Chiral plasmonics is a fascinating research field that is attractive to scientists from diverse backgrounds. Physicists study light–matter interactions, chemists seek ways to analyze enantiomeric molecules, biologists study living objects, and material engineers focus on scalable production processes. Successful access to this emergent field for an interdisciplinary community depends on overcoming three main issues. First, understanding the physical background of chiral plasmonics requires proper introduction in easy language. Second, pitfalls in the characterization of chiroplasmonic features can prevent accurate interpretation. Third, simple and robust methods capable of covering macroscopic substrate areas must be available. This tutorial-style review addresses these issues with the goal to provide a comprehensive introduction into chiral plasmonic nanostructures. It starts with a brief introduction of the relevant physics involved in chiral light–matter interactions. A brief guide about how to adequately characterize samples follows. Subsequently, an overview of fabrication techniques that produce chiral substrates over large areas is given, and the strengths and weaknesses of the different approaches are discussed. The focus is on simple and robust processes that do not require clean room facilities and can be implemented by a much larger scientific audience.

1. Introduction

Plasmonic effects in noble metal nanostructures are probably one of the most widely recognized forms of nanotechnology. The tremendous success and interdisciplinary use of plasmonic materials has been stipulated by efforts to condense the underlying physics and properties of localized surface plasmon resonance (LSPR) in simplified terms, understandable by a wide community. The interesting properties of plasmonic particles attracted attention beyond the physics and nanophotonics community, as they benefit multiple disciplines such as chemistry,[1–3] energy conversion,[4,5] biology,[6,7] nanomedicine,[8–10] sensing technology,[11–17] anti-counterfeit engineering,[18] color design,[19] imaging,[20] and many more.[21–23] Surface enhanced Raman spectroscopy (SERS) played a major role in this advancement, as the technique is inherently attractive to a broad range of scientists with backgrounds in chemistry, biology, or engineering.[11–17] Conversely, these disciplines contributed significantly to the development and refinement of the SERS sensors we have today.

Within the last decade, chiral plasmonics has emerged as a new research direction within the field of plasmonics.[28–44] Chirality and chiral molecules are abundant in biological systems, such as our body, and their handedness plays a significant role in many biological and chemical systems.[45] Enantiomers may, for example cause subordinate differentiations like the odor of lemons and oranges, but also cause seriously differentiating health effects of pharmaceutical drugs.[45,46] The emergence of chiral nanostructures has not only caused fundamental interest in this new class of metamaterials itself, but also raised hope to translate some of the key findings, similarly to traditional plasmonics.[28–44]

Encoding chiral responses is promising to numerous disciplines as it can manipulate electromagnetic fields or enhance the sensitive detection of chiral molecules.[28–44] Chiral plasmonics however, has yet to attract scientists from different scientific disciplines to investigate and harvest emerging properties. We identify three potential bottlenecks preventing a more widespread use of chiral plasmonics: i) Chirality per definition requires breaking the mirror symmetry. In comparison to other plasmonic applications where planar structures are sufficient, chiral plasmonics often requires the production of 3D structures. Inherently, this complicates the design of suitable chiroplasmonic substrates. Current chiroplasmonic substrates are typically produced by multi-step nanofabrication methods in cleanrooms, which are not commonly available, especially...
outside the nanophotonics community. ii) Understanding the chiroptical response of nanostructures is far from trivial and has been controversially discussed within the community over time. There are several pitfalls in the interpretation and characterization of chiral plasmonic systems, or such that seem to be chiral. iii) More generally, there seems to be a lack of common and understandable language that can be easily followed by an interdisciplinary audience. Aspects that seem trivial to experienced researchers in the field may not be clear to everyone and may require a more tutorial explanation.

While there has been a number of excellent reviews and books covering different aspects of the wide field of chiral plasmonics in detail, we believe that there is a need for an easily-accessible introduction for a broad, nonspecialist audience. Here, we aim to address these issues in a tutorial style review. We seek to provide basic understanding and design guidelines to lower the entry barrier for researchers from different backgrounds. Our review is structured as follows. First, we briefly introduce the definition of chirality and explain the different concepts that can be utilized to achieve chirality. Second, we explain basic principles of chiral plasmonics in an (hopefully) easily understandable and unbiased language. We hope that this facilitates access to the field and simplifies the understanding of the subsequent topics of the review. Third, we introduce and discuss fabrication methods to prepare chiral plasmonic substrates that do not rely on sophisticated nanofabrication equipment and cleanroom infrastructure and can thus be available to a broad, interdisciplinary audience with an interest in such systems. We restrict ourselves to substrate-based large-area approaches, as they are easy to handle and manufacture. While wet-chemical approaches are certainly equally useful for the same interdisciplinary audience, there have been several recent reviews covering colloidal and suspension-based approaches and we therefore exclude such systems from our review. We also exclude all aspects of induced chirality, i.e., chirality transfer from molecules to achiral plasmonic structures, which are similarly covered in recent reviews.

2. What is Chirality in the Context of Chiral Optics and Why Does It Matter

Every living being is confronted with chirality on a daily basis, and chirality has been the answer to why you should not eat pizza with an alien as pointed out by Richard P. Feynman’s riddles. The perhaps most obvious example to us humans are hands, which ultimately also contribute to the terminology of handed objects. In 1904, Lord Kelvin called “any geometrical figure, or group of points, “chiral,” stating that it exhibits chirality if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself.” This means, for example, that the mirror image of a right hand cannot be superimposed with the original image. Or, in other words: your left hand resembles the mirror image of your right hand; there is no possibility of twisting, rotating or flipping your hands in a way that the same fingers overlay with each other in the same order. This simple, binary, mathematical concept has decisive consequences in chemistry, biology, and, of course in electromagnetism.

The greatest consequences of chirality can be observed in (bio)chemistry. Although composed of the same atoms, R(+) and S(−)-limonene result in the typical smells of oranges and lemons, respectively, which our human nose differentiates easily. Our human body requires carbohydrates, but can only process sugars with one type of handedness, the specifically common one on our planet. The presence of this homochirality on earth is still puzzling science, and, as famously put by Richard Feynman in his “Symmetry in Physical Law” lecture, an alien species might famish without their own nourishment of a certain handedness. Even nonchiral objects can form chiral structures. In this case, the chirality results from the self-organization of these objects into defined structural arrangements. Cholesteric liquid crystals of cellulose nanoparticles are a typical example of such a chiral phase.

Chirality typically reveals itself to an observer by a chiroptical response, where light absorption differs between the two rotation directions of circular polarization. At the same time a plane of linearly polarized light will be rotated while passing through such a chiral medium, thus termed optical rotation or circular birefringence (CB). This rotation will vary with wavelength; embodied in an effect called optical rotatory dispersion (ORD). Both ORD and circular dichroism are mathematically connected by the Kramers–Kronig relation, hence one must come along with the other. These effects result from the optical activity, i.e., from the enantioselective response from a chiral material with chiral light. Before we can discuss those effects, we introduce different key concepts that make a structure chiral and explain why this depends on the point of view and the underlying substrate.

If an object is laid on a substrate it can be considered chiral if it is either “truly” chiral by itself or if it is “mimicking” chirality (Figure 1b,c). True chirality is common for molecules. A chiral center, i.e., a point where the handedness of a molecule is determined, can be formed by different spatial arrangements of the atoms or functional groups surrounding this center, thus breaking the mirror symmetry. This concept can be transferred to plasmonic nanostructures, as exemplarily shown by pillars arranged in an isosceles triangle on a substrate (Figure 1b). Configurational chirality results if all three pillars are made from the same material, but differ in their heights. If only the central one would have a different height, a mirror symmetry would exist around this particle. Constitutional chirality results if the pillars have the same geometry, but differ in the material of the two satellite pillars. In the example, one of the pillars is grey (i.e., made from silicon), while the other one is yellow (i.e., made from gold). If only the one pillar with an equidistance to the other two pillars (in the example the top left pillar) would be of a different material, mirror symmetry would be retained, resulting in an achiral assembly.

In free space, the absence of mirror symmetry as the definition of chirality prevents planar objects from being chiral. However, when placed on a substrate, a seemingly planar object, i.e., an object that was extruded from a planar figure, can mimic chirality. The asymmetric, windmill-like nanostructure shown in Figure 1c,d, left is a typical example, as are gammaindor structures often used in the nanooptics community. These objects themselves possess a mirror symmetry, as they can be superimposed with their mirror images by simply
flipping them (Figure 1d, left). The mirror symmetry is broken, however, if the object is placed on a substrate (Figure 1c, left). In contrast to truly chiral objects, the chiroptical behavior of such structures may depend on the direction of light illumination.\cite{52,53,55-57} This means that the sign of the chiroptical response may change when the illumination occurs from the substrate side (see also Figure 8b). Such objects are therefore referred to as pseudo chiral. Similarly, heterogeneous or homogenous achiral structures can be rendered into chiral objects if the $k$ vector is at an oblique incidence, leading to extrinsic chirality. d) Planar objects in free space, i.e., without a substrate, are achiral. Similarly, azimuthal rotation of extrinsically chiral objects on their tilted plane can restore mirror symmetry.

3. The 101 of Chiral Plasmonics

Before we discuss chiral plasmonics, we briefly introduce the principles of plasmonics that will be required to follow this review. A more in-depth introduction can be found in several existing review articles.\cite{21–27} This section introduces the physical principles of plasmonics, building the foundation for chiral plasmonics. We start our discussion with individual nanostructures exhibiting plasmonic resonances. These structures can then be integrated into periodic arrays known as metasurfaces or metamaterials when formed from 2D and 3D building blocks, respectively.\cite{66}

3.1. Introduction to Plasmonics

3.1.1. Surface Plasmon Polaritons (SPPs)

A SPP can be defined as a quantum of oscillations in surface charge density,\cite{67} which, in simple words, can be described as the free-electron cloud at the surface of a conducting material. At metal-dielectric interfaces, SPPs arise from the collective interaction of an electromagnetic field with the free conduction electrons of the metal. SPPs are traveling and decaying (i.e., small tilts in the substrate) may lead to small chiral signals that are still on the order of (or higher than) molecular chiral signals.\cite{59–61} The same principle applies to production imperfections, which often cannot be avoided.\cite{62}

Now that we have seen the different ways to achieve chirality, we can address the ambiguous aspects of optical chirality. Although we may have a structurally chiral object, such as a helix, we can observe different obstacles when taking illumination into account. First, we may not measure the same optical activity depending on how we look at (illuminate) an object. Perpendicular illumination of a helix can differ from tangential illumination (Figure 2a).\cite{60,63,64} Second, the definition of chirality is a binary one, and although quantification seems intuitively tempting, it is not possible. The thought experiment in Figure 2b underlines this problem of chiral connectedness.\cite{65} Imagine a helix with clockwise rotation (red). We can continuously transform this helix into a helix with anti-clockwise rotation and a different diameter (blue) by bending the wire. The different diameters of the two helices preserve structural chirality during the entire transformation process (2,3). This means the intermediate steps (2,3) also present chiral objects. Yet, we can expect that there is a stage in between, with no measurable optical chirality. This underlines that quantification of structural chirality is not only impossible, it also highlights that a chiral object does not necessarily exhibit measurable optical activity.\cite{65} As an important consequence of this consideration, a racemic ensemble of chiral objects (Figure 2c, i), i.e., an array of equal parts of both enantiomers, will also not lead to any macroscopically observable measurable in the far-field (device level) (Figure 2c, ii). However, it will have chiral near-fields on the nanoscale that can be employed for enhanced chiral sensing (nano/molecular level), which can then also lead to measurable quantities.\cite{60,64,65}
oscillations, typically found in continuous or perforated metallic films, while LSPRs typically occur in confined nanoparticles.

