subtends a tunable angle. The relative angle between the AuNRs and the handedness of the 3D chiral nanostructure can be actively controlled by two DNA locks, which are extended from the sides of the DNA origami template. Specifically designed DNA strands work as fuel to drive the plasmonic nanostructure to desired states with distinct 3D conformations by altering the relative angle between the two DNA bundles and hence the AuNRs. Unreactive waste is produced during a cycle. The red and blue beams indicate the incident left- and right-handed circularly polarized light, respectively. The four arms of the two DNA locks are labelled *a*, *b*, *c* and *d* (see Figure 16(b)). Through toehold-mediated strand displacement reactions, the plasmonic nanostructure can be driven to either the left- or right-handed state by adding removal strands R_1 or R_2 and back to its relaxed state by adding return strands $\bar{R}_1$

or $\bar{R}_2$. Figure 16(c) shows the operation of the three-state cycle. The system can be driven to either the left- or right-handed state by adding R_1

or R_2 and back to its relaxed state by adding $\bar{R}_1$ or $\bar{R}_2$. This DNA-enabled unprecedented level of spatial and temporal control could significantly advance the development of active plasmonics and metamaterials.

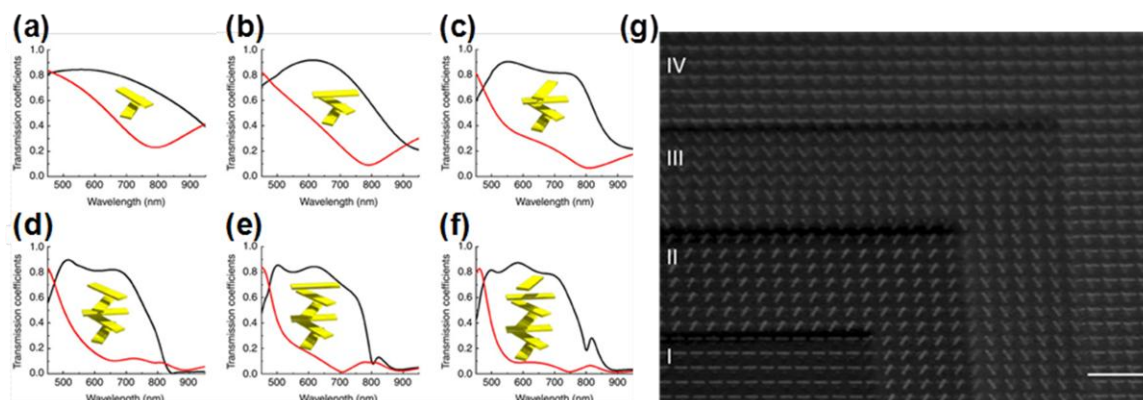


Figure 15. Transmission of LCP and RCP light of multilayer stacked rotated metasurfaces with the number of layers from two to seven (a–f). The insets illustrating one unit cell of the corresponding twisted metamaterial slab along the propagation direction. (g) Multilayer SEM view of the fabricated four-layer structures marked by I, II, III, IV. Scale bar: 1 μm . Adapted from Ref. [103] with permission.

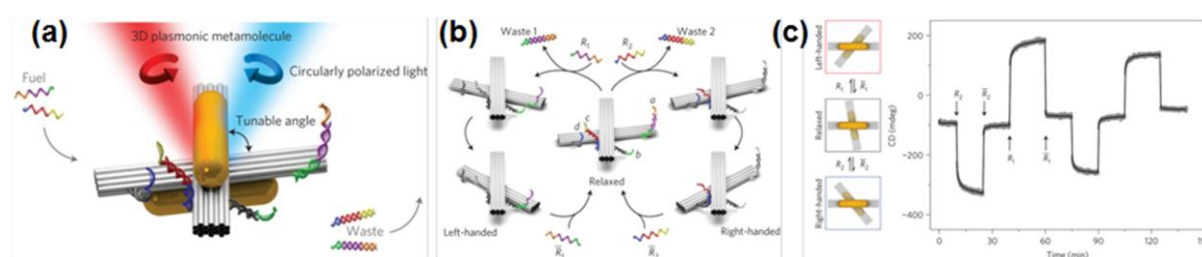


Figure 16. (a) Schematic diagram of a reconfigurable 3D plasmonic metamolecule. (b) Schematic switching mechanism. (c) Cycling the 3D plasmonic metamolecules between three states. The CD signal was monitored over time at a fixed wavelength of 725 nm. Adapted from Ref. [127] with permission.

