Research article

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Dynamic tuning of enhanced intrinsic circular dichroism in plasmonic stereo-metamolecule array with surface lattice resonance

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Abstract: Enhancing the circular dichroism signals of chiral plasmonic nanostructures is vital for realizing miniaturized functional chiroptical devices, such as ultrathin wave plates and high-performance chiral biosensors. Rationally assembling individual plasmonic metamolecules into coupled nanoclusters or periodic arrays provides an extra degree of freedom to effectively manipulate and leverage the intrinsic circular dichroism of the constituent structures. Here, we show that sophisticated manipulation over the geometric parameters of a plasmonic stereo-metamolecule array enables selective excitation of its surface lattice resonance mode either by left- or right-handed circularly polarized incidence through diffraction coupling, which can significantly amplify the differential absorption and hence the intrinsic circular dichroism. In particular, since the diffraction coupling requires no index-matching condition and its handedness can be switched by manipulating the refractive index of either the superstrate or the substrate, it is therefore

possible to achieve dynamic tuning and active control of the intrinsic circular dichroism response without the need of modifying structure parameters. Our proposed system provides a versatile platform for ultrasensitive chiral plasmonics biosensing and light field manipulation.

Keywords: chiral plasmonics; circular dichroism; plasmon hybridization; plasmonic metamolecule; surface lattice resonance.

1 Introduction

Circular dichroism (CD) characterized by the differential absorption of left-handed (LCP) and right-handed circularly polarized (RCP) light is an intrinsic property of chiral compounds, which provides a powerful spectroscopy tool for structural and conformational analyses of complex biomolecules [1, 2]. However, the CD signals of naturally occurring materials are typically very weak due to their small dipole moments and hence a weak coupling with the incident light, and therefore can be detectable only at high concentrations or large volumes. This constitutes a significant long-standing obstacle for realizing compact chiroptical nanophotonic devices with naturally occurring chiral compounds, and has sparked a considerable amount of research interests in designing artificial man-made structures with enhanced CD signals [3–8].

Over the past decade, the extraordinary CD responses of plasmonic chiral nanostructures have gained considerable attention, where the excitation of localized surface plasmon resonances (LSPRs) significantly enhances the light-structure interaction strength due to their extremely large dipole moments, and the generated CD signals are thus orders of magnitude larger than that of natural compounds [9–17]. Such enhanced plasmonic chirality is also featured with flexible modulation of both CD resonance magnitude and frequency through manipulating the structural geometry and constituents [4, 18, 19]. Thus far, strong intrinsic CD responses have been observed in three-dimensional plasmonic helices [20–30], spirals [31–33], nanopillars [34], twisted nanoparticles (e. g., split-ring resonators (SRRs) [35, 36], gammadions [37], arcs [38], and

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rods [11, 39–43]), and oligomer clusters [44–54]. Even handed planar structures exhibit remarkable CD despite the fact that they are not truly chiral [55–66], and their chiral responses can be strongly enhanced with the formation of Fano resonances [66, 67], which are promising platforms to manipulate chiral light-matter interactions at the nanoscale [68]. More interestingly, the CD resonance frequency and strength can be controlled by photoinduced optical handedness switching effects [69], phase-changing materials [70, 71], external magnetic fields [72], excitation power [73], and (DNA) origami templates [74–83], which pave the way for realizing chiroptically active devices.

Recently, plasmonic chiral metasurfaces consist of metallic nanostructures organized in C_4 symmetry has been demonstrated to exhibit intrinsic CD responses without invoking the birefringence effect [11, 48–51]. Under such symmetrical arrangement, the metasurfaces CD responses are definitely characterized by the differential transmission of LCP and RCP incidences, which is identical to that of the differential absorption. In analogy to molecular physics, the constituent nanostructures in such metasurfaces can be termed artificial plasmonic “molecules” [84, 85]. Essentially, the transmission CD signals of the chiral metasurfaces with C_4 symmetry are governed by the differential absorption cross section of constituent plasmonic “molecules.” However, the absorption cross section of a single plasmonic “molecule” cannot be increased significantly by simply increasing its structural size compared with that of its scattering [86], and the differential absorption of the plasmonic “molecule” is therefore relatively weak. As a result, very dense arrays of chiral nanostructures are used to enlarge the transmission CD magnitude. In this case, the absorption of the matched circularly polarized incidence can be enhanced, but the absorption of the opposite circularly polarized incidence that intends to be transmitted is enhanced simultaneously. This obstacle would be more obvious when plasmon resonances shift to the visible and near-infrared frequencies. For example, the transmission CD magnitude can be as large as 0.4 for a very dense stereo-metamaterial composed of twisted SRR dimers in the near-infrared spectral range [87–92], but the magnitude is less than 0.1 for a sparse array made of similar constituent structures [93]. Although the CD response for a similar stereo-metamaterial designed by a deep learning method can be enlarged to about 0.8 [94], the light transmission is blocked due to the presence of a gold film mirror in the structure, and the birefringence effect is also involved in the CD response.

In addition to single plasmonic “molecules,” the plasmonic responses of metal nanoparticle arrays are governed by surface propagating modes caused by the

electromagnetic coupling between unit cells, e. g., extraordinary optical transmission (EOT) related to surface plasmon polaritons [95], and surface lattice resonance (SLR) modes caused by diffraction coupling between LSPRs and Rayleigh anomalies (RAs) [96–100]. Radiative losses can be effectively suppressed with the excitation of SLR modes, which leads to sharp resonances with large Q-factors [101–103]. What's more important is that the optical interaction between the nanoparticles and the incident field can be enhanced by the surface propagating modes, and the absorption of nanoparticle arrays can hence be strongly amplified [104]. This indicates that the coupling between the constituent structures in plasmonic arrays be possibly used for enhancing the CD responses. Several pioneer works have demonstrated the CD responses of planar plasmonic nanostructure arrays associated with the excitations of surface propagating modes. Maoz et al. and Wang et al. have reported respectively the enhanced CD in plasmonic nanohole arrays with the EOT effect [105, 106], and the CD responses can also be tuned by adjusting the array period. It has been demonstrated a large differential transmission for LCP and RCP incidences in achiral nanoparticle arrays with the excitation of two different SLRs [107, 108], and Cotrufo et al. have shown that the surface lattice resonance in a handed planar rod array plays an important role in determining the spin-dependent emission of light [109]. Nevertheless, these structures are not truly chiral, and the CD responses are related to their extrinsic chirality. Besides that, the excitation of the SLR modes in those structures requires to fulfill the index-matching conditions, the enhanced CD for the SRR arrays can only be observed under oblique incidences [107, 108], and the CD magnitude for the nanohole arrays is still relatively weak [105, 106].

In this work, we investigate the chiroptical response of a plasmonic stereo-metamolecule array and show that the CD resonance strength can be significantly leveraged by selectively exciting SLR modes. Although the intrinsic differential absorption of the constituent stereo-metamolecules is quite weak, their periodic counterpart exhibits an SLR-enhanced CD signal of up to 0.7, which is about 6 times larger than that without diffraction coupling. This observation can be explained within the framework of a modified plasmonic Born–Kuhn model. Moreover, since the enhanced CD does not rely on index-matching conditions, it is therefore possible to realize dynamic tuning or active control of the chiroptical response without modifying the structure geometry. Our results highlight the robustness and significance of achiral SLR in chirality enhancement, which can

be a general scheme for a wide range of chiral meta-material designs such as stereo-SRR dimers and oligomer clusters.

2 Results and discussion

2.1 CD of single stereo-SRR dimers

Figure 1a illustrates the configuration and geometric parameters of a gold stereo-SRR dimer with the upper SRR rotated clockwise by an angle θ with respect to the y -axis. Here, the horizontal displacement d between the two SRRs is intentionally introduced to enhance near-field coupling at the gap area [88–92], and the vertical displacement s can be used to manipulate the coupling and the phase retardation. Depending on the relative position and twist angle, the SRR dimer can be left-handed (L-Enantiomer) or right-handed (D-Enantiomer). The spacer layer (e. g., solidifiable photopolymer, PC403) is supposed to have the same refractive index as the silica substrate ($n_{\text{silica}} = n_{\text{spacer}} = 1.50$), while the superstrate

material is set to be air ($n_{\text{sup}} = 1.00$). When circularly polarized light is incident normally onto the structure from the air side, plasmonic coupling between the electric dipole mode of the upper SRR and the quadrupole mode of the lower one results in the formation of hybridized bonding dipole-quadrupole (BDQ) and anti-bonding dipole-quadrupole (ABDQ) resonance modes (Figure 1b) [84, 85]. Plasmon hybridization between two electric dipole modes of the dimer is neglected here due to their significant phase mismatch. More detailed information can be found in Figure S1. Such hybridization modes can be selectively excited by RCP and LCP incidences, depending on the phase retardation between the two SRRs. As a result, the difference in excitation efficiency of the two circular polarized incidences is expected to generate CD signals around the resonance frequency of the SRR dimer.