The excitation of SPPs requires both energy and momentum conservation to be met since the rate at which electromagnetic waves propagate in a medium or at the interface is heavily dependent on its wavelength. This dependence can be explained through the dispersion relation, which describes the relationship between energy, written in terms of angular frequency $\omega$, and momentum, written in terms of the wavevector $k$. The dispersion relation elucidates that the wavevector of a surface plasmon at a given energy is larger than the free-space wavevector of light. The resulting momentum mismatch prevents free-space light from directly exciting SPPs on the metal-dielectric interface.[67,68] This can be circumvented, for example, by utilization of total internal reflection in prism coupling, highly focused optical beams arising from a high numerical aperture and the appropriate patterning of metal surfaces leading to grating coupling.[69]

Excitation of SPPs causes the charges present on the metal-dielectric interface to collectively oscillate, thus emitting waves with lesser frequency than the bulk plasma frequency. The SPP frequency is denoted as

$$\omega_{\text{SPP}} = \frac{\omega_p}{\sqrt{1 + \varepsilon_d}}$$

(1)

where $\omega_p$ is the plasma frequency of electrons in a bulk metal and $\varepsilon_d$ is the dielectric function of the dielectric medium.[70]

As the wavenumber of the SPP is larger than that of propagating electromagnetic waves in free space, an increased penetration of the electromagnetic wave into the bulk metal results, causing ohmic losses in the metal.[67] Thus, the SPP propagation into the bulk metal (i.e., perpendicular to the interface) decays exponentially, and the resulting evanescent wave exhibits a penetration depth in the nanometer range in both metal and dielectric media.[71] In the dielectric medium, the penetration depth $\delta_d$ can be written as

$$\delta_d = \frac{1}{k} \left| \varepsilon_d + \varepsilon_m \right|^2$$

(2)

where $k$ denotes the magnitude of the wave vector in free space and $\varepsilon_m$ is the dielectric function of the metal.[70] As SPPs travel along the metal-dielectric interface, they exhibit a high sensitivity to changes in their dielectric environment. The parameters of the incident light beam will change due to the refractive index and thus vary the SPP excitation.[71]

### 3.1.2. Localized Surface Plasmon Resonances (LSPRs)

While the high sensitivity of SPPs to their dielectric environment holds promise for a variety of applications, including all-optical sensing, challenges such as high-fabrication costs hindered the mass production of SPP-based devices. In contrast, the phenomenon of LSPR, which arises from the non-propagating confinement of light across a single subwavelength metallic nanostructure, opened the door to a variety of scalable applications due to, for instance, their solution-processability.[69]

This light–matter interaction occurring in subwavelength nanoparticles changes the net electric field, which is heavily dependent on the size and shape of the particle. Mie theory can analytically calculate the fields scattered and absorbed by a spherical nanoparticle,[71] while light–matter interactions in nonspherical nanoparticles can be numerically computed, for example by solving Maxwell’s equations with finite element methods.[72]
method, discrete dipole approximation, finite difference time domain or the boundary value problem.\[^{73}\]

The behavior of sufficiently small metallic nanoparticles can be approximated in the quasi-static electric-dipole limit, where the excitation by an electromagnetic field polarizes the free-electron cloud at the nanoparticle surface. The electric dipole moment is written as \( p = \alpha E \), for incident electric field \( E \) and electric dipole polarizability \( \alpha \). For a spherical nanoparticle, \( \alpha \) is defined as\[^{67}\]

\[
\alpha(\omega) = 4\pi\epsilon_0 a^3 \left( \frac{\epsilon_1(\omega) - \epsilon_2}{\epsilon_1(\omega) + 2\epsilon_2} \right)
\]

where \( a \) is the radius of the nanoparticle, \( \epsilon_1(\omega) \) is the dielectric function of the nanoparticle and \( \epsilon_2 \) is the dielectric function of the surrounding medium. In the quasi-static limit, electric fields radiated by a dipolar nanoparticle are written as\[^{74}\]

\[
E_d = E + E_{\text{scat}} = \frac{1}{4\pi\epsilon_0 a^3} \left[ 3n(p)p - p \right]
\]

where \( E_{\text{scat}} \) denotes the scattered electric field and \( n \) is the unit vector along the direction of propagation.

When the frequency of an incident electromagnetic plane wave matches the resonant frequency of the nanoparticle, a strong oscillation of the free-electron cloud, induced from displacement and Coulombic restoring forces, leads to the LSPR. The consequent strong enhancement in scattering and absorption efficiency of the metal nanoparticle is quantified by the scattering and absorption cross-sections

\[
\sigma_{\text{scat}} = \frac{k^4}{6\pi\epsilon_0} |\alpha(\omega)|^2 \quad \text{(5)}
\]

\[
\sigma_{\text{abs}} = \frac{k^2}{\epsilon_0} \text{Im}[\alpha(\omega)] \quad \text{(6)}
\]

Equations (5) and (6) make apparent how the frequency-dependence of \( \sigma_{\text{scat}} \) and \( \sigma_{\text{abs}} \) strongly depends on the electric dipole polarizability, and thus, the related material functions.\[^{67}\]

### 3.1.3. Coupling of Resonances and Surface Lattice Resonances

In addition to the response of a single isolated particle in a homogenous environment, the behavior of plasmonic resonators drastically changes when two or more resonators are in close proximity. Similarly to orbital physics in chemistry, the dipolar modes of nanoparticles can exhibit mode hybridization, which results in the appearance of new resonances.\[^{75-82}\] Moreover, we note that the coupling of multiple metallic nanoparticles can exhibit physically meaningful effects in the form of multipolar resonances,\[^{83,84}\] or oligomers, where smaller individual nanoparticles are coupled to produce collective modes over the entire oligomer.\[^{82-87}\]

Going the next consequent step and assembling many plasmonic resonators next to each other in a defined lattice can significantly change the interaction between them.\[^{88,89}\] Surface lattice resonances (SLRs) arise in plasmonic systems when sub-wavelength metallic nanoparticles are arranged in ordered, periodic, diffractive lattices.\[^{90-94}\] In comparison to LSPR, SLR results in higher-quality-factor resonances,\[^{95-99}\] which can go experimentally up to quality factors (\( \Delta \lambda / \lambda \)) above 2400.\[^{39}\] Further, SLRs exhibit near-field effects distributed over larger surface areas than highly confined LSPRs with longer lifetime due to lesser radiative losses.\[^{96-99}\]

Due to their diffractive nature, SLRs are most effectively excited when the incident electromagnetic field matches the lattice periodicity. In certain simplified cases, where each nanoparticle in the lattice is well-approximated in the dipole limit, the SLR spectral response can be computed analytically from a dipole summation model,\[^{90,100}\] while more complex systems are best treated numerically.

### 3.2. Introduction to Chiral Plasmonics

Section 3.1.2 illustrates how sufficiently sub-wavelength plasmonic nanoparticles give rise to localized surface plasmon resonances which are well-approximated in the quasi-static electric dipole limit, with dipole moment \( p = \alpha E \) for electric dipole polarizability \( \alpha \) and incident electric field \( E \). Similarly, a chiral optical effect is achieved in the quasi-static dipole limit by magnetoelastic cross coupling as\[^{101,102}\]

\[
\begin{pmatrix}
    p \\
    m
\end{pmatrix} = \begin{pmatrix}
    \alpha_C & i\alpha_M \\
    -i\alpha_C & \alpha_M
\end{pmatrix} \begin{pmatrix}
    E \\
    H
\end{pmatrix} \quad \text{(7)}
\]

where \( \alpha_C \) and \( \alpha_M \) are the chiral and magnetic dipole polarizabilities, respectively, and \( H \) denotes the incident magnetic field. In the case of metallic nanoparticles, the magnetic dipole moment \( m = 0 \) and the polarizabilities are scalar. Thus, a chiral metallic nanoparticle can be modeled in the quasi-static dipole limit as \( p = \alpha_C E + i\alpha_M H \), where the factor \( i \) denotes a phase shift between electric and magnetoelastic dipole moments. The electric field radiated by a chiral metallic nanoparticle in the quasi-static electric dipole limit is described by Equation (4). Further, because \( m = 0 \) in metallic nanoparticles, the magnetic field upon interaction with a chiral metallic nanoparticle can be approximated as the incident magnetic field \( H_0 = H \).\[^{102,103}\]

In contrast to bi-anisotropic media, which exhibit different optical properties along perpendicular axes and magnetoelastic cross-coupling arises due to intrinsic material properties,\[^{101,104}\] metallic nanoparticles are composed of isotropic media and chiral optical effects arise from the interplay between the nanoparticle shape and the polarization state of the incident electromagnetic field.\[^{105}\] Based on the conservation law of optical chirality in lossy, dispersive media,\[^{106}\] chiroptical effects can be generated in a single nanoparticle when i) an achiral nanoparticle interacts with chiral (e.g., circularly polarized) light, ii) a chiral nanoparticle interacts with achiral (e.g., linearly polarized) light, or iii) a chiral nanoparticle interacts with chiral light.

In all cases, either the chirality of the incident electromagnetic field or the chiral geometry of the metallic nanoparticle imposes a chiral character on the oscillation of the free-electron cloud at the nanoparticle surface. This, in turn, induces a magnetoelastic dipole moment \( \alpha_C \), and the resulting phase shift
between electric and magnetic dipole moments results in the generation of chiral electromagnetic fields.\(^\text{[35]}\)

To realize the described chiral coupling in metallic nanoparticles, overlapping electric and magnetoelectric dipole moments must be excited, which can be achieved by means of intrinsic or extrinsic chirality. The perhaps most simple way to achieve this is by circumventing the need for 3D in the nanostructure geometry. Varying the angle of light incident on an achiral metasurface (see, e.g., Figure 1c) affects the generation of chiral optical fields from achiral elements by leveraging the effects of extrinsic chirality. Here, the sign of the chiroptical response depends purely on the tilting direction of the metasurface, with respect to the incident light. For metasurfaces, studies in k-space polarization have shown that the surface lattice resonance can also generate chiral electromagnetic fields, and spectrally tunable sharp circular dichroism.\(^\text{[61,107]}\) The effect of induced chirality can also play a non-negligible role in intrinsically chiral metamaterials, where each unit-cell-element exhibits a 3D chiral geometry, and thus should be kept in mind for the optical characterization, especially when dealing with small intrinsic CD signals.\(^\text{[102,108,109]}\)

Intrinsically chirality in complex resonators has been achieved in a variety of chiral geometries in both theory and experiment, which are discussed in detail in previous reviews.\(^\text{[33,34,47,110,111]}\) Examples include nanohelices,\(^\text{[112–114]}\) chiral nanoprisms,\(^\text{[115–117]}\) self-assembled chiral nanostructures,\(^\text{[118–123]}\) as well as more sophisticated geometries.\(^\text{[124,125]}\) Some complex-shaped chiral particles can simultaneously be sensitive to the orientation of linearly polarized light, arranging such resonators in a C3 or C4-symmetric arrangement has been demonstrated to circumvent such linear birefringence artefacts.\(^\text{[85,126]}\)

### 4. How to Characterize Chiral Metamaterials?

This chapter lays out a framework for the mathematical representation and quantitative measurement of the interaction between polarized light and matter, which is fundamental to the understanding of chiral light–matter interactions. We start by introducing the polarization ellipse and Poincaré sphere as means of visualizing the polarization state of light, after which we describe the Stokes parameters, measurables which quantify said polarization state, and the related measurement technique, Stokes polarimetry. We then discuss the matrix representation of polarizing media by Mueller and Jones matrix formalism, before classifying optically active—including chiral—media and discussing spectroscopic means for their characterization, including CD and ORD spectroscopy.