4.2. Sensing

4.2.1. Biosensing and chirality determination

CD spectroscopy is a very powerful technique to probe the bio/chemo-molecular structure due to the inherent twist, or chiral symmetry, of circularly polarized radiation. However, such a spectroscopic technique has limitations in sensitivity, especially for small chiral molecules, since the absorption cross sections for left- and right-circularly polarized light only differ by less than one part per thousand [128]. The root reason for such weak chiroptical interaction lies in the mismatch between the chiral length scale of light (set by the wavelength of light), with the chiral length scale of molecules, which is typically orders of magnitude smaller. Recently, it has been shown that the use of plasmonic chiral systems can breach this natural ceiling to chiroptical sensitivity. Even handed planar, i.e., two-dimensional, plasmonic structures have demonstrated extremely strong interaction with circularly polarized light [129–132] as well as with chiral molecules [133,134]. Hendry and co-workers have demonstrated ultrasensitive detection and characterization of biomolecules using planar chiral plasmonic nanostructures [135]. They used plasmonic gammadion nanostructures to generate superchiral electromagnetic fields under optical excitation (Figure 17a). Such superchiral fields greatly enhance the interaction between the biomolecules and structures and hence enable a highly sensitive detection signal. The differences in the effective refractive indices of chiral samples exposed to left- and right-handed superchiral fields are found to be up to 106 times greater than those observed in optical polarimetry measurements, thus allowing picogram quantities of adsorbed molecules to be characterized. By adsorbing different proteins onto the plasmonic gammadion nanostructures, a clear spectral change can be observed, as shown in Figure 17(b)&(c). More importantly, such superchiral fields can even help probe chiral supramolecular structure by the induced dissymmetrical shift [see Figure 17(d)]. This could form the

basis for assaying technologies that can detect amyloid diseases and certain types of viruses.

4.2.2. Surface Enhanced Raman Scattering (SERS)

SERS is a very sensitive spectroscopic technique that can detect and trace amounts of chemical and biological molecules via significant enhancement of Raman scattering when molecules are adsorbed on a metal surface (e.g., silver and gold). In a chiral plasmonic structure, the spiral or chiral turns/bends may function as hot spots to achieve a sensitive SERS signal. Zhou *et al.* investigated the SERS performance using helical silver zigzag-like nanorod arrays [136,137]. They have shown that enhancement increases as the number of zigzags N increases up to $N = 4$ due to the increase of the number of hot spots as shown in Figure 18. Above $N = 5$, the SERS intensity reaches saturation and starts to decrease due to the number change of effective hot spots. The top multiple arms can block the incident light to strike at the bottom hot spots in a silver nanorod film, which causes a disproportionate increase in the SERS intensity as the number of arms of the helical zigzag-like nanorods increases.

5. SUMMARY AND OUTLOOK

The emerging field of chiral plasmonics leverages the strengths and advantages of both plasmonics and advanced fabrication technologies. Thus far, the reported results by many research groups worldwide have demonstrated an accelerating pace of progress thanks to rapid advances in many aspects including micro-/nanofabrication, chemical synthesis protocols, characterization, and numerical simulations. Although chiral plasmonics presents great opportunities to explore new science and applications, current research methodologies and capabilities