The absorption cross-section (Abs) spectra of the single modified stereo-SRR dimer (D-Enantiomer) under RCP and LCP incidences are shown in the upper panel of Figure 2a. As expected from our qualitative reasoning, the RCP mode is located at a lower energy (990 nm), which

Figure 1: Geometric configuration and plasmon hybridization of a modified gold stereo-SRR dimer. (a) Schematic views of the modified stereo-SRR dimer, showing geometric parameters such as ring radius $r = 90$ nm, width $w = 40$ nm, gap width $g = 30$ nm, thickness $h = 40$ nm, vertical separation $s = 60$ nm, horizontal separation $d = 90$ nm and twisted angle $\theta = 60^\circ$. The refractive index of the substrate $n_{\text{sub}} = n_{\text{silica}} = n_{\text{spacer}} = 1.50$, and the superstrate $n_{\text{sup}} = 1.00$. (b) Plasmon hybridization between the electric dipole and quadrupole modes in a D-Enantiomer, forming an antibonding dipole-quadrupole (ABDQ) and a bonding dipole-quadrupole (BDQ) resonance.

Figure 2: CD response of a single modified gold stereo-SRR dimer. (a) Absorption cross-section spectra of a single D-Enantiomer under LCP and RCP incidences (upper panel) and corresponding differential absorption (ΔAbs) spectrum, i. e., CD spectrum (lower panel). (b, c) Near-field enhancement ($|E/E_0|$, left panels) and surface charge (right panels) distribution profiles at the ABDQ (b) and (c) BDQ resonance wavelengths.

corresponds to the bonding mode (BDQ), whereas the LCP mode lies at a higher energy (880 nm), corresponding to the antibonding mode (ABDQ). In addition, the resonance shoulder around 1100 nm under the LCP incidence is attributed to the excitation of a hybridized dipole mode (Figure S1). As a result, a positive differential absorption ($\Delta Abs = Abs_{LCP} - Abs_{RCP}$) peak occurs at 880 nm and a negative one at 987 nm as shown in the lower panel of Figure 2a, leading to the CD response of the stereo-SRR dimer. The corresponding near-field and surface charge distribution profiles at the two CD peaks are rendered in Figure 2b,c, respectively. Clearly, the surface charge profiles confirm the electric dipole mode of the upper ring and the quadrupole mode of the lower ring at their resonance wavelengths. However, there is a π phase difference for the quadrupole mode of the lower ring at the two resonances, confirming our analysis of hybridized ABDQ and BDQ modes.

2.2 Enhanced CD with surface lattice resonances

In order to highlight the importance of SLR in enhancing plasmonic chiroptical effects, we arrange chiral stereo-SRR dimers in a C_4 -symmetric supercell to avoid circular birefringence (Figure 3a). The supercell has a period $p = 890$ nm and the center-to-center distance between two adjacent dimers is 450 nm. The simulated transmission and absorption spectra of the array under RCP and LCP incidences as well as the corresponding transmission CD spectrum are plotted in Figure 3b. An ensemble CD spectrum by assuming no coupling between adjacent dimers is also overlaid as a dotted line for comparison. One can immediately see two pronounced positive and negative CD peaks at 831 and 949 nm for the array, both blue-shifted compared to the reference spectrum. This can be attributed to the effective mode volume overlapping between SRR

dimers in the array (Figure S2 in Supporting Information). The positive CD peak increases slightly compared with that of the single dimer (red circle), while the negative CD peak at 949 nm (blue solid circle) is enhanced to 0.70, which is 6 times larger than the ensemble CD spectrum. This is a clear evidence that electromagnetic coupling between adjacent dimers plays an important role in the chiroptical signal enhancement. In fact, it has recently been demonstrated that the coupling between a localized plasmon resonance and the Bragg resonance of a periodic lattice be used to improve the resonance quality factor and light absorption [110]. It should be noted from Figure 3b that there is another resonance peak located at 1078 nm, which is the bonding

dipole-dipole (BDD) mode of the chiral stereo-SRR, whose near-field and surface charge distribution profiles can be found in Figure S3.

The above observation of enhanced CD in the array of C_4 -arranged chiral stereo-SRR dimers can be attributed to the emergence of SLR modes due to collective oscillation of LSPRs in each unit cell. In short, for a periodic plasmonic nanoparticle array, Rayleigh anomalies that are associated with light diffracted parallel to the array surface, occur at [96–99],

$$\lambda_{(ij)_{\text{med}}} = \frac{p \times n_{\text{med}}}{\sqrt{i^2 + j^2}} \quad (1)$$

where n_{med} is either the refractive index of the superstrate (n_{sup}) or the substrate (n_{sub}), and $(i, j)_{\text{med}}$ denotes the diffraction order. When the incident angle is just across RAs at a plasmon resonance band, the unit cells diffractively couple to each other, creating a propagating SLR mode. The spectral positions of relevant RAs are denoted by the gray dashed lines in Figure 3b. As a result, plasmonic non-radiative absorption is increased by the enhanced interaction between incident field and lossy metal but plasmonic radiative scattering is suppressed due to diffraction coupling, leading to an overall sharp resonance peak with high Q-factor [104]. Therefore, the absorption of a chiral plasmonic nanostructure array is expected to be greatly enhanced under an appropriate circularly polarized incidence but negligible for the opposite one, leading to a pronounced CD peak. It is worth to emphasize that, although the refractive indexes of the superstrate and substrate are not equal ($n_{\text{sub}} = 1.50$, $n_{\text{sup}} = 1.00$), the index-matching condition here is not a necessary requirement to realize strongly enhanced CD response.

The sharp resonance and CD peak located at 949 nm (blue solid circle) occurs on the long-wavelength side of the $(1, 0)_{\text{sup}}$ RA (please note that to simplify the expression, the rest degenerate RAs in Figure 3b are not indicated here), and the resonance quality factor is larger than that of the localized resonances shown in Figure 2a, which are the signatures of coupling light into SLR mode [104]. Besides that, the near-field distributions shown in Figure S4 demonstrate that there are relatively strong field enhancements between the unit cells, and propagating waves are observed along both x - and y -directions, which further reveal the excitation of the SLR. The corresponding field pattern for a single stereo-SRR in the unit cell (Figure 4) is consistent with Figure 2c, demonstrating that, indeed, it is the BDQ mode. As expected, the excitation efficiency of BDQ mode inherits from its single structure situation. This

Figure 3: CD responses of a stereo-SRR dimer array organized in C_4 symmetry. (a) Schematic views of the stereo-SRR dimer array. (b) The transmission (upper panel) and absorption (middle panel) spectra with RCP (blue lines) and LCP (red lines) incidences, and the corresponding CD in transmission of the array (solid line, lower panel). The dotted line in lower panel is calculated from equation $\Delta T = 4 \times \Delta \text{Abs}/p^2$, which is the ensemble average of CD response calculated by neglecting the coupling between dimers. The vertical dashed lines denote the spectral positions of corresponding RAs, and the tick labels on the right side represent the converted cross section values by multiplying the area of the unit cell (p^2).

Figure 4: Near-field enhancement (left panels) and charge distribution (right panels) of one dimer in the supercell array at the positive and negative CD peaks shown in Figure 3, where the ABDQ (a) and BDQ (b) modes are excited. BDQ mode are greatly enhanced compared with single dimer situation due to the diffraction coupling.

behavior is also confirmed in Figure 4b where near-field is greatly enhanced. In this case, the BDQ mode is efficiently excited by RCP incidence, giving rise to enhanced absorption ($Abs \sim 0.84$), whereas LCP illumination stands on the opposite side with negligible absorption ($Abs \sim 0.14$). It should be noted that although the $(1, 1)_{sub}$ RA in the substrate is around the same spectral range, it is almost overlapped with the maximum point of the sharp resonance. This behavior does not satisfy the relation between an RA and SLR mode, and it should not be the main contribution of the enhancement. This can also be verified in Figure 4b that the field enhancement around the upper rings are stronger than that of the lower ones, demonstrating that the SLR is caused by the diffraction coupling of the BDQ mode in the superstrate. Actually, the $(1, 1)_{sub}$ RA mostly interacts with the BDD mode at 1078 nm (Figure S3) and is beyond the scope of this study. We therefore dismiss the $(1, 1)_{sub}$ SLR hereafter throughout this paper.

The broad resonance peak at 831 nm is attributed to the ABDQ mode (Figure 4a), and interestingly, exhibiting weak chiroptical enhancement (Figure 3b). This is from the fact that, the ABDQ mode is located, on one hand, at the short-wavelength side of $(1, 0)_{sup}$ RA, thus no $(1, 0)_{sup}$ SLR resonance, and on the other hand far away from $(2, 0)_{sup}$ RA, yielding weak diffraction coupling. As a result, chiral stereo-SRR dimer arrays at this band restore to uncoupled situation, where the corresponding CD signal is comparable to that of ensemble CD spectrum. This phenomenon can be confirmed in Figure 4a where the near-field enhancement is also comparable with that of the single dimer (Figure 2b). Another example sharing the same mechanism is the hybridized magnetic dipole-dipole mode centered at 2100 nm. As shown in Figure 5 and Figure S5, the CD response of the stereo-SRR dimer array appears in its magnetic dipole-dipole coupling range. When the

magnetic resonance wavelength is far away from the RAs, there is no diffraction coupling between unit cells. As a result, the CD response of the array is almost identical to that for an ensemble of the same number of single SRR dimers without diffraction coupling (lower panel, Figure 5). The maximum CD in transmission is only about 0.12, and it is in accordance with the experimental results reported in previous studies [93]. Considering that the magnitude of differential absorption cross sections for the hybridized magnetic dipole resonances are comparable with that of the ABDQ and BDQ modes (Figures 2 and S4), the excitation of SLRs can be an effective approach for enhancing the intrinsic CD responses.