#### 4.1. Representations of Polarized Light—Polarization Ellipse and Poincaré Sphere

Polarized light can be mathematically described as the linear superposition of two electromagnetic plane waves as

\[
E(\mathbf{r}, t) = \Re\left[ (E_0 e^{i \delta_1} + E_0 e^{i \delta_2}) e^{i (\omega t - k \cdot r)} \right]
\]

where \(E_0\), \(E_1\), and \(E_2\) are the real electromagnetic field amplitudes along two orthogonal axes 1, 2, and \(\delta_1\) and \(\delta_2\) denote the respective phase with wavevector \(k\), angular frequency \(\omega\), spatial coordinate \(r\) and temporal coordinate \(t\). For simplified notation, we consider a z-propagating plane wave, polarized along the x- and y-axes, denoted as

\[
E(\mathbf{r}, t) = \Re\left[ (E_0 e^{i \delta_1} + E_0 e^{i \delta_2}) e^{i z - \omega t} \right]
\]

To visualize the polarization state of light, \(r\) and \(t\) can be eliminated from Equation (9), resulting in the definition of the orientation angle \(\psi\), describing the rotation of the ellipse axes, and ellipticity angle \(\chi\), describing the ellipse opening angle. Together, \(\psi\) and \(\chi\) describe the polarization ellipse as\(^\text{[127]}\)

\[
\tan 2\psi = \frac{2E_0 e^{i \delta_1} E_0 e^{i \delta_2}}{E_0 e^{i \delta_1} - E_0 e^{i \delta_2}} \cos \delta, \quad 0 \leq \psi \leq \pi
\]

\[
\sin 2\chi = \frac{2E_0 e^{i \delta_1} E_0 e^{i \delta_2}}{E_0 e^{i \delta_1} + E_0 e^{i \delta_2}} \sin \delta, \quad -\pi/4 < \chi < \pi/4
\]

The polarization ellipse is shown in Figure 3a. Note that for linearly polarized light, the polarization ellipse collapses to a line, while for circularly polarized light, where \(\chi = \pm 45^\circ\), the polarization ellipse is represented by a circle, and only an ellipse for the more general case of elliptically polarized light.

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**Figure 3.** Quantitative descriptions of the polarization state of light. a) Representation of the polarization ellipse with orientation angle \(\psi\) and ellipticity angle \(\chi\). b) Representation of the Poincaré sphere with azimuthal coordinate \(2\psi\) and polar coordinate \(2\chi\). c) Indication of polarization states on the surface of the Poincaré sphere, where RCP and LCP denote right- and left-handed circularly polarized light, \(X\) and \(Y\) denote horizontal and vertically polarized light while \(+45^\circ\) and \(-45^\circ\) denote linearly polarized light oriented at \(\pm 45^\circ\).
When visualizing the relationship between different polarization states, an alternative spherical representation, known as the Poincaré sphere, provides instructive information.127 As shown in Figure 3b, the Poincaré sphere of radius 1 is described by the azimuthal coordinate $2\varphi$ and polar coordinate $2\chi$. Each point on the surface of the Poincaré sphere represents a polarization state of light. Note that $\varphi$ and $\chi$ are identical to the orientation and ellipticity angles of the polarization ellipse. As shown in Figure 3c, linear polarization states are represented on the equator of the Poincaré sphere, while RCP and LCP are located at the north and south poles, and the remaining surface of the Poincaré sphere represents elliptical polarization states.127

4.2. Stokes Parameters—Measurables Describing the Polarization Properties of Light

After visualizing the instantaneous polarization state of light, we now introduce measurable quantities that characterize this polarization state. The Stokes polarization parameters quantify the polarization state of light by a series of intensity measurements.74,127 Using an $x$-$y$ linear polarization basis as shown in Figure 3, the Stokes parameters are written as

$$S_0 = E_{0x}^2 + E_{0y}^2$$

$$S_1 = E_{0x}^2 + E_{0y}^2$$

$$S_2 = 2E_{0x}E_{0y}\cos\delta$$

$$S_3 = 2E_{0x}E_{0y}\sin\delta$$

where $E_{0x}$ and $E_{0y}$ are the real electric field amplitudes along $x$ and $y$, and $\delta = \delta_x - \delta_y$ represents the phase difference between $x$ and $y$ components as introduced above. The Stokes parameters are commonly written in vector form, known as the Stokes vector

$$\begin{pmatrix}
S_0 \\
S_1 \\
S_2 \\
S_3
\end{pmatrix} = \begin{pmatrix}
E_{0x}^2 + E_{0y}^2 \\
E_{0x}^2 + E_{0y}^2 \\
2E_{0x}E_{0y}\cos\delta \\
2E_{0x}E_{0y}\sin\delta
\end{pmatrix}$$

The Stokes parameters can be interpreted physically as follows: the zeroth Stokes parameter $S_0$ represents the total light intensity; the first Stokes parameter, $S_1$, represents the differential intensity of $x$- and $y$-polarized light; the second Stokes parameter, $S_2$, describes the differential intensity of $+45^\circ$ and $-45^\circ$ linearly polarized light; while the third Stokes parameter $S_3$, quantifies the differential intensity of right and left circularly polarized light. The four Stokes parameters are related as $S_0^2 \geq S_1^2 + S_2^2 + S_3^2$, where equality is achieved for fully polarized light and the inequality is valid when unpolarized light is present.

We can now express the Stokes parameters in terms of measurable quantities. The measurement is achieved by so-called Stokes polarimetry, where each Stokes parameter arises from the relative intensity measurement of two defined polarization states.128,129 Figure 4 shows the measurement components constituting Stokes polarimetry.127,129 The optical source of interest is sequentially analyzed by a quarter-wave plate, providing a quarter-wavelength phase shift on incident light, with optical (fast) axis at $\varphi$, and a linear polarizer, with optical axis at $\theta$. The Stokes parameters are recorded by four sequential measurements with varying $\varphi$ and $\theta$.

$$S_0 = I(0',0') + I(90',90')$$

$$S_1 = I(0',0') - I(90',90')$$

$$S_2 = I(45',45') - I(135',135')$$

$$S_3 = I(0',45') - I(0',135')$$

In addition to the static-polarizer configuration129 shown in Figure 4, Stokes polarimetry can also be achieved with higher sensitivity for configurations utilizing a liquid crystal variable retarder,130 plasmonic nanomaterial-based polarimetry130,131 or photoelastic modulators.15 Stokes polarimetry has proven a valuable tool in characterizing the polarization response of 2D and 3D chiral plasmonic nanostructures.97,127

4.3. Mueller and Jones Matrix Representation or the Polarization Properties of Matter

While the Stokes parameters quantify the polarization state of light, we now consider the mathematical formalism by which the polarizing properties of a medium are described to fully quantify linear light–matter interactions. The mathematical representation of a polarizing medium can be achieved by the Mueller matrix,72,112,133 a $4 \times 4$ transformation matrix relating the input Stokes vector $S_{in}$ to the output Stokes vector $S_{out}$ as

$$S_{out} = M \cdot S_{in}$$

$$\begin{pmatrix}
S_{0t} \\
S_{1t} \\
S_{2t} \\
S_{3t}
\end{pmatrix} = \begin{pmatrix}
m_{11} & m_{12} & m_{13} & m_{14} \\
m_{21} & m_{22} & m_{23} & m_{24} \\
m_{31} & m_{32} & m_{33} & m_{34} \\
m_{41} & m_{42} & m_{43} & m_{44}
\end{pmatrix} \begin{pmatrix}
S_0 \\
S_1 \\
S_2 \\
S_3
\end{pmatrix}$$
To better illustrate the principle of Mueller matrices, we consider two illustrative examples of polarizing elements. A linear polarizer with a transmission axis oriented along \( x \) is described by the Mueller matrix

\[
M_{\text{LinPol}} = \begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{23}
\]

Indeed, for \( \gamma \)-polarized incident light, \( S_{\text{in}} = [1, -1, 0, 0] \), Equation (22) leads to \( S_{\text{out}} = M_{\text{LinPol}} S_{\text{in}} = 0 \), which is expected, as a linear polarizer oriented in \( x \) fully attenuates \( \gamma \)-polarized incident light. Similarly, the Mueller matrix of a quarter-wave plate, which imposes a phase retardation on light propagating along its optical (fast) axes, is described as

\[
M_{\text{QWP}} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \tag{24}
\]

When incident linearly polarized light oriented at 45° with \( S_{\text{in}} = [1,0,1,0] \) passes through a quarter-wave plate described by \( M_{\text{QWP}} \), we obtain \( S_{\text{out}} = M_{\text{QWP}} S_{\text{in}} = [1, 0, 0, 1] \), corresponding to the Stokes vector of right-handed circularly polarized light.

For samples with unknown polarizing properties, the Mueller matrix can be recorded by Mueller matrix polarimetry, shown schematically in Figure 5, where both backscattering and transmission modes of operation are illustrated. The Mueller matrix polarimeter is composed of a frequency-modulated polarization state generator (PSG), for the incident light and a polarization state analyzer (PSA) to modulate the light emerging from the sample. Both PSG and PSA constitute a photoelastic modulator (PEM) and a polarizer component. While frequency modulation of the polarized light is achieved by the PEM, the polarizing elements are sequentially rotated in orientation. The input light is varied between four polarization states and the resulting output Stokes vectors are analyzed to obtain the 16 elements of the Mueller Matrix.[132–135]

For complex media, the Mueller Matrix can be decomposed to account for the depolarization (\( M_D \)), retardance (\( M_R \)) and diam- attenuation (\( M_B \)) as[133,136]

\[
M = M_S \cdot M_R \cdot M_D \tag{25}
\]

where the linear superposition of each component contributes to the realistic representation of complex polarizing media.[136–138]

Mueller matrix polarimetry has been demonstrated to successfully characterize the anisotropic optical properties of metallic nanostructures.[139,140]

For systems containing fully polarized light, the matrix representation of a polarizing medium can be described by the \( 2 \times 2 \) Jones matrix[132]

\[
J = \begin{pmatrix} f_{xx} & f_{xy} \\ f_{yx} & f_{yy} \end{pmatrix} \tag{26}
\]

representing a linear relationship between the incident and outgoing electric field vector as \( E_{\text{out}} = J \cdot E_{\text{in}} \). Jones matrices have been demonstrated to describe 2D and 3D chiral plasmonic nanostructures where depolarization effects are negligible.[117,141]

### 4.4. Chiroptical Spectroscopy and the Characterization of Optically Active Matter

We now discuss spectroscopic methods, among which CD spectroscopy is the most common, to quantify chiral light–matter interactions. When polarized light interacts with optically active matter, its polarization state changes due to material anisotropy.[112] The phenomena of birefringence and dichroism are characteristic properties of optically active matter which can be leveraged for their spectroscopic characterization. When light traverses a birefringent medium, two orthogonal polarization states of light experience differential propagation speeds due to material anisotropy along the optical axes.[142] Circular birefringence denotes a differential propagation speed of RCP and LCP, while linear birefringence describes a differential propagation speed of the orthogonal components of linearly polarized light.[132] Dichroism occurs in optically active media that exhibit differential absorption of orthogonal polarization states of light. Circular dichroism (CD) describes the differential absorption of LCP and RCP light, while linear dichroism occurs for differential absorption of linearly polarized light along orthogonal axes.[143] Chiral matter is an example of optically active matter. We now discuss how the dichroism and birefringence of chiral matter enable its spectroscopic characterization.