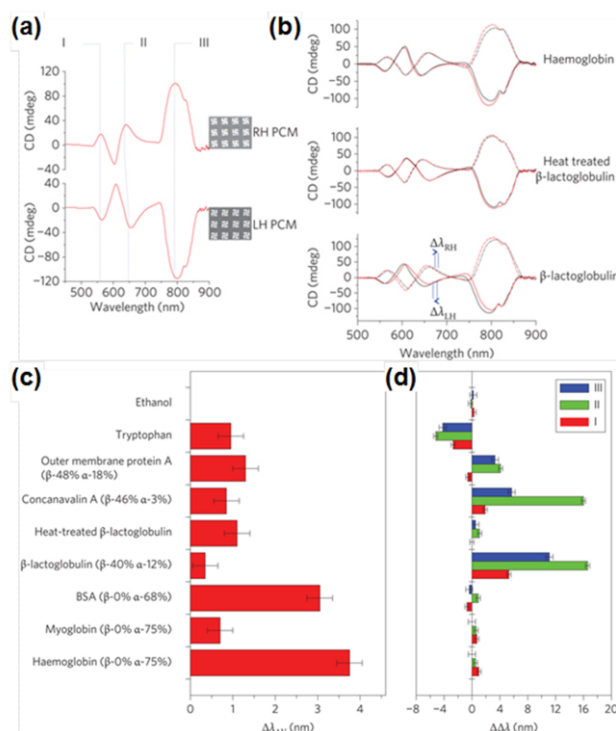


Figure 17. (a) Measured CD spectra from LH/RH planar chiral gammadians in distilled water. Three modes that are sensitive to changes in the local dielectric surroundings have been labelled I, II and III. (b) Induced CD spectral changes by the adsorbed proteins haemoglobin, β -lactoglobulin and thermally denatured β -lactoglobulin. (c) Induced wavelength shift for tryptophan and the six proteins. (d) Corresponding dissymmetrical shift for modes I, II and III. Adapted from Ref. [135] with permission.

still require significant improvements in order to have complete control in terms of construction and execution of the chiral plasmonic devices.

Currently, most designs and results of chiral plasmonics are only for laboratory investigations of fundamental principles or proof-of-concept trials. Although promising, the optical performance of many proposed devices is still relatively poor compared to the conventional bulky counterparts. Therefore, the optical performance has to be further enhanced via new designs or optimization.

Many reports have shown that even for planar 2D chiral plasmonic structures, strong interaction with circularly polarized light as well as with chiral molecules have been demonstrated, despite the fact that some are not truly chiral. With 3D chiral structures, it is therefore expected that much stronger chiral optical responses can be exhibited. However, the fabrication of 3D chiral plasmonic structures still remains experimental challenges, particularly for top-down fabrication. Among bottom-up fabrication techniques, GLAD seems more promising for 3D fabrication but lack the fine control and uniformity in large scale. Therefore, this emerging research field still requires highly innovative techniques/approaches to fulfil the scalable, repeatable, fast, and economic fabrication, particularly for 3D chiral structures.

Lab demonstration and prototypes have to be translated into practical applications eventually. It requires innovations in diverse areas so as to move from the proof-of-concept level to real world practices, including designs, fabrication, illumination and detection, and system integration. An ideal system with specific functions should be simple, compact, robust, and user-friendly, which will be a big challenge ahead of this research field and provide endless opportunities to the scientists and engineers as well.

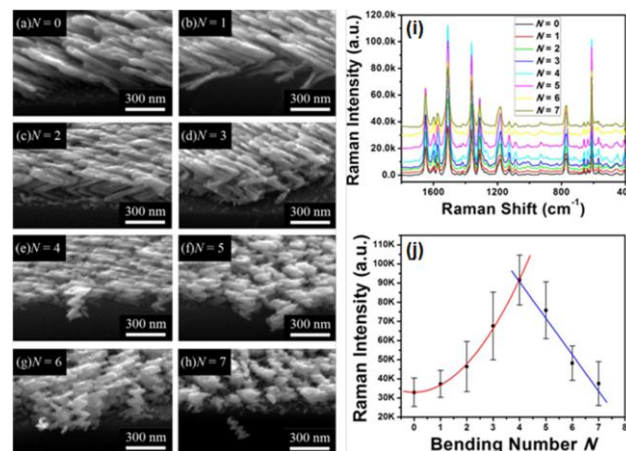


Figure 18. SEM images (a-h) of Ag chiral sculptured films having different number of zigzags and the corresponding Raman signal (i&j) for the different samples with different zigzag numbers. Adapted from Ref. [137] with permission.

ACKNOWLEDGEMENTS

Y. J. Liu, E. S. P. Leong, E. H. Khoo, and W. K. Phua acknowledge financial support from Agency for Science, Technology and Research (A*STAR) under the grant No. 12302FG012. G. Y. Si and H. T. Dai thank the funding support from the National Natural Science Foundation of China under grant No. 61405031 and 61177061, respectively.

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Cite this article as:

Yan Jun Liu *et al.*: Chiral plasmonics: Fabrication and applications. Sci. Adv. Today 1 (2015) 25212.