Figure 5: CD responses related to the magnetic dipole resonance of the stereo-SRR dimer array shown in Figure 3. Upper panel: transmission spectra under RCP (blue lines) and LCP (red lines) incidences; Lower panel: corresponding transmission CD spectrum for the dimer array (solid line) and the CD spectrum calculated for an ensemble of uncoupled single dimers ($\Delta T = 4 \times \Delta Abs / p^2$, dotted line).

2.3 Optimized condition for enhanced CD

SLRs and LSPRs are two resonance modes that stem from distinct physical mechanisms. In other words, SLRs is a collective resonance mode with high Q-factors and can be manipulated by tuning the period of the arrays. In contrast, LSPRs solely depends on the property of metamolecules. Therefore, one is able to tune the two resonances independently in order to get optimized chiroptical effect. We carried out the period sweep of the supercell while keeping dimer distance unchanged within unit cell. The contour plot of the corresponding transmission and absorption spectra (the upper and middle panels), as well as CD signal (the lower panel) for different periods are depicted in Figure 6. The RAs calculated from Equation (1) is superimposed as dashed lines for comparison.

The ABDQ and BDQ modes are excited around, respectively, 840 and 940 nm, which are denoted by the red and blue arrows in the upper and middle panels of Figure 6b. We therefore distinguish the period of supercell in three regions according to the relative position between $(1, 0)_{\text{sup}}$ RAs and LSPRs band. For lattice period $800 \text{ nm} < p < 950 \text{ nm}$, RAs intersect with LSPRs modes, resulting in strong SLR modes. In this case, BDQ mode is effectively excited under RCP incidence. The CD response therefore gets enhanced and reaches maximum when $p = 890 \text{ nm}$. When the period of supercell is smaller than 800 nm , $(1, 0)_{\text{sup}}$ RA are shifted to far short-wavelength side of LSPR modes. Therefore, their diffraction coupling is

relatively weak. For large lattice period ($p > 950 \text{ nm}$), LSPRs lies above $(1, 0)_{\text{sup}}$ RA and thus cannot oscillate collectively. On the contrary, LSPRs start to interact with $(1, 1)_{\text{sup}}$ and $(2, 0)_{\text{sub}}$ higher order RAs. The solid lines in the upper panel of Figure 7a represent the absorption spectra of a sparse array with a large period ($p = 1210 \text{ nm}$). Although the pronounced resonances are spectrally overlapped with higher order RAs (the vertical dashed lines), it has little effect on LSPRs except a resonant blue-shift. The resonance shift can be attributed to the effective mode volume overlapping between neighboring SRR dimers, which is similar to the result in Figure 3b. In contrast, the absorption of the two resonances for the array is comparable with that of the single dimer (lower panel, Figure 7a). In other words, chiroptical effects of these regions restores to uncoupling situation. This behavior, again, can be explained by the near-field distributions of the sparse array (Figure 7b,c) which are almost identical with that of the single dimer situation (Figure 2b,c).

2.4 Enhancing chiroptical effects with other metamolecules

Given the concept that SLRs and LSPRs can be tailored independently, it is possible to exploit SLRs as a universal approach to enhance the chiroptical effects of LSPRs based metamaterials. A typical example is shown in Figure S6 where gold stereo-SRR dimer arrays with spatial shift $d = 0$

Figure 6: (a) Transmission under RCP (upper panel) and LCP (middle panel) incidences, as well as CD spectra (lower panel) for the stereo-SRR dimer arrays with different periods. (b) The corresponding RCP and LCP incidences absorption (upper and middle panels), as well as CD in absorption (lower panel) spectra. The unit has been converted into absorption cross section (μm^2) by multiplying the area of the unit cell. The dashed lines indicate RAs, and the blue and red arrows in Figure 6b denote the BDQ and ABDQ resonances, respectively.

Figure 7: CD responses of a sparse stereo-SRR dimer array. (a) Absorption spectra of the sparse array with $p = 1210$ nm for LCP and RCP incidences (upper panel), and the corresponding CD in absorption spectrum (lower panel). The dotted lines in the upper panel are the absorption spectra of a single dimer scaled by a factor of 4, the dotted line in the lower panel is the ensemble CD single calculated based on the single dimer, the vertical dashed lines denote the spectral positions of several RAs, and the tick labels on the right side represent the converted cross section values by multiplying the area of the unit cell. (b) Near-field enhancement (left panels) and charge (right panels) distributions of the ABDQ, and (c) BDQ hybridized resonances for the sparse array.

can be strongly enhanced by adjusting the lattice spacing. In addition, here, we demonstrate the robustness of SLRs from a new chiral metamolecule, that is, the chiral quadrumer. Figure 8a illustrates the schematic of a chiral quadrumer array composed of two sets of orthogonally corner-stacked gold nanodisk dimers [46]. The quadrumer array is chosen deliberately for the following two reasons. First, it is easier to fabricate such structure with the current nanolithography method, and it is also possible to further enhance the chiral responses of more complex oligomer cluster arrays [47–49]. Second, the intrinsic CD signal for a single chiral quadrumer is extremely weak (Figure S7), especially compared with a single stereo-SRR dimer. Nevertheless, our numerical simulation result indicates that the quadrumer supercell array also exhibits strong CD responses (solid line in the lower panel, Figure 8b). A dip-to-peak profile centered around 1250 nm is observed due to the selective excitation of the hybridized longitudinal

resonances, that is, the antibonding (ABDD) and bonding (BDD) dipole-dipole resonances (inset of Figure 8a). Compared with single chiral quadrumer whose ensemble CD signal is smaller than 0.1 (dotted line, magnified by 5 times for a better visualization), the positive CD peak located at 1320 nm is enhanced by 10 times. As shown in Figure S9, we also simulate the transmission spectra and calculate corresponding transmission CD of these structures under circular polarized illumination from the substrate side, which reveal slightly reduced CD values with negligible polarization conversion, thereby confirming the presence of intrinsic chirality in these structures [50]. The near-field distributions of LSPR modes shown in Figure S8 indicates that the CD peak ($\text{CD} = -0.42$) located at 1103 nm stems from the diffraction coupling of ABDD mode by $(1, 1)_{\text{sub}}$ RA in the substrate. In addition, the sharp peak around 1320 nm is the $(1, 0)_{\text{sup}}$ SLR mode by the diffraction coupling of the BDD mode in

Figure 8: Enhanced CD spectra from chiral gold quadrumer arrays. (a) Schematics of the quadrumer array organized in C_4 symmetry. The supercell parameters are: period $p = 850$ nm, center distance between two adjacent quadrumer in a unit cell $d = 430$ nm, radius of the disk $r = 80$ nm, disk thickness $t = 30$ nm, gap size between the two disks on the same layer $h = 10$ nm, separation between the upper and lower layer $s = 50$ nm, and refractive index of the substrate $n_{\text{sub}} = 1.80$ and the superstrate $n_{\text{sup}} = 1.50$. Inset: the plasmon hybridization scheme between the longitudinal resonances of the two dimers on the upper and bottom layers. (b) The transmission (upper panel) spectra under RCP (blue lines) and LCP (red lines) incidences, and the corresponding CD in transmission of the array (solid line, lower panel). Inset: the charge distributions of the two CD peaks. The dotted line is the ensemble CD in transmission calculated based on the single quadrumer by neglecting the coupling between unit cells (magnified by 5 times for a better visualization), and the vertical dashed lines denote the spectral positions of RAs.

the superstrate. This coupling is even stronger than that of the ABDD mode, whose CD signal in transmission is about 0.60. The CD peak centered at around 900 nm is the transverse hybridized resonance and will not be discussed in this work.

2.5 Dynamic tuning of transmission CD

One important nature of SLR, in general, is that its excitation efficiency depends dominantly on the spectral overlapping between RAs and LSPRs. Considering the fact that the excitation of SLRs don't relying on index-matching conditions, it is therefore envisioned that the chiroptical properties of a given structure can be dynamically controlled by manipulate the frequency detuning of LSPRs, an approach that one can easily play with by modifying the superstrate's index such as flowing in different liquid materials [111], or integrated with a phase-change material

layer [70, 71]. This is of particularly advantageous for practical applications such as polarization engineering approaches, polarization sensitive imaging, and stereo display technologies, where the geometry of functional materials cannot be changed [69–71, 73–79]. For a qualitative assessment, we simulated the CD response of chiral quadrumer array embedded in different superstrates, as shown in Figure 9. The corresponding transmission spectra of chiral quadrumer array under LCP and RCP incidences are represented in Figure S10. As expected, the spectral positions and intensities for both ABDD and BDD modes are strongly modified under different superstrate indexes. When the refractive index is small ($n_{\text{sup}} = 1.00$), CD signals are relatively weak, given by -0.18 and 0.26 for the ABDD and BDD modes, respectively (black line, Figure 9a). The intensities of both CD peaks increase with the increasing refractive index, reaching a maximum value when $n_{\text{sup}} = 1.50$, where the CD in transmission are more than one times stronger than that of $n_{\text{sup}} = 1.00$ situation

Figure 9: Dynamic tuning of CD responses. (a) The CD spectra in transmission under different superstrate indexes for the same chiral quadrumer array, where the sign of CD signal is switched around the spectral positions marked with yellow bars. (b) Transmission spectra under RCP (upper panel) and LCP (middle panel) incidences, as well as the CD responses (lower panel) for the quadrumer array under different superstrate indexes. The dashed lines show the spectral position of RAs, and the dotted lines in the lower panel denote the evolution of ABDD and BDD modes.