#### 4.4.1. Circular Dichroism Spectroscopy

CD spectroscopy is a widely used technique to characterize chiral matter, based on the differential extinction of LCP and RCP.[143] When scattering is negligible, as is the case for sufficiently small molecules or nanoparticles, circular dichroism is obtained from the difference in the absorption as \( \Delta A = A_{\text{LCP}} - A_{\text{RCP}} \). In certain cases, it is instructive to study a normalized form of circular dichroism, known as the dissymmetry factor or g-factor defined as \( g = \frac{2(A_{\text{LCP}} - A_{\text{RCP}})}{A_{\text{LCP}} + A_{\text{RCP}}} \).

Circular dichroism spectroscopy is carried out using the experimental setup shown in Figure 6a. An unpolarized beam is passed through a linear polarizer. The resulting linearly polarized light is converted to LCP or RCP by a quarter-wave
4.4.2. Optical Rotatory Dispersion (ORD) and Chirality Flux Spectroscopy

ORD is a further spectroscopic technique which, based on circular birefringence, is Kramer-Kronig related to CD spectroscopy with the ability to characterize chiral matter.\cite{147,148} In ORD, a sample of interest is excited with linearly polarized light and the rotation plane of the outgoing, elliptically polarized beam is measured.

While CD spectroscopy characterizes the chiral properties of the material in question, chirality flux spectroscopy,\cite{35} shown in Figure 6c, characterizes the chirality of electromagnetic fields generated by chiral matter. Based on the conservation law of optical chirality,\cite{106} in this method a sample is excited with linearly polarized, achiral light, while light emerging from the sample is analyzed by a PEM, acting as a frequency-modulated quarter-wave plate, and a subsequent linear polarizer. In the far-field where detection takes place, the quantity recorded by this technique, known as the chirality flux efficiency,\cite{35} is directly proportional to the third Stokes parameter (Equation (15)), describing the degree of circular polarization. Inspired by optical antenna theory, it has been shown that the chirality flux efficiency measured by this method provides information on the chiral electromagnetic near-fields generated by plasmonic nanostructures.\cite{35}

5. Fabrication

In comparison to fabricating flat metasurfaces, engineering of chiral metamaterials must overcome additional hurdles as manufacturing 3D structures in the nanometer regime is extremely challenging.\cite{39,149,150} and minute structural deviation can rapidly alter the chiroptical properties.\cite{62,64} Serial lithographic methods meet these challenges by a sequential alternation of masks, which requires several, highly precise alignment steps in the course of the fabrication process.\cite{39,149,150} Here, we exemplarily introduce alternative fabrication methods that are able to circumvent these difficulties.

From a fabrication point of view, with no claim to completeness, we identify three general strategies to fabricate such chiral metamaterials (Figure 7): i) Advanced lithography, commonly using (sequential glancing angle) deposition steps with masks produced either via self-assembly or other large-area strategies, ii) deformation of substrates decorated with plasmonic nanoparticles, and iii) templated colloidal assembly. Note that the different processes can also be combined. Colloidal particles are very popular building blocks to create (chiral) plasmonic structures over large areas, but serve different purposes. Colloidal particles can be templates in the fabrication of the actual nanostructure, a process commonly referred to as colloidal lithography. For clarity, we further separate our first category (Section 6) into methods based on colloidal lithography (Section 6.1), from other lithography methods that produce large-area chiral metamaterials (Section 6.2). On the other hand, colloidal particles can also play a role in approach ii) and iii). In these cases, however, the particles serve as individual plasmonic resonators that are directly self-assembled into chiral structures, by manipulation of either the substrate (Section 7)
or the use of patterned substrates serving as a template (Section 8).

6. Advanced Lithography

6.1. Colloidal Lithography to Fabricate Chiral Plasmonic Nanostructures

Colloidal lithography, also known as nanosphere lithography,[151] typically requires a 2D colloidal monolayer as a mask, and nanostructures are generated from deposition steps through open spaces in these regular assemblies[152–154]—although there are exceptions that use individual colloidal particles as masks. The success of colloidal lithography is therefore intimately linked to the ability to create colloidal monolayers with high precision and order over large areas.[155–158] While typical colloidal self-assembly uses polymer or silica colloidal particles to produce monolayers with hexagonal symmetry have long been established, recent advances in colloidal self-assembly,[159] enable access to versatile lattice geometries,[160–165] large inter-particle spacing,[166,167] or enhanced ordering.[158,167,168] Such particle masks improve the optical activity, or significantly alter the optical properties due to near-field and lattice coupling in the fabricated nanostructure arrays.[77,80,90,91,169] Noteworthy, highly defined chiral nanostructures may also be produced by techniques as simple as drop-casting of a colloidal dispersion onto a substrate[151] or onto an air/water interface[170,171] to form a mask.

6.1.1. “Conventional” Colloidal Lithography

For this review solely, the term conventional colloidal lithography shall refer to all techniques where the colloidal monolayer mask is formed by (spherical) particles, and this very mask is directly used in the lithography steps that form the desired nanostructure arrays on the underlying substrate. In a final process step, this particle mask is removed to reveal the nanostructured substrate. The dimensions of the fabricated structures directly relate to the diameter of the colloidal particles used as masks, but have distinct boundaries: importantly, the particle diameter may significantly limit the maximum height of the resulting nanostructures on the substrate, since contact to the colloidal mask needs to be avoided. As evaporated metals require a minimum thickness of around 20 nm to form an homogeneous film, and extra etching steps may reduce the distance of the colloidal mask to the substrate,[171] the diameter of the colloidal particles typically needs to be larger than around 60 nm.[172,173] In the following, we will first describe how conventional colloidal lithography processes can be used to produce chiral planar—and subsequently 3D nanostructures with increasing complexity.

2D Objects: Extrinsic chirality of planar, achiral resonators and pseudo chiral nanostructures are two simple, yet elegant ways to yield chiroptical responses while avoiding the hurdles of manufacturing truly 3D nanostructures.

Figure 7. Simplified overview of the different fabrication approaches for large-area chiral plasmonic metamaterials. Here, we differentiate between three main approaches. i) Advanced lithographic approaches mainly employ evaporation through shadow masks such as nanoapertures; glancing angle deposition, meaning directed materials evaporation from an oblique direction (elevation angle $\alpha$) and different in-plane directions (azimuthal angle $\gamma$); and dry etching (such as physical argon etching). Colloidal lithography methods, where self-assembled colloidal particles serve as masks in the fabrication process, typically fall into this category. ii) Deformation of substrates, form the second approach, where plasmonic resonators are arranged into a chiral assembly via defined manipulations of the underlying substrate. iii) Templated assemblies form the third approach. In this case, an external chemical or physical template provides a basis to direct individual nanoparticles into desired structural motifs on a substrate.
nanostructures underneath.\cite{172,173} Importantly, the masking particles must not touch each other, which would otherwise result in (partially) truncated crescent structures. This separation can be achieved by either using randomly dispersed particles,\cite{172,173} etching of close-packed monolayers,\cite{174,185} or by hard-core/soft-shell particle masks.\cite{98,166}

**Extrinsic Chirality:** Extrinsic chirality has been induced in such planar achiral crescent arrays with mirror symmetry by tilting their substrate against the incident illumination.\cite{186} For randomly arranged crescents, all three resonances become optically active, with different preferences for the handedness of circularly polarized light. The resonance excitation wavelengths are independent of the tilting angle. However, the circular dichroism is increasing with stronger rotation, while the overall sign of the dichroism is solely changed by the rotation direction.\cite{186}

Arranging plasmonic resonators into well-defined lattices allows coupling of localized surface plasmons to grazing diffractions, leading to surface lattice resonances.\cite{90-93} In the case of split-ring resonators, this leads to resonances with a narrow line width.\cite{61,107,187} Tilting such substrates also results in strong extrinsic chirality.\cite{61,107,187} However, due to the nature of the Bragg modes, the surface lattice resonances will shift depending on the angle of incidence, resulting in spectrally tunable circular dichroism.\cite{61} Such extrinsic chiral surface lattice resonances with similar tunable characteristics have been observed in arrays of planar crescents (Figure 8a).\cite{188} Extrinsic chirality can also be found in other structural motifs produced by colloidal lithography, such as non-concentric rings,\cite{189} nano-hole arrays,\cite{190} or shell-like structures.\cite{191}

**Planar Chiral Objects:** Pseudo chiral objects are planar yet exhibit handedness-dependent responses to circularly polarized light at normal incidence.\cite{52,55-57} Tilting these substrates also results in strong extrinsic chirality.\cite{61,107,187} These structures obtain their chiral nature by substrate-induced symmetry breaking or fabrication imperfections,\cite{33,37,52,53,58} without requiring a 3D character, which simplifies the fabrication processes.

One way to realize such pseudo chiral nanostructures is to modify the crescent fabrication process. Evaporating a

---

**Figure 8.** Conventional colloidal lithography can be used to fabricate 2D nanostructures with (pseudo) chiral response. a) The simplest, yet flexible way to generate chiroptical properties uses extrinsic chirality by tilting the substrate with respect to the illumination direction. i) An achiral array of crescent-shaped nanostructures is tilted around the short-axis, forming a chiral entity with the incident light. ii/iii) At normal incidence, no circular dichroism is observed, which changes at oblique illumination. Spectral shifts with rotation angle result from surface lattice resonances caused by the arraying of the crescents in a defined lattice. Reproduced under the terms of Creative Commons (CC BY) license.\cite{188} Copyright 2019, The Authors, published by Springer Nature. b) Planar chiral structures break the symmetry via the underlying substrate. i) Planar crescent chiroptics are fabricated by a two-step evaporation process. First, silica forms an ellipsoidal well. Gold is subsequently deposited into this well, while the surrounding metal is stripped off the substrate. ii) The deposition angle between the two steps define the symmetry of the resulting comma-shaped crescent. iii) These planar crescent chiroptics show a strong CD response in the near IR. They also show the flip in signs upon inversion of the illumination direction, which typically occurs for planar chiral structures. Reproduced under the terms of OSA Open Access Publishing Agreement. Copyright 2018, Optical Society of America. c) More complex nanostructure arrays result from the combination of evaporation shadows casted by multiple neighboring particles of the colloidal monolayer mask. Sequential deposition steps from multiple directions open an entire zoo of new structures. i) Attention needs to be paid to the orientation of the crystal domains of the monolayer mask, as the shadow engineering depends on the lattice orientation of each grain. ii) Complex planar structure arrays with structural chirality can arise from this technique. Reproduced under the terms of the ACS Editor’s Choice. Copyright 2014, American Chemical Society.
dielectric film prior to metal deposition from another azimuth angle (Figure 7a) forms asymmetric, comma-shaped crescents (Figure 8b, i, ii) without the need for physical etching.\[192\] Similarly to the aforementioned extrinsic chiral crescents, the three main resonances show circular dichroism, albeit at normal illumination. Due to the planar chiral character of these structures, the chiroptical response flips signs upon change of the illumination direction (Figure 8b, iii), providing flexibility within a single substrate. Importantly, these crescents exhibit only short-range order. Their structure and optical properties are therefore independent of the lattice orientation and order of the colloidal monolayer used as mask.\[192\] Near-field lithography, which uses the spherical particles as nanoscale lenses to pattern underlying UV-resists,\[193,194\] can produce similar planar chiral structures.\[195\] Planar chiral plasmonic oligomers, consisting of a defined arrangement of nanoparticles with near-field coupling can exhibit pseudo chiral behavior.\[85\] Such structures can form by directed evaporation of metals through nanoscale hole masks formed from the interstitial sites in a close-packed colloidal monolayer, which results in individual triangular nanoparticles.\[196\] Evaporation from different angles thus affords the arrangement of these nanoparticles in a spiral-like oligomer with chiroptical response.\[197\]

**Grain Orientation Dependent Pseudo Chiral Objects:** Planar objects with perhaps ultimate complexity are formed by colloidal lithography with multiple, consecutive evaporation steps, termed shadow sphere lithography (Figure 8c, i).\[153\] These evaporation steps combine several directions, varying both, azimuthal and elevation angles and therefore provide complex patterns by superposition. In addition, different materials evaporated at the different directions provide chemically heterogeneous nanostructures. In contrast to the previous examples, the resulting nanostructures produced in this process critically depend on the grain orientation of the colloidal monolayer mask with respect to evaporation directions. In other words, shadow sphere lithography accesses a completely new set of geometries by exploiting both, the grain orientation and the interparticle spacing within the lattice, which, for polymer particles, can be controlled by plasma etching.\[153,171\] As a consequence, assembled colloidal monolayers, which are typically polycrystalline, produce a manifold of distinct nanostructure arrays within one single substrate. This is in stark contrast to nanostructures shown above that result from shadowing of a single sphere, and not multiple ones. If a monocristalline colloidal monolayer mask is achieved, an initial registration between the evaporation angle and the lattice grain orientation would be required for a defined structure fabrication process. The resulting structures (Figure 8c, ii) can be planar 2D or 3D, show sharp and highly complex features, yet their chiroptical properties remain unexplored.\[153\]

**3D Objects:** Next, we discuss structures that are intrinsically chiral by themselves. This means that despite being manufactured onto substrates, they show a truly 3D nature, which will reflect in their chiroptical effects.

**Chirality in Nanohole Arrays:** Nanosized apertures and their arrays played a major role in the development of the field of plasmonics. Extraordinary transmission (EOT), meaning more light is transmitted as expected by classical geometrical optics, results from plasmonic resonances around nanoholes in metallic thin films.\[92,198,199\] Such structural motifs allow a simple tailoring of the resonance wavelength via the size and periodicity of the array. Chirality in nanohole arrays can be implemented by manipulating the shape of the holes themselves. Chiral holes with a screw-like shape were previously fabricated by ion milling into thin silver films.\[200,201\] This concept can be transferred to colloidal lithography by evaporating metallic films on nonclose packed arrays of particles from several azimuthal directions (Figure 9a).\[202\] Each deposition step thus forms an ellipsoidal hole. Consecutive evaporation from different azimuthal directions lead to a partial overlap of these individual nanohole layers. These overlaps amount to a continuous solid film with arrays of screw-like holes. By choosing either clockwise or counter clockwise rotation between the consecutive deposition steps, the handedness of the chiral hole arrays is determined. The resulting spectra (Figure 9a, iii) show optical activity for multiple resonances, including LSPR, SPP and near the point of EOT.\[202\] It should be noted that even in single layers of ellipsoidal nanoholes in an hexagonal array chiral effects may occur for individual grains with certain hole orientations.\[203\]

**Moiré Patterns:** Moiré patterns provide an alternative strategy to achieve 3D chiral objects.\[204,205\] Such patterns occur when two lattices are stacked above each other with a twist in between both lattice orientations.\[206\] Chiral metamaterials can thus be achieved by stacking two achiral metal nanohole arrays above each other.\[207,208\] Introducing a twist between both arrays while considering their individual mirror symmetries, leads to the formation of chiral moiré pattern. While the rotation direction determines the handedness, the actual twisting angle determines the spectral features (Figure 9b).\[207\] Similar to shadow sphere lithography, such chiral moiré patterns are sensitive to the lattice orientation of the colloidal mask, which makes the alignment of individual grains very difficult. However, at the same time, structural variety is encoded within a single substrate. While this complicates accurate characterization as the optical properties need to be measured within each individual grains, the absence of far-field CD signals on the entire substrate might be an advantage for enhancing of molecular signals.\[207\] On the other side, other large-area methods such as nanoimprint lithography can also be used to generate similar structures over entire substrates.\[204,205\] Using a dielectric spacer layer that is responsive to external triggers between the metal nanohole arrays adds another degree of freedom and makes the metamaterial dynamically controllable.\[208\] The interconnected nature of the metal film in nanohole arrays also provides mechanic stability, which allows the transfer of Moiré pattern on arbitrarily shaped surfaces and flexible substrates.\[209\] Moiré metamaterials and a range of additional fabrication methods can be found in recent reviews on the subject.\[204,205\]

**Individual 3D Chiral Nanostructures:** Individual rather than interconnected 3D nanostructures can also be produced by colloidal lithography. Crescent-shaped structures again serve
as instructive examples on how a fabrication process needs to be altered to produce a chiral nanostructure. Inspired by on-edge lithography,\cite{210,211} the mirror symmetry of an individual crescent is broken by introducing a dielectric step onto which the metallic crescent is evaporated under a different azimuthal angle (Figure 9c, i).\cite{214} The direction of the twisting between the two deposition steps determines the handedness of the chiral crescents. The chiral origin and sign of CD of the two main dipolar resonances can be understood by a multipole decomposition.\cite{214,223,254} The strength of the resulting circular dichroism can be controlled via the twisting angle, peaking at ±90°, or the thickness of the underlying dielectric step.\cite{214}

**Chiral Surface Lattice Resonances:** Collective excitation of arrays of plasmonic resonators leads to narrow surface lattice resonances with longer life-times and thus overcome problems typically associated with plasmonic systems.\cite{90–95} While optical activity of extrinsic chiral systems has been shown for surface lattice resonances for a while,\cite{61} it has only recently been demonstrated and described for intrinsic chiral systems, leading to CD signals with narrow bandwidth.\cite{98,212,213} Arranging resonators in a C4-symmetry does not hinder the excitation of the SLR and can suppress contributions of linear birefringence as shown in simulation for stereo split-ring resonators and for planar-chiral systems.\cite{212,213} Arranging the 3D intrinsic chiral crescents with broken mirror-symmetry into a hexagonal lattice provided by nonclose packed colloidal particles\cite{166} allows the coupling the dipolar plasmon resonances to lattice modes, and thus to form chiral surface lattice resonances (Figure 9c).\cite{98,214} Although demonstrated in a proof-of-principle experiment of large-areas,\cite{98} their quality factors is not yet comparable to state-of-the-art fabrication methods\cite{95} or theoretical findings.

6.1.2. Hole-Mask Lithography

We refer to hole-mask lithography as techniques based on material deposition through a hole/aperture, to contrast them to conventional colloidal lithography, which uses colloidal particles directly as masks. As illustrated in Figure 10a, i, those apertures are formed by depositing non-close packed spheres on a polymeric spacing layer that is on top of the target substrate.
Directed evaporation of gold normal to the surface forms a nanohole array on the polymeric spacing layer. Plasma etching subsequently degrades the organic polymer material selectively in the areas unprotected by the gold film, creating nanoscale apertures. These apertures finally serve as evaporation masks to form 2D and 3D structures on the now accessible underlying target substrate (Figure 10a, i) [196,215–218]. In a final step, the hole-mask along with the polymer spacer layer can be removed by organic solvents [196]. These 2D masking patterns may also be made from top-down lithography techniques, and hence do not depend on the spherical character of the particles. Compared to conventional colloidal lithography, the height of the produced nanostructures is only limited by the polymeric spacer layer, and not by the diameter of the colloidal particles. Note that in a similar fabrication scheme, the interstitial sites of a colloidal monolayer can be directly used as aperture as well, within the limitation of the constraints mentioned above [219].

Deposition through a hole-mask normal to the surface results in the formation of a planar disk for low height-to-width ratios [196]. Complex structures, including chiral ones, arise from controlled variations in the evaporation direction, the deposition thickness, a continuous change of the evaporation direction, or...
repetitive depositions from different directions.\textsuperscript{[202,205–208]} In this chapter we discuss the different approaches with increasing complexity. Structures presented in the following were exclusively prepared by spin coating or drop-casting colloidal dispersions with rapid drying, leading to sparsely and randomly distributed colloidal particles on the substrate. Hence, the resulting chiral nanostructures only exhibit short-range order. Lattice effects stemming from the arrangement of the chiral structures in period arrays have not been reported at the time of this review. Using more sophisticated colloidal masks to create the nanohole apertures may therefore be a strategy to modify further and tailor the chiroptical responses of such nanostructures.

Extrinsic Chirality: Continuous evaporation of metals onto a hole-mask substrate using different angles along one geodesic produces anisotropic disc-shaped nanostructures (Figure 10a, ii top left).\textsuperscript{[196]} Such nanostructures show a strong extrinsic chiral response if the incident angle of the illuminating light (or, the tilting angle of the substrate) is above the critical angle of internal reflection due to evanescent fields.\textsuperscript{[200]} For a 45° tilting, the difference in reflection for the two circular polarizations reaches up to 90% (Figure 10a, iii). The handedness itself is controlled by the sample angle (in-plane rotation).\textsuperscript{[209]}

3D Chiral Nanostructures: Hole-mask lithography allows the fabrication of curved nanostructures by tilting the substrate during the evaporation process while constantly rotating the substrate in the azimuthal plane. This protocol allows producing split-ring resonators similar to the crescents shown above.\textsuperscript{[216,219]} Sequential evaporation from different directions can also be used to produce symmetric planar double crescent structures,\textsuperscript{[220]} which exhibit Fano resonances.\textsuperscript{[225]} Controlled variation of the azimuthal rotation speed during the metal deposition process varies the thickness along the split-ring resonators, with thicker areas resulting from slower rotation (Figure 10b, i). This variation in thickness produces chiral split-ring resonators with a true 3D character.\textsuperscript{[224]} The resulting structures exhibit three resonances with strong differential transmission (Figure 10b, ii).\textsuperscript{[222]} Such structures can also be placed in Fabry–Pérot nanocavities for strong coupling, resulting in a mode-splitting of the chiral resonances.\textsuperscript{[223]} Elliptical birefringence is typically associated with such 3D split-ring resonators due to the C1 symmetry.\textsuperscript{[85,224,225]} Repetitive evaporation from multiple angles can overcome this problem by keeping 120° between the orientations of the individual structures, leading to a C3-symmetry with a true-chiral response independent of the propagation direction.\textsuperscript{[231]} To our knowledge, there have been no similar successful attempts to produce such symmetries using conventional colloidal lithography processes. The produced chiral nanostructures can be lifted off the substrate and dispersed in hydrogel films.\textsuperscript{[216]} The resulting random orientation of the plasmonic nanostructures affords densely packed films with isotropic optical responses.\textsuperscript{[227]}