(red line, Figure 9a). By further increasing n_{sup} (>1.50), the intensities of the CD peaks start to decrease, where the CD in transmission with $n_{sup} = 2.00$ are comparable with that of $n_{sup} = 1.00$ (cyan line, Figure 9a).

The transmission spectra under RCP and LCP incidences as well as CD spectra are depicted in Figure 9b. The dashed lines denote the spectral positions of the RAs, and the dotted lines in the lower panel of Figure 9b schematically show the evolution of ABDD and BDD modes. The RAs from the substrate stay unchanged with increasing n_{sup} , whereas the LSPRs band and RAs from the superstrate shift to lower energies. Nevertheless, the RAs in the superstrate red shift more rapidly compared with that of the LSPRs. Therefore, when n_{sup} is small enough (e. g., $n_{sup} = 1.00$), resonance band of the quadrumer locates far away from the RAs. The corresponding SLRs cannot be effectively excited, thereby leading to weak CD responses. When n_{sup} increases, the ABDD and BDD modes start to intersect with $(1, 1)_{sub}$ and $(1, 0)_{sup}$ RAs, respectively. In this case, strong diffraction coupling takes place between

nearby unit cells, yielding enhanced CD responses. A further increase in refractive index ($n_{sup} > 1.50$) separate the LSPRs band and RAs again, which is the reason of decreasing CD responses. Interestingly, the sign of CD signals can be switched progressively around the spectral position marked with yellow bars in Figure 9a, which means that the quadrumer array has flipped into “opposite enantiomer” simply by changing its cover materials.

2.6 Modified Born–Kuhn model

The modified plasmonic Born–Kuhn model can be used to describe the underlying physics for the SLR-enhanced chiroptical response. The plasmonic Born–Kuhn model has found tremendous success in explaining the plasmonic chiroptical effects [11, 46], where the optical activity of plasmonic chiral materials can be interpreted as the coupling between two oscillators resonating perpendicularly to each other. The schematic is shown in the inset of Figure 10, where

Figure 10: Comparison between the calculated CD in transmission (circular points) and the fitted spectra from the Born-Kuhn model (solid line) for the chiral quadramer array shown in Figure 8. Inset: the plasmonic Bohn-Kuhn model with only the longitudinal resonances of the upper and bottom layers are considered. The fitting parameters are $\omega_{01} = 242.84$ THz, $\omega_{02} = 258.20$ THz, $\gamma_1 = 3.65 \times 10^{12} \text{ s}^{-1}$, $\gamma_2 = 2.28 \times 10^{13} \text{ s}^{-1}$, and $\kappa_{12} = 1.08 \times 10^{28} \text{ s}^{-2}$.

a yellow oscillator ($u_1 = A_1 e^{-i\omega t}$) is placed at the upper layer and a blue oscillator ($u_2 = A_2 e^{-i\omega t}$) is located at the bottom layer. In the modified Born-Kuhn model, each oscillator represents the collective SLR modes of top (bottom) resonance layer only. This treatment is a natural way of modeling longitudinal propagating resonances as the upper (lower) nanostructure layer plays, respectively, the dominate role when the RAs of the superstrate (substrate) are involved in the formation of SLRs. The coupling between the superstrate (substrate) RAs with the opposite side of layer is neglected. As a result, these oscillators inherit from the basic properties of RAs such as non-resonant features and independent spectral position determined only by surrounding materials themselves. In this way, the two collective resonances are independent. The damping of the collective resonances would be weaker than that of the localized resonances.

As a result, the dynamic equation of the SLR-enhanced chiral metamaterial responding to circularly polarized waves is given by the following Lorentzian equations of two coupled oscillators [46],

$$\begin{bmatrix} \omega_1^2 - \omega^2 - i\omega\gamma_1 & \kappa_{12} \\ \kappa_{12} & \omega_2^2 - \omega^2 - i\omega\gamma_2 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = - \begin{bmatrix} g_1 E_y e^{ik(z-s/2)} \\ g_2 E_x e^{ik(z+s/2)} \end{bmatrix} \quad (2)$$

where $\omega_{1(2)}$ denotes the resonance frequency, $\gamma_{1(2)}$ is the damping of the corresponding oscillator, κ_{12} is the coupling strength of the two oscillators, s is the vertical distance between the two dimers, and $g_{1(2)}$ denotes the coupling

strength of the oscillator with the incident field. The CD responses are related to the nonlocality tensor $\Gamma(\omega)$ [112], and one can get an analytical expression of the CD in transmission with a detailed derivation shown in the method section [46],

$$\Delta T = T_{RCP} - T_{LCP} = \frac{4\omega^2}{2c^2} \text{Im} \left\{ 4\pi e N_0 s \frac{g_1 g_2 \frac{\kappa_{12}}{\omega_2^2 - \omega^2 - i\omega\gamma_2}}{(\omega_1^2 - \omega^2 - i\omega\gamma_1) - \frac{\kappa_{12}^2}{\omega_2^2 - \omega^2 - i\omega\gamma_2}} \right\} \quad (3)$$

where N_0 is the charge carrier density. Equation (3) forms the central result of the modified Born-Kuhn model and agrees well with the simulation spectra from the quadramer array, as shown in Figure 10. In addition, it has been shown that the diffraction coupling in the superstrate is stronger than that of the substrate, and the fitted result, indeed, reveals that the damping of the upper oscillator that embedded in the superstrate is weaker than that of the lower one in the substrate ($\gamma_1 < \gamma_2$), indicating a more effectively coupling with the RA in the superstrate, and the intensity of the positive CD peak is stronger than that of the negative one. Note that, in addition to the longitudinally hybridized resonance considered in the Born-Kuhn model, the transversely hybridized resonance for the upper and lower nanodisk dimers leads to the chiral resonance at around 900 nm, which explains the difference between the FDTD calculation and the Born-Kuhn model results in this spectral range.

3 Conclusion

In conclusion, we have shown that the excitation of SLRs can significantly enhance the chiroptical response of plasmonic metamaterials up to 10 times, with a maximum of CD around 0.7. For a matched circularly polarized incidence, the diffraction coupling between an LSPR and RAs results in strong optical interactions, thereby leading to an amplified absorption. As a result, enhanced CD responses can be achieved simply by choosing a proper period of the array even though the intrinsic chirality of constitutional metamolecules is small. In addition, SLRs and LSPRs are two robust plasmonic effects with distinct underlying physics. Their combination showcases a new degree of freedom to design plasmonic chiral nanostructures. As a demonstration, the phenomenon of “chirality inversion” is observed in the chiral quadramer arrays simply by

changing its cover materials. Although this work focuses on the physics of SLR enhanced plasmonic chirality, the proposed structures can be readily fabricated by the current state-of-the-art nanofabrication techniques, e. g., two-step electron-beam lithography. This technique has been used to successfully fabricate stacked metasurfaces, including stacked split-ring resonator [89], corner-stacked gold nanorods [11], and twisted metamaterial [15, 113]. Our approach could be beneficial in the following two aspects. First, the enhanced CD peaks inherit from the propagation property of SLRs, that is, sharp resonance peaks with high Q-factors, which is *a priori* for practical applications such as biosensing and polarization manipulation [114]. Second, the spectral position of RAs can be dynamically tuned by superstrate, thereby leading to the active control of material chirality. Considering that a propagating SLR mode does not process any chiral properties, it is counterintuitive that the SLR can be used to enhance chirality. Therefore, our results will open the door to novel plasmonic designs in a wide range of applications, which will definitely find applications in broader areas.

4 Methods

Electromagnetic Simulation: The finite-difference time-domain method was used to simulate the optical responses of the single plasmonic nanostructure and the supercell arrays. The dielectric constants of gold were taken from literature [115]. A normal incident pulse along the $-z$ direction was used as the excitation source. Perfectly matched layers were set at all sides as the boundaries for single nanostructures simulation, while periodic boundary condition was imposed in x - and y -directions, and PMLs were set at the top and bottom for supercell simulation.