3D Chiral Oligomers: Defined arrangements of several individual nanoparticles are often termed plasmonic oligomers.\textsuperscript{[75,86,87]} The plasmonic resonances of the individual nanoparticles are coupled to produce collective modes of the entire oligomer.\textsuperscript{[75,86,87]} Such oligomers can exhibit chirality if the individual nanoparticles are not equal and the structure exhibits a 3D character—much like chiral molecules are formed from the 3D arrangement of different atoms.\textsuperscript{[62,85,228]} Hole-mask lithography is well suited to produce such oligomers, which are formed by defined assemblies of small nanopillars (Figure 10c). Configurational symmetry arises from pillars of equal diameter and material, but varying heights (Figure 10c, i).\textsuperscript{[229]} The near-field coupling and small gaps lead to strong chiral hot spots between the individual nanopillars.\textsuperscript{[229]} Such oligomers can additionally couple to underlying stacks of gold and cobalt layers, leading to magneto-optical and chiro-optical materials with tunable chirality.\textsuperscript{[230]}

Configurational chirality results from oligomers with pillars of different materials.\textsuperscript{[229,231]} Such heterogeneous planar structures show strong substrate-induced chirality.\textsuperscript{[232,233]} The addition of a different material can also provide additional functionality to the oligomer and has been used, for example, for an active control of the circular dichroism. A trimer of equally shaped nanopillars, where one consists of ferromagnetic nickel allows controlling optical transmission via an applied magnetic field (Figure 10c, ii).\textsuperscript{[234]} Other materials, such as palladium and magnesium are also interesting for active applications, like chiral plasmonic hydrogen sensors.\textsuperscript{[231,235,236]}

6.1.3. On-Particle Lithography

In contrast to all previous methods, on-particle lithography does not only use the colloidal monolayer as a mask or template, but integrates the particles as a part of the final nanostructure. The character of the nanostructures results from decorating plasmonic patches onto the inherently 3D colloidal particles. On-particle lithography takes advantage of defined angles and shadowing effects to place these patches at defined locations of the spherical colloidal particles and with controlled mutual orientation. It therefore requires a defined arrangement of the colloidal particles, typically as hexagonally close packed monolayers.\textsuperscript{[237]} The key advantage of this approach toward chiral nanostructures is its simplicity. Aside from the colloidal monolayer itself, the only instrumental requirement is a device for the directed deposition of the plasmonic metals.

The approach follows the common scheme of glancing angle depositions.\textsuperscript{[238,239]} Directed metal evaporation from two different angles will form two patches on the surface of the spherical colloidal particle with defined and controllable mutual orientations (Figure 11a, i). These two patches, which often asymmetrically overlap, break the symmetry and create the chiral character. Enantiomeric structures can be formed by changing the orientation of the two patches, i.e., by clockwise or counterclockwise azimuthal rotation in between the evaporation steps (Figure 11a, ii).\textsuperscript{[240]} The shadowing effect of neighboring colloidal particles during the evaporation process is important for the chiral character, as the sixfold symmetry of the hexagonal pattern would otherwise result in racemic structures.\textsuperscript{[243]} The choice of azimuthal and elevation angle give access to a wide variety of patch shapes that will determine the optical properties.\textsuperscript{[240,244]} The g-factor (or CD) of these two-patch gold structures demonstrates the chiral character, which is obtained by this comparably simple fabrication process.
(Figure 11a, ii). Noteworthily, the CD signal can be enhanced by employing a cavity, which can be achieved by depositing gold and silica films below the colloidal monolayer.[243] Such structures display strong chiral signals at visible wavelengths, which sets them apart from several of the methods introduced above, which often operate in the near IR region.[240,241,243] The
optical performance of patchy particle ensembles can also be improved by postproduction with thermal annealing, leading to much higher quality factors ($\Delta \alpha / \lambda$) of the resonances.$^{[244]}$

Without careful preparation protocols, the assemblies of a colloidal monolayer may result in small grains and low order.$^{[175–178]}$ As a consequence, the glancing angle deposition results in the simultaneous formation (Figure 11b, i) of multiple chiral morphologies within a single substrate, as the shadowing effect changes with crystal orientation.$^{[241,245]}$ This phenomenon is similar to the shadow-sphere lithography approach described above (Figure 8c). The macroscopic CD signal from such chiral plasmonic substrate is the superposition of individual contributions of all distinct structures present in each grain and therefore difficult to interpret.$^{[245]}$ The individual grains show much more detailed spectra originating from uniform and defined nanostructures,$^{[245]}$ as even minute differences in seemingly similar chiral structures can cause strong differences in CD signals (Figure 11b, ii, note that the spectra are not correlated to the above SEM images).$^{[62]}$

Using defined arrangements of separated plasmonic patches rather than conductively connected patches adds another degree of freedom in on-colloid lithography. In addition, the disconnection of the individual patches makes the process less dependent on the polycrystalline nature and the orientation of the grains.$^{[237,246,247]}$ Chiral plasmonic structures can be created, for example, by arranging the individual patches in a helical fashion by multiple metal depositions with $120^\circ$ azimuthal sample rotation between each deposition (Figure 11c, i).$^{[248]}$ The individual gold or silver patches can be separated by reactive evaporation of silica or MgF$_2$ to ensure that they are disconnected from each other.$^{[246,248]}$ At the same time, it is also possible to omit the passivation step and to produce connected helical structures with a chiral character.$^{[248]}$ As mentioned above, such chiral nanostructures can exhibit resonances in the visible range. The spectral positions of these resonances can be easily tailored by patch thicknesses and the material choice, but, especially, by the diameter of the colloidal particle that forms the basis of the nanostructure. The resulting plasmonic resonances of the multipatch structures can be easily shifted from the visible to the near infrared by increasing the particle size (Figure 11c, ii).$^{[237,246,248]}$

**Altered On-Particle Lithography:** The geometry of the colloidal particles themselves can also be altered to control the shape of the resulting nanostructures.$^{[247,249,250]}$ A more conical shape of the base used for deposition can be, for example, achieved by forming a frustum made of silicon on top of the spherical colloidal particles by continuous evaporation. The metal patches forming the chiral plasmonic properties, are then deposited on top of the conical surface features, producing structures known as Swiss rolls.$^{[240]}$ Figure 11d, i shows another example of a process leading to nanocone structures which are subsequently modified by on-particle lithography.$^{[249,250]}$ The colloidal monolayer is deposited on top of a photoresist layer, which can be shaped into nanocone and truncated nanocone arrays by controlled reactive ion etching using the colloidal particles as a shadow mask.$^{[249,250]}$ Glancing angle metal deposition on top of these structures then creates the chiral nanostructure array, much like in the classical on-particle lithography approach. The polymeric nature of the photoresist layer allows transferring of the chiral nanostructured films to other substrates such as flexible PDMS or hydrogels (Figure 11d, ii). Transfer of these structures onto hydrogels and immersion in water does not alter the optical properties over time (Figure 11d, iii). The dissolution of the photoresist gives direct access to the interior of the nanopores and can potentially allow subsequent functionalization$^{[231]}$ of the nanopore regions with high field enhancements (Figure 11d, iv)$^{[249,256]}$

6.1.4. Helical Evaporated Nanostructures

Besides our macroscopic hands, helices are probably the most obvious handed object and there have been tremendous efforts to fabricate helically shaped nanoparticles and understand their (chiral) optical properties.$^{[64,222,252–264]}$ However, it seems that chiral lattice resonances$^{[61,98,212,213]}$ have not been reported for such helical arrays, although the combination of controlled fabrication and tunable CD signals of such helix arrays may provide flexibility to observe such collective modes. In the following, we introduce approaches to create such arrays of helical nanostructures over large areas and showcase the flexible design with respect to shape and material.

The evaporation of material on a continuously rotating substrate to gain optically active materials dates back to 1959.$^{[262–264]}$ Defined structures result from a shadowing effect caused by defined, yet minute surface unevenness onto which metal is evaporated at a very steep angle.$^{[238,239]}$ The helical shape finally results from a continuous rotation of the substrate. Different fabrication strategies to combine these steps have emerged, which we will briefly introduce. i) When a dielectric is evaporated onto substrate at a very steep angle, adatoms condense on the surface, and geometrical shadowing of those “particles” prevents further film formation.$^{[238,239]}$ Continuous evaporation at high angles with a controlled rotation of the substrate growths those initial adatoms into helices.$^{[238,239]}$ Consecutive coating of these dielectric helices with a metal forms core–shell like plasmonic helices.$^{[239]}$ ii) Following the more spontaneous formation of surface roughness, constant co-deposition of silver and titanium can form randomly distributed helical plasmonic resonators in a single step.$^{[235]}$ iii) Finally, a more ordered fabrication method takes advantage of colloidal templating to create a regular topography as the starting point for the helical deposition. Micelle lithography is used to create arrays of nanoscale gold nanoparticles on a substrate (Figure 12a, i)$^{,265,266}$ Gold nanoparticle- or precursor-loaded micelles are self-assembled into a monolayer with high order onto a desired target substrate (Figure 12a, ii)$^{,113,265,266}$ Subsequent removal of the organic material by oxygen plasma forms the nanoparticle array.$^{265,266}$

Consecutive metal evaporation at very low temperatures and steep angles will deposit material on top of a gold nanoparticle while shadowing other parts of the surface. The helical shape is then induced by substrate rotation with the rotation speed controlling the pitch of the helix (Figure 12b).$^{113,260,267}$ The process provides ample degrees of freedom to tailor material composition (Figure 12b, iii–v), and shape and constitution of the formed helical structures (Figure 12c, i)$^{,113,215,260,267}$ For instance, palladium/silver alloys (Figure 12b, iii,iv) can be hydrogenated, which strongly alters the circular dichroism, to produce chiral hydrogen sensors.$^{[235]}$ Similarly, this change in properties provides active control over the plasmonic chirality.$^{[43]}$
As mentioned above, numerous studies investigating chiral helices have been reported, ranging from single or arrays of helices with a 180° rotation, to helices with multiple rotations showing higher order chiral modes, to even intertwined helices. Most relevant in the context of large-area substrates are helices with only half turns. Their optical properties can be interpreted by the excitation of fundamental resonances of first and higher orders (Figure 12c, iii). Sufficient distance between substrate and metal source needs to be provided to reach a collimated deposition process. Different materials can be combined either simultaneously or in sequence. Arrays of nano-scale helical structures result from the continuous rotation-glancing angle deposition process. This means electric dipoles form along the screw direction of the helix. The sign of the CD spectra can either be rationalized by a hybridization scheme, were the rotation distribution of the electric field in space of LCP or RCP favors the arrangement of the dipoles along the structure, or by a multipole decomposition of electric and magnetic moments.

6.2. Other Advanced Lithographic Methods

The methods hereinafter are not, or not entirely based on particle templates; yet, if particles appear, they act as resonating building blocks rather than simple templates, which separates the approaches from the methods discussed above. Some of the approaches have the potential of large-area applications, although they may have been demonstrated on a small scale.

6.2.1. Prestructuring the Substrate

The difficulty to directly manufacture 3D metallic nanostructures can be partially mitigated by creating a prepattern onto a substrate, which is subsequently decorated with plasmonic structures to create chirality. On-particle lithography, discussed above, takes advantage of this principle by using the colloidal particles themselves as 3D structures to be decorated. In the following, we outline other (potential) approaches to create large-area chiral nanostructures via prestructuring of the substrate. In on-edge lithography (Figure 13a), a 1D grating on a substrate serves as the topography.