Born–Kuhn model: From the Lorentzian equations that describing the motion of the two coupled oscillators (Equation (2)), one can get the amplitudes of the two oscillators [46],

$$A_1 = \frac{g_1 E_y e^{-iks/2} - \frac{\kappa_{12} g_2}{\omega_2^2 - \omega^2 - i\omega\gamma_2} E_x e^{iks/2}}{\omega_1^2 - \omega^2 - i\omega\gamma_1 - \frac{\kappa_{12}^2}{\omega_2^2 - \omega^2 - i\omega\gamma_2}} e^{ikz} \quad (4)$$

$$A_2 = \frac{-g_2 E_x e^{ik(z+s/2)} - \kappa_{12} A_1}{\omega_2^2 - \omega^2 - i\omega\gamma_2} \quad (5)$$

Suppose that the charge and the velocity of an electron are, respectively, $-e$ and v , the current density at a point r can be written as $J(r) = -ev\delta(r)$, and the total current density can be calculated as,

$$J_x = -eN_0 g_2 \frac{du_2}{dt} \quad (6)$$

$$J_y = -eN_0 g_1 \frac{du_1}{dt} \quad (7)$$

where N_0 is the charge carrier density, and $J_z = 0$. Since the polarization $P(\omega, r) = J(\omega, r)/(-i\omega)$, one can get the nonzero polarization components,

$$P_x = eN_0 \left[\frac{g_2^2}{\omega_2^2 - \omega^2 - i\omega\gamma_2} E_x - \frac{\frac{\kappa_{12} g_2}{\omega_2^2 - \omega^2 - i\omega\gamma_2} g_1 E_y e^{-iks} - \left(\frac{\kappa_{12} g_2}{\omega_2^2 - \omega^2 - i\omega\gamma_2} \right)^2 E_x}{\omega_1^2 - \omega^2 - i\omega\gamma_1 - \frac{\kappa_{12}^2}{\omega_2^2 - \omega^2 - i\omega\gamma_2}} \right] e^{ikz} \quad (8)$$

$$P_y = eN_0 \left[\frac{g_1^2 E_y - \frac{\kappa_{12} g_2}{\omega_2^2 - \omega^2 - i\omega\gamma_2} g_1 E_x e^{iks}}{\omega_1^2 - \omega^2 - i\omega\gamma_1 - \frac{\kappa_{12}^2}{\omega_2^2 - \omega^2 - i\omega\gamma_2}} \right] e^{ikz} \quad (9)$$

where the approximation $e^{\pm iks} \approx 1 \pm iks$ has been used. The first-order approximation of the linear constitutive equation can be used to deduce the nonlocality tensor,

$$P_i(\omega) = \frac{1}{4\pi} \left\{ \sum_{j=x,y,z} [\varepsilon_{ij}(\omega) - \delta_{ij}] E_j(\omega) + \sum_{j=x,y,z} \sum_{n=x,y,z} \Gamma_{ijn}(\omega) \frac{\partial E_j(\omega)}{\partial r_n} \right\} \quad (10)$$

where ε_{ij} is the material permittivity tensor, Γ_{ijn} is the material nonlocality tensor, and δ_{ij} is the Kronecker delta symbol. Then, one can obtain the nonzero components of the nonlocality tensor by comparing Equations (8) and (9) with Equation (10),

$$\Gamma_{xyz} = -\Gamma_{yxz} = 4\pi e N_0 s \frac{\frac{\kappa_{12} g_2}{\omega_2^2 - \omega^2 - i\omega\gamma_2} g_1}{\omega_1^2 - \omega^2 - i\omega\gamma_1 - \frac{\kappa_{12}^2}{\omega_2^2 - \omega^2 - i\omega\gamma_2}} \quad (11)$$

By considering the propagation direction in an isotropic medium, one can get,

$$\Gamma = \Gamma_{xyz} \quad (12)$$

The ellipticity of the propagation wave per length unit can be written as [112],

$$\sin 2\eta = \tanh \left[\frac{\omega^2}{c^2} \text{Im}\{\Gamma\} \right] \quad (13)$$

where the first-order approximation can be used since $\eta \ll 1$,

$$\eta = \frac{\omega^2}{2c^2} \text{Im}\{\Gamma\} \quad (14)$$

The ellipticity and transmission for LCP and RCP incidences fulfills the following relation,

$$\tan \eta = \frac{\sqrt{T_{RCP}} - \sqrt{T_{LCP}}}{\sqrt{T_{RCP}} + \sqrt{T_{LCP}}} \quad (15)$$

Considering that $\eta \ll 1$, one can obtain,

$$\eta = (T_{RCP} - T_{LCP})/4 \quad (16)$$

By substituting Equation (14) to Equation (16), one can get the analytical expression of the CD in transmission (Equation 3), which is used to fit the simulated spectrum to obtain the properties of individual oscillators [46].

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References

- [1] N. Berova, P. L. Polavarapu, K. Nakanishi, and R. W. Woody, *Comprehensive Chiroptical Spectroscopy*, Wiley: New York, 2012.
- [2] L. D. Barron, *Molecular Light Scattering and Optical Activity*, New York, Cambridge University Press, 2009.
- [3] M. Qiu, L. Zhang, Z. Tang, W. Jin, C.-W. Qiu, and D. Y. Lei, “3D metaphotonic nanostructures with intrinsic chirality,” *Adv. Funct. Mater.*, vol. 28, pp. 1803147, 2018. <https://doi.org/10.1002/adfm.201803147>.
- [4] H.-E. Lee, H.-Y. Ahn, J. Mun, et al., “Amino-acid- and peptide-directed synthesis of chiral plasmonic gold nanoparticles,” *Nature*, vol. 556, pp. 360–365, 2018. <https://doi.org/10.1038/s41586-018-0034-1>.
- [5] J. Karst, N. H. Cho, H. Kim, et al., “Chiral scatterometry on chemically synthesized single plasmonic nanoparticles,” *ACS Nano*, vol. 13, pp. 8659–8668, 2019. <https://doi.org/10.1021/acsnano.9b04046>.
- [6] J. Liu, Z. Ni, P. Nandi, U. Mirsaidov, and Z. Huang, “Chirality transfer in Galvanic replacement reactions,” *Nano Lett.*, vol. 19, pp. 7427–7433, 2019. <https://doi.org/10.1021/acs.nanolett.9b03117>.
- [7] H. E. Lee, R. M. Kim, H. Y. Ahn, et al., “Cysteine-encoded chirality evolution in plasmonic rhombic dodecahedral gold nanoparticles,” *Nat. Commun.*, vol. 11, pp. 263, 2020. <https://doi.org/10.1038/s41467-019-14117-x>.
- [8] Z. Liu, Y. Xu, C. Y. Ji, et al., “Fano-enhanced circular dichroism in deformable stereo metasurfaces,” *Adv. Mater.*, 2020, Art no. e1907077. <https://doi.org/10.1002/adma.201907077>.
- [9] Y. Tang, A. E. Cohen, “Optical chirality and its interaction with matter,” *Phys. Rev. Lett.*, vol. 104, pp. 163901, 2010. <https://doi.org/10.1103/physrevlett.104.163901>.
- [10] Y. Tang, A. E. Cohen, “Enhanced enantioselectivity in excitation of chiral molecules by superchiral light,” *Science*, vol. 332, pp. 333–336, 2011. <https://doi.org/10.1126/science.1202817>.
- [11] X. Yin, M. Schäferling, B. Metzger, and H. Giessen, “Interpreting chiral nanophotonic spectra: the plasmonic Born–Kuhn model,” *Nano Lett.*, vol. 13, pp. 6238–6243, 2013. <https://doi.org/10.1021/nl403705k>.
- [12] C. Helgert, E. Pshenay-Severin, M. Falkner, et al., “Chiral metamaterial composed of three-dimensional plasmonic nanostructures,” *Nano Lett.*, vol. 11, pp. 4400–4404, 2011. <https://doi.org/10.1021/nl202565e>.
- [13] M. Zhang, V. Pacheco-Pena, Y. Yu, et al., “Nanoimprinted chiral plasmonic substrates with three-dimensional nanostructures,” *Nano Lett.*, vol. 18, pp. 7389–7394, 2018. <https://doi.org/10.1021/acs.nanolett.8b03785>.
- [14] Y. Chen, X. Yang, and J. Gao, “3D Janus plasmonic helical nanoapertures for polarization-encrypted data storage,” *Light Sci. Appl.*, vol. 8, pp. 45, 2019. <https://doi.org/10.1038/s41377-019-0156-8>.
- [15] Y. Zhao, M. A. Belkin, and A. Alù, “Twisted optical metamaterials for planarized ultrathin broadband circular polarizers,” *Nat. Commun.*, vol. 3, pp. 870, 2012. <https://doi.org/10.1038/ncomms1877>.
- [16] R. Ji, S.-W. Wang, X. Liu, H. Guo, and W. Lu, “Hybrid helix metamaterials for giant and ultrawide circular dichroism,” *ACS Photonics*, vol. 3, pp. 2368–2374, 2016. <https://doi.org/10.1021/acsphotonics.6b00575>.
- [17] S. Mokashi-Punekar, Y. Zhou, S. C. Brooks, and N. L. Rosi, “Construction of Chiral, Helical Nanoparticle Superstructures: Progress and Prospects,” *Adv. Mater.*, 2019, Art no. e1905975. <https://doi.org/10.1002/adma.201905975>.
- [18] M. Hentschel, M. Schäferling, X. Duan, H. Giessen, and N. Liu, “Chiral plasmonics,” *Sci. Adv.*, vol. 3, 2017, Art no. e1602735. <https://doi.org/10.1126/sciadv.1602735>.
- [19] Y. Luo, C. Chi, M. Jiang, et al., “Plasmonic chiral nanostructures: chiroptical effects and applications,” *Adv. Opt. Mater.*, vol. 5, pp. 1700040, 2017. <https://doi.org/10.1002/adom.201700040>.
- [20] J. K. Gansel, M. Thiel, M. S. Rill, et al., “Gold helix photonic metamaterial as broadband circular polarizer,” *Science*, vol. 325, pp. 1513–1515, 2009. <https://doi.org/10.1126/science.1177031>.
- [21] A. Radke, T. Gissibl, T. Klotzbücher, P. V. Braun, and H. Giessen, “Three-dimensional bichiral plasmonic crystals fabricated by direct laser writing and electroless silver plating,” *Adv. Mater.*, vol. 23, pp. 3018–3021, 2011. <https://doi.org/10.1002/adma.201100543>.
- [22] A. G. Mark, J. G. Gibbs, T.-C. Lee, and P. Fischer, “Hybrid nanocolloids with programmed three-dimensional shape and material composition,” *Nat. Mater.*, vol. 12, pp. 802–807, 2013. <https://doi.org/10.1038/nmat3685>.
- [23] M. Esposito, V. Tasco, M. Cuscunà, et al., “Nanoscale 3D chiral plasmonic helices with circular dichroism at visible frequencies,” *ACS Photonics*, vol. 2, pp. 105–114, 2015. <https://doi.org/10.1021/ph500318p>.
- [24] H.-H. Jeong, A. G. Mark, T.-C. Lee, et al., “Active nanorheology with plasmonics,” *Nano Lett.*, vol. 16, pp. 4887–4894, 2016. <https://doi.org/10.1021/acs.nanolett.6b01404.s001>.
- [25] D. Kusters, A. de Hoogh, H. Zeijlemaker, H. Acar, N. Rotenberg, and L. Kuipers, “Core-shell plasmonic nanohelices,” *ACS Photonics*, vol. 4, pp. 1858–1863, 2017. <https://doi.org/10.1021/acsphotonics.7b00496.s001>.
- [26] J. Cheng, G. Le Saux, J. Gao, et al., “GoldHelix: gold nanoparticles forming 3D helical superstructures with controlled morphology and strong chiroptical property,” *ACS Nano*, vol. 11, pp. 3806–3818, 2017. <https://doi.org/10.1021/acsnano.6b08723>.
- [27] M. Esposito, V. Tasco, F. Todisco, et al., “Programmable extreme chirality in the visible by helix-shaped metamaterial platform,” *Nano Lett.*, vol. 16, pp. 5823–5828, 2016. <https://doi.org/10.1021/acs.1021/acs>.
- [28] Z. Liu, H. Du, J. Li, L. Lu, Z.-Y. Li, and N. X. Fang, “Nano-kirigami with giant optical chirality,” *Sci. Adv.*, vol. 4, 2018, Art no. eaat4436. <https://doi.org/10.1126/sciadv.aat4436>.
- [29] I. V. A. K. Reddy, A. Baev, E. P. Furlani, P. N. Prasad, and J. W. Haus, “Interaction of structured light with a chiral plasmonic metasurface: giant enhancement of chiro-optic response,” *ACS Photonics*, vol. 5, pp. 734–740, 2018. <https://doi.org/10.1021/acsphotonics.7b01321>.

- [30] M. Rajaei, J. Zeng, M. Albooyeh, et al., “Giant circular dichroism at visible frequencies enabled by plasmonic ramp-shaped nanostructures,” *ACS Photonics*, vol. 6, pp. 924–931, 2019. <https://doi.org/10.1021/acsp Photonics.8b01584>.
- [31] B. Frank, X. Yin, M. Schäferling, et al., “Large-area 3D chiral plasmonic structures,” *ACS Nano*, vol. 7, pp. 6321–6329, 2013. <https://doi.org/10.1021/nn402370x>.
- [32] R. Verre, L. Shao, N. Odebo Länk, et al., “Metasurfaces and Colloidal Suspensions Composed of 3D Chiral Si Nanoresonators,” *Adv. Mater.*, vol. 29, pp. 1701352, 2017. <https://doi.org/10.1002/adma.201701352>.
- [33] Y. Fang, R. Verre, L. Shao, P. Nordlander, and M. Käll, “Hot electron generation and cathodoluminescence nanoscopy of chiral split ring resonators,” *Nano Lett.*, vol. 16, pp. 5183–5190, 2016. <https://doi.org/10.1021/acs.nanolett.6b02154.s002>.
- [34] B. Yeom, H. Zhang, H. Zhang, et al., “Chiral plasmonic nanostructures on achiral nanopillars,” *Nano Lett.*, vol. 13, pp. 5277–5283, 2013. <https://doi.org/10.1021/nl402782d>.
- [35] Y. Chen, J. Gao, and X. Yang, “Chiral metamaterials of plasmonic slanted nanoapertures with symmetry breaking,” *Nano Lett.*, vol. 18, pp. 520–527, 2017. <https://doi.org/10.1021/acs.nanolett.7b04515>.
- [36] S. Yang, Z. Liu, S. Hu, et al., “Spin-selective transmission in chiral folded metasurfaces,” *Nano Lett.*, vol. 19, pp. 3432–3439, 2019. <https://doi.org/10.1021/acs.nanolett.8b04521>.
- [37] A. V. Rogacheva, V. A. Fedotov, A. S. Schwanecke, and N. I. Zheludev, “Giant gyrotropy due to electromagnetic-field coupling in a bilayered chiral structure,” *Phys. Rev. Lett.*, vol. 97, pp. 177401, 2006. <https://doi.org/10.1103/physrevlett.97.177401>.
- [38] Y. Cui, L. Kang, S. Lan, S. Rodrigues, and W. Cai, “Giant chiral optical response from a twisted-arc metamaterial,” *Nano Lett.*, vol. 14, pp. 1021–1025, 2014. <https://doi.org/10.1021/nl404572u>.
- [39] K. W. Smith, H. Zhao, H. Zhang, et al., “Chiral and achiral nanodumbbell dimers: the effect of geometry on plasmonic properties,” *ACS Nano*, vol. 10, pp. 6180–6188, 2016. <https://doi.org/10.1021/acsnano.6b02194>.
- [40] A. F. Najafabadi and T. Pakizeh, “Analytical chiroptics of 2D and 3D nanoantennas,” *ACS Photonics*, vol. 4, pp. 1447–1452, 2017. <https://doi.org/10.1021/acsp Photonics.7b00179>.
- [41] Z. Wang, H. Jia, K. Yao, W. Cai, H. Chen, and Y. Liu, “Circular dichroism metamirrors with near-perfect extinction,” *ACS Photonics*, vol. 3, pp. 2096–2101, 2016. <https://doi.org/10.1109/piers.2016.7735089>.
- [42] S. Fasold, S. Lin, T. Kawde, et al., “Disorder-enabled pure chirality in bilayer plasmonic metasurfaces,” *ACS Photonics*, vol. 5, pp. 1773–1778, 2018. <https://doi.org/10.1021/acsp Photonics.7b01460>.
- [43] T. Liu, L. V. Besteiro, T. Liedl, M. A. Correa-Duarte, Z. Wang, and A. O. Govorov, “Chiral plasmonic nanocrystals for generation of hot electrons: toward polarization-sensitive photochemistry,” *Nano Lett.*, vol. 19, pp. 1395–1407, 2019. <https://doi.org/10.1021/acs.nanolett.8b05179>.
- [44] A. Kuzyk, R. Schreiber, Z. Fan, et al., “DNA-based self-assembly of chiral plasmonic nanostructures with tailored optical response,” *Nature*, vol. 483, pp. 311–314, 2012. <https://doi.org/10.1038/nature10889>.
- [45] X. Shen, A. Asenjo-García, Q. Liu, et al., “Three-dimensional plasmonic chiral tetramers assembled by dna origami,” *Nano Lett.*, vol. 13, pp. 2128–2133, 2013. <https://doi.org/10.1021/nl400538y>.
- [46] X. Duan, S. Yue, and N. Liu, “Understanding complex chiral plasmonics,” *Nanoscale*, vol. 7, pp. 17237–17243, 2015. <https://doi.org/10.1039/c5nr04050g>.
- [47] C. Song, M. G. Blaber, G. Zhao, et al., “Tailorable plasmonic circular dichroism properties of helical nanoparticle superstructures,” *Nano Lett.*, vol. 13, pp. 3256–3261, 2013. <https://doi.org/10.1021/nl4013776>.
- [48] M. Hentschel, L. Wu, M. Schäferling, P. Bai, E. P. Li, and H. Giessen, “Optical properties of chiral three-dimensional plasmonic oligomers at the onset of charge-transfer plasmons,” *ACS Nano*, vol. 6, pp. 10355–10365, 2012. <https://doi.org/10.1021/nn304283y>.
- [49] M. Hentschel, M. Schäferling, B. Metzger, and H. Giessen, “Plasmonic diastereomers: adding up chiral centers,” *Nano Lett.*, vol. 13, pp. 600–606, 2013. <https://doi.org/10.1021/nl3041355>.
- [50] M. Hentschel, M. Schäferling, T. Weiss, N. Liu, and H. Giessen, “Three-dimensional chiral plasmonic oligomers,” *Nano Lett.*, vol. 12, pp. 2542–2547, 2012. <https://doi.org/10.1021/nl300769x>.
- [51] V. E. Ferry, M. Hentschel, and A. P. Alivisatos, “Circular dichroism in off-resonantly coupled plasmonic nanosystems,” *Nano Lett.*, vol. 15, pp. 8336–8341, 2015. <https://doi.org/10.1021/acs.nanolett.5b03970>.
- [52] X. Lan and Q. Wang, “Self-assembly of chiral plasmonic nanostructures,” *Adv. Mater.*, vol. 28, pp. 10499–10507, 2016. <https://doi.org/10.1002/adma.201600697>.
- [53] E. Vinegrad, D. Vestler, A. Ben-Moshe, A. R. Barnea, G. Markovich, and O. Cheshnovsky, “Circular dichroism of single particles,” *ACS Photonics*, vol. 5, pp. 2151–2159, 2018. <https://doi.org/10.1021/acsp Photonics.8b00016.s001>.
- [54] L. Hu, T. Liedl, K. Martens, Z. Wang, and A. O. Govorov, “Long-range plasmon-assisted chiral interactions in nanocrystal assemblies,” *ACS Photonics*, vol. 6, pp. 749–756, 2019. <https://doi.org/10.1021/acsp Photonics.8b01676>.
- [55] E. Hendry, R. V. Mikhaylovskiy, L. D. Barron, M. Kadodwala, and T. J. Davis, “Chiral electromagnetic fields generated by arrays of nanoslits,” *Nano Lett.*, vol. 12, pp. 3640–3644, 2012. <https://doi.org/10.1021/nl3012787>.
- [56] B. Hopkins, A. N. Poddubny, A. E. Miroshnichenko, and Y. S. Kivshar, “Circular dichroism induced by Fano resonances in planar chiral oligomers,” *Laser Photonics Rev.*, vol. 10, pp. 137–146, 2016. <https://doi.org/10.1002/lpor.201500222>.
- [57] A. B. Khanikaev, N. Arju, Z. Fan, et al., “Experimental demonstration of the microscopic origin of circular dichroism in two-dimensional metamaterials,” *Nat. Commun.*, vol. 7, pp. 12045, 2016. <https://doi.org/10.1117/12.2239083>.
- [58] P. Yu, J. Li, C. Tang, et al., “Controllable optical activity with non-chiral plasmonic metasurfaces,” *Light-Sci. Appl.*, vol. 5, 2016, Art no. e16096. <https://doi.org/10.1038/lsa.2016.96>.
- [59] L. Kang, Q. Ren, and D. H. Werner, “Leveraging Superchiral Light for Manipulation of Optical Chirality in the Near-Field of Plasmonic Metamaterials,” *ACS Photonics*, vol. 4, pp. 1298–1305, 2017. <https://doi.org/10.1021/acsp Photonics.7b00057>.
- [60] J. García-Guirado, M. Svedendahl, J. Puigdollers, and R. Quidant, “Enantiomer-selective molecular sensing using racemic nanoplasmonic arrays,” *Nano Lett.*, vol. 18, pp. 6279–6285, 2018. <https://doi.org/10.1021/acs.nanolett.8b02433>.
- [61] T. S. H. Yoo, J. Berthelot, G. Guida, et al., “Circularly polarized images with contrast reversal using pseudochiral metasurfaces,” *ACS Photonics*, vol. 5, pp. 4068–4073, 2018. <https://doi.org/10.1021/acsp Photonics.8b00730>.