Figure 12. Fabrication of the nanoscale helices as the prototypical handed object. For large area processes, a controlled surface topography needs to be introduced to the substrate, which templates the helical structures by glancing angle deposition. a) Micelle lithography can form very small gold nanoparticles as suitable surface topography. i) Micelles can either be loaded with gold particles directly, or with precursor molecules that decompose into nanoparticles. Top and bottom part) Reproduced with permission. Copyright 2000, American Chemical Society. Middle part) Reproduced with permission under the STM Permission Guidelines (PG) Signatory. Copyright 1990, IOP Publishing. ii) These micelles form ordered monolayers on the target substrate, e.g., by convective deposition. Removal of the organic material by oxygen plasma creates the nanoparticle array. Reproduced with permission under the STM Permission Guidelines (PG) Signatory. Copyright 2013, Nature Publishing Group. b) Glancing angle deposition deposit material with a defined direction onto the nanoparticle array. i) A very steep deposition angle creates a shadowing effect. Reproduced with permission under the STM Permission Guidelines (PG) Signatory. Copyright 2013, Nature Publishing Group. ii) The helical shape is induced by the controlled rotation of the substrate during the deposition. Reproduced with permission. Copyright 2014, The Royal Society of Chemistry. iii) Sufficient distance between substrate and metal source needs to be provided to reach a collimated deposition process. Different materials can be combined either simultaneously or in sequence. iv) Arrays of nano-scale helical structures result from the continuous rotation-glancing angle deposition process. Reproduced with permission. Copyright 2017, Wiley-VCH. v) Multiple revolutions and high pitch lengths are possible. Reproduced with permission. Copyright 2014, The Royal Society of Chemistry. c) i) Examples of the degrees of freedom for the two evaporation steps after composition and shape. Reproduced with permission under the STM Permission Guidelines (PG) Signatory. Copyright 2013, Nature Publishing Group. ii, iii) The high aspect ratio and helical shape leads to strong chiroptical properties. Multiple dipolar and higher order modes are excited inside the helices. An overlap of magnetic and electric multipoles results from their 3D nature. Reproduced with permission. Copyright 2014, Wiley-VCH.
Figure 13. Other advanced lithographic methods for large-area fabrication of chiral plasmonic nanostructures. a) On-edge-lithography combines substrate prepatternning and planar lithography i) An L-shaped nanostructure is deposited through a hole-mask onto a 1D grating, resulting in one part being on top of the grating and the perpendicular part appearing at lower positions. ii) The cleavage of the L into two perpendicular slaps resembles a Born–Kuhn type resonator with a coupled mode splitting. Reproduced with permission.[210] Copyright 2012, Wiley-VCH. b) Stencil lithography produces 3D structures by considering the time-depended clogging of a planar hole mask with complex shape. i) Continuous deposition through the mask will clog finer features first, leading to a longer deposition and thus increased height on mask areas with wider features. ii) Helical-like spirals as an example
(on top and in between the creating), thus forming a 3D structure (Figure 13a). In this specific case, the L-shaped resonator breaks into two slabs, one which sits on the upper part of the grating, and one, perpendicular to the first one, on the substrate below the grating. This arrangement forms a Born–Kuhn type resonator[51] which produces strong circular dichroism.[209] The cleavage of the structure, i.e., the disruption of the L into two slabs, gives access to two hybrid plasmonic modes and thus alters the optical properties.[208] It depends on the individual layer thickness (gold film thickness vs grating edge height) and can be employed to engineer the optical properties.[208,214] Despite evoking a chiral response from a planar achiral mask, the method also allows elevating already chiral 2D planar structures, such as starfish-shaped nanoobjects, leading to orders-of-magnitude stronger chiral signals compared to their flat counterparts.[211]

6.2.2. Advanced Stencil Lithography

Stencil Lithography employ nanoscale apertures as evaporation mask, much like hole-mask colloidal lithography introduced above.[196,268] During evaporation, the metal flux continuously clogs these nano apertures. Especially with small features, this clogging process changes the shape of the mask, and thus, the structure formed on the substrate (Figure 13b, i).[269] 2D stencils can be engineered to form chiral 3D structures as demonstrated by the spiral split-ring resonators shown in Figure 13b, ii.[269] The trick in the process is that the smaller parts of the opening clog first, and thus form structures with lower heights, while the larger part of the structure can grow much longer because the mask remains open for longer times.[269] Structures have been prepared by both gold and aluminum, demonstrating material versatility. The clogging process is material specific, and thus the height aspect ratio varies between materials.[269]

6.2.3. Imprint Lithography with Glancing Angle Deposition

The next set of techniques described in this subchapter combine substrate pre patterning approaches with glancing angle deposition from different azimuthal directions.

Multiple twisted stacks of slab arrays demonstrated strong broadband circular dichroism.[225] Ideal arrays are made from individual slabs with perfect registration. However, it has been shown that perfect alignment of the individual slabs in-between individual layers is not necessarily required due to the pure lattice effects leading to the chiral response.[225] Therefore, simpler fabrication techniques can be employed to create such stacks. Stacks of twisted metallic gratings, known as chiral nano woodpiles, are one such example.[220] The fabrication process first forms a dielectric 1D grating by embossing an ethylene(tetrafluoroethylene) (ETFE) mold into a softened sacrificial polymer layer.[219] In a second step, directed metal deposition from an angling glancing angle forms the metal stripes.[222] These metallic gratings can be embedded into another polymer layer, allowing the stacking of multiple layers with controlled angles in between the individual slabs.[222] The resulting structure combines plasmonic and photonic features, leading to strong handedness-dependent reflection around the combined photonic and plasmonic bands.[222] Making such structures from aluminum could also shift the response toward the visible range, but has yet only been demonstrated by focused ion beam milling.[221]

Another way toward chiral nanostructures using nanoimprint lithography is based on nanopore arrays (Figure 13c, i). Hard polydimethylsiloxane (hPDMS) nanopillar arrays are embossed into a photoresist layer, producing nanopore arrays.[274,275] Three consecutive glancing angle metal depositions with 45° twisting in-between each deposition forms films with chiral nano pore openings. These substrate exhibit g-factors of 0.21 and a differential transmission of around 4% (Figure 13c, ii). Alternatively, nanopores can also be created over large areas via anodization of aluminum, followed by a similar evaporation procedure.[276] These structures were then successfully transferred to silica substrates, and used in the detection of chiral molecules.[272] In general, nanopore arrays are interesting structures in the context of biomedical and plasmonic sensing, as they have a large surface area and specific region of high sensitivity can be site-specifically functionalized to selectively bind desired molecules of interest.[231,277,278] Nanoimprint lithography can also be used to produce L-shaped Born–Kuhn type resonators[51] in the cm² range.[279] Such structures show typical mode splitting, with two resonances showing different preferences for the handedness of circularly polarized light.[279]

Alternatively, it is also possible to use the indentation of planar chiral objects, such as multi-armed structures resembling starfish or shrunken into polymer films.[280] In this case, a simple perpendicular metal deposition directly generates a 3D-mimicking structures. One planar chiral object will form at the bottom of the indentation, while the inverse structure forms as a hole in the otherwise continues film, resulting in a coupling of their individual resonances.[280,281] Similarly, this approach allows incorporation of flexoelectric materials to gain active control over chiroptical signals by triggering mechanical deformation upon applying an external voltage.[282]
6.2.4. Interference Lithography

Another large area fabrication approach to yield gratings as a basis for chiral metamaterials is laser interference lithography.[283] Interference patterns of two laser beams result in a 1D gratings in a photoresist after development (Figure 13d, i), which can either be used to produce gold gratings via a lift-off approach, or as gratings of photoluminescent colloidal quantum dots via a PDMS stamping.[283] Directly overlaying of such a metallic and an emitting particle grating via stacking results in chiral Moiré (Figure 13d, i). In contrast to the Moiré pattern introduced above, which showed variations along the substrate as a result of the polycrystallinity of the colloidal monolayer template, the stacking of two individual substrates allows precise control over the entire substrate (Figure 13d, ii).[283] The resulting circular dichroism and polarization of photoluminescence can be reversibly tuned by the stacking angle (Figure 13d, iii) as the individual layers are independently fabricated prior overlaying.[283]

7. Substrate Deformation

A second general approach to create chiral nanoobjects is the deformation of a substrate coated with 2D nanostructures. From an engineering perspective, a twisted or rolled 2D plane loses flatness, and therefore becomes 3D. Manufacturing the required planar objects is much easier than directly fabricating their 3D counterparts.[40,149,150] The common denominator of the different processes introduced in this chapter is to create such chiral materials from planar structures by the deformation of their underlying substrates.

7.1. Self-Rolling Films

Internal strain gradients in thin films can be exploited to induce self-rolling and the creation of defined, layered rolls.[284,285] This strategy was recently employed at small scales to create chiral nano-kirigami structures.[150,286,287] On a larger scale, metallic nanohole arrays have been subjected to the process to create rolls of metallic meshes made of nanohole arrays resembling carbon nanotubes.[288]

More precise engineering of films can provide predictive self-rolling, so that nanostructures deposited on the initially flat film can be precisely stacked above each other in one roll, and even form a complex chiral metamaterial (Figure 14a, i).[289] Such materials can, for example resemble a Born–Kuhn type resonators with two stacked slabs (Figure 14a, ii). Even stacking of more layers was demonstrated, leading to a chiroptical response in the visible.[289] Such rolls are not only inherently 3D chiral metamaterials, they are also attractive for on-chip applications with an integration of microfluidics.[290,291]

7.2. Twisting of Substrates and Active Control

Besides rolling up a flat nanostructure array on a polymer film, twisting of the substrate prior to deposition constitutes a second strategy to employ substrate deformation to create a chiral nanostructured material. Such a twisting process was used to assemble gold nanoparticles into chiral s-like chains with opposite handedness (Figure 14b, i).[292] In this experimentally simple procedure, flexible substrates were twisted in a defined direction (left or right-handed twisting can provide enantiomers) and subsequently coated with multiple layers of gold nanoparticles via a layer-by-layer deposition method.[292] Releasing the twisting of the polymer films unveils the formation of chain-like structures with opposite handedness (Figure 14b, ii), which exhibit two CD resonances in the visible (Figure 14b, iii, 0% strain, curves with shaded red and blue).[292]

Additionally, the approach provides active control over the strength of the circular dichroism. Lateral stretching of the prepared chiral gold nanoparticle films strongly enhanced the circular dichroism (Figure 14b, iii 10–50% strain).[292] This active modulation via applying an external strain is completely reversible (Figure 14b, iv), and was demonstrated over 10 000 cycles.[292] Such active control may also lead to a spectral tuning or selective switching of chiral surface lattice resonances by exploiting the possibility to change lattice parameters in complex structures reversibly.[293,294]

8. Templated Assembly for Chiral Nanostructures

Templated assembly techniques use a prestructured substrate to guide the self-assembly process into defined arrangements. Colloidal gold particles can thus be precisely arranged into certain (chiral) positions determined by mechanical, physical, chemical, or more biological motives.[295–298] While templated assembly techniques have been very successful in producing complex and deterministic nanostructure arrays, it has only recently emerged as a promising technique to create chiral nanostructures. In the following, we select few representative examples of such chiral structures. Interestingly, many of these reported structures do not only provide chirality, but also add active control or response to the environment. Some of the employed techniques may have demonstrated structure formation on a smaller scale, but may provide avenues and inspiration toward large area fabrication of (active) chiral substrates.

8.1. Capillary Assembly

The assembly of nanorods, or more general of particles forming defined clusters known as plasmonic molecules provide defined hot spots with high near-field enhancements.[75,87] These hot spots have been employed in the sensing of chiral molecules and the study of the interaction between chiral molecules and matter.[41,299–301] Most of these examples rely on wet-chemical ligand functionalization to form plasmonic molecules in dispersion or induced chirality due to chemical molecules. A substrate-bound alternative to create such defined clusters is capillary assembly, which employs a defined surface topography that templates the self-assembly process.[295–298,302–304] A dispersion of colloidal particles is dragged over this structured substrate. At the meniscus front, individual particles[299] or defined sequences or particles[297] are thus deterministically placed into the topographic features to form the desired colloidal
clusters. Figure 15a shows how capillary assembly is employed to create planar chiral plasmonic molecules made from a defined arrangement of three gold rods, which were assembled in triangular templates. The relative orientation of triangular surface features to the meniscus determines the symmetry of the resulting assembly, which can be either the two chiral enantiomers or an achiral structure (Figure 15a, ii). Three different plasmonic resonances with enhanced near-fields primarily in-between the rods arise, which can exhibit handedness-dependent extinction (Figure 15a, iii–iv).

8.2. Physico-Chemical Contrast

A second possibility to place particles into defined arrangements is the use of physio-chemical surface contrasts. For example, gold surfaces are easily functionalized with thiol molecules, which self-assemble in the form of a dense monolayer on the gold surface, thus controlling the surface chemistry and providing specific binding motifs. A localized functionalization with such specific binding motifs can be provided by exploiting a preformed materials contrast, given, for example by preformed gold nanostructures on the surface. Partial passivation of a gold nanostructure with a silica or titania layer can control the localized placement of such additional particles within a single nanostructure (Figure 15b, i), opening possibilities to create complex, chiral assemblies. DNA origami, i.e., exploiting the highly specific binding motifs of complementary DNA strands on different particles, is an important chemical tool to achieve such defined assemblies. This topic has been recently reviewed in depth elsewhere and we therefore only show one instructive example of its capabilities. A chiral plasmonic nano clock can be formed by two gold
Figure 15. Templated assembly to create chiral plasmonic nanostructures. a) i) Capillary assembly forces gold nanorods into chiral trimer structures using triangular-shaped surface topographies. The polymeric topography can subsequently be removed, leaving the chiral nanostructure on the surface. ii) The relative flow direction of the meniscus determines whether the molecule is left-handed, achiral or right-handed. iii) The plasmonic molecule formed by the three nanorods shows an enhancement of the electromagnetic near-field for the three modes. iv) The scattering spectra show the handedness-dependent excitation of the resonances for circularly polarized light. Reproduced with permission.[305] Copyright 2019, American Chemical Society. b) Material contrast and localized chemical surface functionalization can be used to place particles into certain (chiral) positions or relative orientations within a preformed nanostructure. i) Partial passivation of a gold crescent allows localized functionalization at one of the two tips with thiol chemistry, and thus a selective binding of gold nanoparticles via electrostatic attraction. Reproduced with permission.[184] Copyright 2019, Wiley-VCH. ii) DNA origami can control the relative position of two stacked nanorods. DNA fuel allows the active rotation of the two, leading to an active CD signal. Reproduced under the terms of Creative Commons (CC 4.0) license.[317] Copyright 2019, The Authors, Published by Springer Nature. c) Chemo- and thermomechanical properties of thin films can be employed to fold planar structures into 3D object. i) Planar structures with asymmetric arms are formed on a substrate and coated with a bilayer of titanium and gold nanoparticles. i) Strain in this bilayer is induced by a ligand-exchange in the nanoparticle layer, which curls the arms and folds the planar structure into a 3D object. ii) The arms bend in a helical way if the imprint mask was planar chiral. iii) The differential transmission shows inverse signals for both enantiomers (black, red) in the infrared (dashed lines). Thermal annealing bends the structure further (see i, red overlay), resulting in a blue shift of the resonances. Reproduced with permission.[318] Copyright 2020, American Chemical Society. d) Chiral phases in phase-separated polymers and polymeric particles can be used as a matrix to create chiral nanoparticle structures over large areas. i) Cellulose nanoparticles can form cholesteric chiral phases into which gold nanoparticles can be embedded. Adapted with permission.[327] Copyright 2015, American Chemical Society. ii) This material combination results in macroscopic photonic-plasmonic films. iii) In the example, plain cellulose nanocrystal assemblies (black) show a CD signal in the infrared. Incorporation of gold nanorods leads to a chiral response at 600 nm (blue), which increases in intensity increasing nanorod concentration (green to red). Reproduced with permission.[328] Copyright 2014, American Chemical Society. iv) Gyroid phases in block copolymers can be selectively replaced by plasmonic materials, leading to 3D chiral metamaterials over large areas. Reproduced with permission.[329] Copyright 2020, Wiley-VCH.
nanorods that are bound together via DNA strains. Different steps (positions) can be reached by adding the respective DNA fuels, leading to the rotation of one gold rod with respect to the other, and thus allows completely active and reversible control over the CD signal (Figure 15b, i).[317]

8.3. Chemo- and Thermomechanically Responsive Films

A different strategy to employ a prestructured substrate to create 3D chiral structures is to employ strains that are build up in thin films to guide a subsequent folding process, in which a planar structure folds up into a 3D object. Conceptually, this approach is similar to the self-rolling films discussed above. However, in the following approaches, it is the structure itself that folds up in a predesigned pattern—and not the complete substrate. Figure 15c highlights an example of complex, chiral nanostructure arrays fabricated using chemo- and thermomechanically responsive thin films.[318] The process elegantly combines several fabrication steps discussed above. Imprint lithography is used to fabricate planar surface nanostructures consisting of a central square with asymmetric arms (Figure 15c, i) on a substrate covered with a thin chromium layer. Consecutive evaporation of titanium and spin-coating of a gold nanoparticle dispersion results in a bilayer made of titanium and ligand-capped gold nanoparticles on the structured chromium surface. The trick employed to actuate these structures is to partially remove the flat chromium layer underneath the arms of the bilayer-coated nanostructure by chemical etching. A ligand exchange of the molecules coating the gold nanoparticles to ligands with a shorter chain subsequently reduces the interparticle distance in the gold nanoparticle layer. This change in the nanoparticle layer, in turn, causes an internal non-uniform strain in the bilayer, resulting in the curling of the arms. For initially planar chiral arms (Figure 15c, ii), this process forms arrays of 3D chiral structures over square millimeter dimensions. These structures show strong circular dichroism in the infrared (Figure 15c, iii dashed lines). Short annealing at elevated temperatures (160 °C) result in a mechanical tuning of the structure, which increases the curling and leads to a blue shift of the resonances (Figure 15c, iii solid lines).[318]

8.4. Matrix-Induced Chiral Self-Assembly

The last set of examples uses different matrices that provide a scaffold to guide the self-assembly of plasmonic nanoparticles into chiral 3D structures. Candidates for such chiral matrices that have been employed for this process are cholesteric phases of cellulose nanocrystals,[50,319] and gyroid phases formed by phase-separating block-copolymers films.[320,321]

8.4.1. Cholesteric Phases of Cellulose Nanocrystals

Cellulose nanocrystals are made of rod-like nanoparticles that can be extracted from abundant cellulose by acid hydrolysis.[50] At sufficiently high concentrations, these anisotropic particles self-assemble into a cholesteric phase, which is composed of layers of helically twisted rods.[50,322–326] These chiral assembly structures can subsequently be loaded with plasmonic particles and rods (Figure 15d, i).[30,327] As we see in Figure 15d, ii, such composites form stable, macroscopic films.[328] The resulting optical properties are complex and determined by the combination of the photonic properties of the cellulose nanocrystal assembly, and the plasmonic resonances of the decorating nanoparticles.[327,328] The presence of gold nanorods within this assembly induced a distinct CD resonance in the visible region, which is increasing in intensity with increasing gold nanorod concentration (Figure 15d, iii).[328]

8.4.2. Gyroid Phases in Block-Copolymers

The second strategy to use a chiral matrix takes advantage of gyroid phases in block copolymers (Figure 15d, iv).[329] Block-copolymers form gyroid phases with periodicities in the sub-100 nm range. One of the blocks can be selectively removed and replaced by plasmonic materials such as gold and silver.[320,329] The remaining block can be subsequently removed by plasma treatment, leaving behind a fully metallic 3D metamaterial with optical properties in the visible (Figure 15d, iv).[329] Block-copolymers are also used in 2D patterns for substrates,[329] which seems to remains unexplored for chiral plasmonic substrates.

9. Conclusion

We hope that you now understand the basics of chiral plasmonics and have found a suitable approach to create chiral structures over large areas. We see that the field of chiral plasmonics is not only continuously growing, but also maturing toward real-life applications. While a continuous gain in the understanding of the chiral light–matter interactions explains how chirality and electromagnetic fields work at the nanoscale, we must acknowledge that the field of chiral plasmonics will need to deliver on promises made in the past. Whether chiral plasmonic substrates work as polarizers, sensors, emitters, on-chip components, and as diagnostics tools will require fulfilling at least the two following aspects: the resilience of such substrates in real-life scenarios and applications, and scalable fabrication techniques that must emerge at feasible costs. This aspect is especially challenging since the fabrication of chiral plasmonic substrates requires the minute control of plasmonic material at the nanoscale in 3D.

In this review, we identified three general approaches toward the parallel fabrication of chiral nanostructures: advanced and complex lithography, the twisting deformation of substrates, and the template-assisted assembly. Colloidal particles play a significant role in several of the shown approaches, as they can flexible building blocks to design nanoscale masks, but can also be assembled directly into chiral structures.

Finally, we would like to address some aspects that we believe will dominate the forefront of large-area substrate fabrication and application-driven development in different communities in the coming years:
Perhaps most apparent is the implementation of substrates with active control over optical properties. Most advances toward this goal have not been achieved using large-area methods, but typically with more conventional top-down approaches or via DNA self-assembly. Implementing precise control and actuation over chiral structures over large areas requires combination of different, sophisticated fabrication techniques but will be required for displays or active optical components.

Chiral nanostructures on flexible substrates are important for three reasons; they can be used in wearable (on-skin) devices and diagnostic tools, they can cover other materials with near arbitrary shape, and finally, they can provide active control over chirality or spatial properties by changing, e.g., the periodicity in surface lattice resonances.[284]

The precise fabrication of substrates with gradients are of interest for different (transforming) optical components and in sensing. While there have been several approaches toward such substrates,[331–333] they have not necessarily included chiral properties.

Integration into functional (on-chip) devices will add to the fabrication complexities and may require the combination of different sets of techniques but is needed for miniaturization and real-world applications.

The success of chiral plasmonics will depend in no small part on whether different scientific communities will pick up concepts and identity, adopt, and exploit some of the fascinating properties of chiral for their specific purposes and applications. We hope that this tutorial review conveys fundamental concepts, and real-world applications.

Acknowledgements

This project received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement No 861950, project POSEIDON. A.S.P., J.J.M., and L.V.P. gratefully acknowledge funding from the Jacobs School of Engineering at UC San Diego. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

N.V. and E.S.A.G. designed the scope and outline of the article. E.S.A.G. wrote the introduction, chirality, and fabrication chapters with help of N.V. A.S.P., J.J.M., and L.V.P. wrote the chiral plasmonic theory and characterization chapters. All authors contributed to the final manuscript.

Keywords

chirality, colloidal lithography, large-area substrates, plasmonics, surface patterning

Received: February 22, 2021
Revised: April 8, 2021
Published online:

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