- [62] S. Zu, T. Han, M. Jiang, F. Lin, X. Zhu, and Z. Fang, “Deep-subwavelength resolving and manipulating of hidden chirality in achiral nanostructures,” *ACS Nano*, vol. 12, pp. 3908–3916, 2018. <https://doi.org/10.1021/acsnano.8b01380>.
- [63] N. J. Greybush, V. Pacheco-Pena, N. Engheta, C. B. Murray, and C. R. Kagan, “Plasmonic optical and chiroptical response of self-assembled au nanorod equilateral trimers,” *ACS Nano*, vol. 13, pp. 1617–1624, 2019. <https://doi.org/10.1021/acsnano.8b07619>.
- [64] Y. Hwang, S. Lee, S. Kim, J. Lin, and X.-C. Yuan, “Effects of Fano resonance on optical chirality of planar plasmonic nanodevices,” *ACS Photonics*, vol. 5, pp. 4538–4544, 2018. <https://doi.org/10.1021/acsp Photonics.8b01007>.
- [65] T. Han, S. Zu, Z. Li, M. Jiang, X. Zhu, and Z. Fang, “Reveal and control of chiral cathodoluminescence at subnanoscale,” *Nano Lett.*, vol. 18, pp. 567–572, 2018. <https://doi.org/10.1021/acs.nanolett.7b04705>.
- [66] S. Zu, Y. Bao, and Z. Fang, “Planar plasmonic chiral nanostructures,” *Nanoscale*, vol. 8, pp. 3900–3905, 2016. <https://doi.org/10.1039/c5nr09302c>.
- [67] Y. Bao, Z. Hu, Z. Li, X. Zhu, and Z. Fang, “Magnetic plasmonic Fano resonance at optical frequency,” *Small*, vol. 11, pp. 2177–2181, 2015. <https://doi.org/10.1002/sml.201402989>.
- [68] S. Zu, T. Han, M. Jiang, et al., “Imaging of plasmonic chiral radiative local density of states with cathodoluminescence nanoscopy,” *Nano Lett.*, vol. 19, pp. 775–780, 2019. <https://doi.org/10.1021/acs.nanolett.8b03850>.
- [69] S. Zhang, J. Zhou, Y.-S. Park, et al., “Photoinduced handedness switching in terahertz chiral metamolecules,” *Nat. Commun.*, vol. 3, pp. 942, 2012. <https://doi.org/10.1038/ncomms1908>.
- [70] X. Yin, M. Schäferling, Michel, A.-K., et al., 2015. Active chiral plasmonics. *Nano Lett.* 15, 4255–4260. <https://doi.org/10.1021/nl5042325>.
- [71] X. Duan, S. Kamin, F. Sterl, H. Giessen, and N. Liu, “Hydrogen-regulated chiral nanoplasmonics,” *Nano Lett.*, vol. 16, pp. 1462–1466, 2016. <https://doi.org/10.1021/acs.nanolett.5b05105>.
- [72] I. Zubritskaya, N. Maccaferri, X. Inchausti Ezeiza, P. Vavassori, and A. Dmitriev, “Magnetic control of the chiroptical plasmonic surfaces,” *Nano Lett.*, vol. 18, pp. 302–307, 2017. <https://doi.org/10.1021/acs.nanolett.7b04139>.
- [73] S. P. Rodrigues, S. Lan, L. Kang, et al., “Intensity-dependent modulation of optically active signals in a chiral metamaterial,” *Nat. Commun.*, vol. 8, pp. 14602, 2017. <https://doi.org/10.1038/ncomms14602>.
- [74] R. Schreiber, N. Luong, Z. Fan, et al., “Chiral plasmonic DNA nanostructures with switchable circular dichroism,” *Nat. Commun.*, vol. 4, pp. 2948, 2013. <https://doi.org/10.1038/ncomms3948>.
- [75] A. Kuzyk, R. Schreiber, H. Zhang, A. O. Govorov, T. Liedl, and N. Liu, “Reconfigurable 3D plasmonic metamolecules,” *Nat. Mater.*, vol. 13, pp. 862–866, 2014. <https://doi.org/10.1038/nmat4031>.
- [76] A. Kuzyk, Y. Yang, X. Duan, et al., “A light-driven three-dimensional plasmonic nanosystem that translates molecular motion into reversible chiroptical function,” *Nat. Commun.*, vol. 7, pp. 10591, 2016. <https://doi.org/10.1038/ncomms10591>.
- [77] A. Kuzyk, M. J. Urban, A. Idili, F. Ricci, and N. Liu, “Selective control of reconfigurable chiral plasmonic metamolecules,” *Sci. Adv.*, vol. 3, 2017, Art no. e1602803. <https://doi.org/10.1126/sciadv.1602803>.
- [78] X. Wu, L. Xu, W. Ma, et al., “Propeller-like nanorod-upconversion nanoparticle assemblies with intense chiroptical activity and luminescence enhancement in aqueous phase,” *Adv. Mater.*, vol. 28, pp. 5907–5915, 2016. <https://doi.org/10.1002/adma.201601261>.
- [79] Z. Wang, L. Jing, K. Yao, et al., “Origami-based reconfigurable metamaterials for tunable chirality,” *Adv. Mater.*, vol. 29, pp. 1700412, 2017. <https://doi.org/10.1002/adma.201700412>.
- [80] L. M. Kneer, E.-M. Roller, L. V. Besteiro, R. Schreiber, A. O. Govorov, and T. Liedl, “Circular dichroism of chiral molecules in dna-assembled plasmonic hotspots,” *ACS Nano*, vol. 12, pp. 9110–9115, 2018. <https://doi.org/10.1021/acsnano.8b03146>.
- [81] T. Man, W. Ji, X. Liu, et al., “Chiral metamolecules with active plasmonic transition,” *ACS Nano*, vol. 13, pp. 4826–4833, 2019. <https://doi.org/10.1021/acsnano.9b01942>.
- [82] C. Zhou, L. Xin, X. Duan, M. J. Urban, and N. Liu, “Dynamic plasmonic system that responds to thermal and aptamer-target regulations,” *Nano Lett.*, vol. 18, pp. 7395–7399, 2018. <https://doi.org/10.1021/acs.nanolett.8b03807>.
- [83] G. Yao, J. Li, Q. Li, et al., 2019. Programming nanoparticle valence bonds with single-stranded DNA encoders. *Nat. Mater.* <https://doi.org/10.1038/s41563-41019-40549-41563>.
- [84] E. Prodan, C. Radloff, N. J. Halas, and P. A. Nordlander, “Hybridization model for the plasmon response of complex nanostructures,” *Science*, vol. 302, pp. 419–422, 2003. <https://doi.org/10.1126/science.1089171>.
- [85] P. Nordlander, C. Oubre, E. Prodan, K. Li, and M. I. Stockman, “Plasmon hybridization in nanoparticle dimers,” *Nano Lett.*, vol. 4, pp. 899–903, 2004. <https://doi.org/10.1021/nl049681c>.
- [86] P. K. Jain, K. S. Lee, I. H. El-Sayed, and M. A. El-Sayed, “Calculated absorption and scattering properties of gold nanoparticles of different size, shape, and composition: applications in biological imaging and biomedicine,” *J. Phys. Chem. B*, vol. 110, pp. 7238–7248, 2006. <https://doi.org/10.1021/jp057170o>.
- [87] M. Decker, R. Zhao, C. M. Soukoulis, S. Linden, and M. Wegener, “Twisted split-ring-resonator photonic metamaterial with huge optical activity,” *Opt. Lett.*, vol. 35, pp. 1593, 2010. <https://doi.org/10.1364/ol.35.001593>.
- [88] N. Liu, H. Liu, S. Zhu, Giessen, H., 2009. Stereometamaterials. *Nat. Photonics* 3, 157–162. <https://doi.org/10.1038/nphoton.2009.4>.
- [89] N. Liu, H. Guo, L. Fu, S. Kaiser, H. Schweizer, and H. Giessen, “Three-dimensional photonic metamaterials at optical frequencies,” *Nat. Mater.*, vol. 7, pp. 31–37, 2007. <https://doi.org/10.1038/nmat2072>.
- [90] D. A. Powell, K. Hannam, I. V. Shadrivov, and Y. S. Kivshar, “Near-field interaction of twisted split-ring resonators,” *Phys. Rev. B*, vol. 83, pp. 235420, 2011. <https://doi.org/10.1103/physrevb.83.235420>.
- [91] S. M. Hein, and H. Giessen, “Retardation-induced phase singularities in coupled plasmonic oscillators,” *Phys. Rev. B*, vol. 91, 2015, Art no. 205402. <https://doi.org/10.1103/PhysRevB.91.205402>.

- [92] G. R. Keiser, A. C. Strikwerda, K. Fan, V. Young, X. Zhang, and R. D. Averitt, “Decoupling crossover in asymmetric broadside coupled split-ring resonators at terahertz frequencies,” *Phys. Rev. B*, 88, 2013, Art no. 024101. <https://doi.org/10.1103/PhysRevB.88.024101>.
- [93] H. Liu, Cao, J. X., Zhu, S. N., N. Liu, R. Ameling, H. Giessen, 241403(R. Lagrange model for the chiral optical properties of stereometamaterials. *Phys. Rev. B* 81, 2010. <https://doi.org/10.1103/PhysRevB.81.241403>.
- [94] W. Ma, F. Cheng, and Y. Liu, “Deep-learning-enabled on-demand design of chiral metamaterials,” *ACS Nano*, vol. 12, pp. 6326–6334, 2018. <https://doi.org/10.1021/acsnano.8b03569>.
- [95] T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, and P. A. Wolff, “Extraordinary optical transmission through sub-wavelength hole arrays,” *Nature*, vol. 391, pp. 667–669, 1998. <https://doi.org/10.1038/35570>.
- [96] S. Zou, N. Janel, Schatz, G.C., 2004. Silver nanoparticle array structures that produce remarkably narrow plasmon lineshapes. *J. Chem. Phys.* 120, 10871–10875. <https://doi.org/10.1063/1.1760740>.
- [97] V. G. Kravets, F. Schedin, and A. N. Grigorenko, “Extremely narrow plasmon resonances based on diffraction coupling of localized plasmons in arrays of metallic nanoparticles,” *Phys. Rev. Lett.*, vol. 101, 2008, Art no. 087403. <https://doi.org/10.1103/PhysRevLett.101.087403>.
- [98] A. Vitrey, L. Aigouy, P. Prieto, García-Martín, J.M., González, M.U., 2014. Parallel collective resonances in arrays of gold nanorods. *Nano Lett.* 14, 2079–2085. <https://doi.org/10.1021/nl500238h>.
- [99] G. Vecchi, V. Giannini, and J. Gómez Rivas, “Shaping the fluorescent emission by lattice resonances in plasmonic crystals of nanoantennas,” *Phys. Rev. Lett.*, vol. 102, pp. 146807, 2009. <https://doi.org/10.1103/PhysRevLett.102.146807>.
- [100] D. Wang, M. R. Bourgeois, W.-K. Lee, et al., “Stretchable nanolasing from hybrid quadrupole plasmons,” *Nano Lett.*, vol. 18, pp. 4549–4555, 2018. <https://doi.org/10.1021/acs.nanolett.8b01774>.
- [101] W. Zhou, M. Dridi, Suh, J. Y., et al., 2013. Lasing action in strongly coupled plasmonic nanocavity arrays. *Nat. Nanotechnol.* 8, 506–511. <https://doi.org/10.1038/nnano.2013.99>.
- [102] D. Wang, A. Yang, W. Wang, et al., 2017. Band-edge engineering for controlled multi-modal nanolasing in plasmonic superlattices. *Nat. Nanotechnol.* 12, 889–894. <https://doi.org/10.1038/nnano.2017.126>.
- [103] A. Yang, Z. Li, , Knudson, M. P., et al., 2015. Unidirectional lasing from template-stripped two-dimensional plasmonic crystals. *ACS Nano* 9, 11582–11588. <https://doi.org/10.1021/acsnano.5b05419>.
- [104] G. Vecchi, V. Giannini, and J. Gómez Rivas, “Surface modes in plasmonic crystals induced by diffractive coupling of nanoantennas,” *Phys. Rev. B*, vol. 80, 2009, Art no. 201401(R). <https://doi.org/10.1103/PhysRevB.80.201401>.
- [105] Maoz, B.M., A. Ben Moshe, D. Vestler, O. Bar-Elli, G. Markovich, 2012. Chiroptical effects in planar achiral plasmonic oriented nanohole arrays. *Nano Lett.* 12, 2357–2361. <https://doi.org/10.1021/nl300316f>.
- [106] Z. Wang, Y. Wang, G. Adamo, et al., 2016. Novel chiral metasurface with controllable circular dichroism induced by coupling localized and propagating modes. *Adv. Opt. Mater.* 4, 883–888. <https://doi.org/10.1002/adom.201600063>.
- [107] I. De Leon, M. J. Horton, S. A. Schulz, J. Upham, P. Banzer, and R. W. Boyd, “Strong, spectrally-tunable chirality in diffractive metasurfaces,” *Sci. Rep.*, vol. 5, pp. 13034, 2015. <https://doi.org/10.1038/srep13034>.
- [108] L. Mao, K. Liu, S. Zhang, and T. Cao, “Extrinsically 2D-chiral metamirror in near-infrared region,” *ACS Photonics*, 2020, <https://doi.org/10.1021/acsp Photonics.1029b01211>.
- [109] M. Cotrufo, Osorio, C. I., Koenderink, A. F., 2016. Spin-dependent emission from arrays of planar chiral nanoantennas due to lattice and localized plasmon resonances. *ACS Nano* 10, 3389–3397. <https://doi.org/10.1021/acsnano.5b07231>.
- [110] X. Zhang, Z.-G. Zhang, Q. Wang, S.-N. Zhu, H. Liu., 2019. Controlling thermal emission by parity-symmetric fano resonance of optical absorbers in metasurfaces. *ACS Photonics* 6, 2671–2676. <https://doi.org/10.1021/acsp Photonics.9b00024>.
- [111] A. Yang, , Hoang, T. B., M. Dridi, et al., 2015. Real-time tunable lasing from plasmonic nanocavity arrays. *Nat. Commun.* 6, 6939. <https://doi.org/10.1038/ncomms7939>.
- [112] Y. P. Svirko and N. I. Zheludev. *Polarization of Light in Nonlinear Optics*, New York, John Wiley & Sons, 1998.
- [113] Y. Zhao, A. N. Askarpour, L. Sun, J. Shi, X. Li, and A. Alu, “Chirality detection of enantiomers using twisted optical metamaterials,” *Nat. Commun.*, vol. 8, pp. 14180, 2017. <https://doi.org/10.1038/ncomms14180>.
- [114] H.-H. Jeong, A. G. Mark, M. Alarcón-Correa, et al., “Dispersion and shape engineered plasmonic nanosensors,” *Nat. Commun.*, vol. 7, pp. 11331, 2016. <https://doi.org/10.1038/ncomms11331>.
- [115] P. B. Johnson and R. W. Christy, “Optical Constants of the Noble Metals,” *Phys. Rev. B*, vol. 6, pp. 4370–4379, 1972. <https://doi.org/10.1103/PhysRevB.6.4370>.

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